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The Distribution and Decomposition of
Organic Phosphorus and Organic Nitrogen
in River Ecosystems of Korea



by

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Organic Phosphorus and Organic Nitrogen
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PREFACE

Eutrophication is the response in water due to overenrichment by nutrients, primarily phosphorus (P) and nitrogen (N), and can occur under natural or anthropogenic conditions. In aquatic ecosystems eutrophication might induce biological and chemical changes, with symptoms ranging from excessive algae blooms and greenish waters to anoxia caused by oxygen depletion during decomposition of elevated biomass input to waters. In addition, eutrophication might trigger cyanobacterial blooms which can result in the production of neuro- and hepato-toxins posing severe risks to human and animal health. Nitrogen and phosphorus concentrations in many rivers have increased over time. The effect of increasing N concentration depends on P availability. In combination with increased N concentration, similar changes have occurred with P in many rivers. This has often altered the stoichiometric balance of N and P which may not only affect the total production in freshwater systems, but also its quality.

Transformations between various N-compounds in the aquatic ecosystems offer significant management potential for stream and rivers. Nitrogen is a key component of proteins and nucleic acids. Most phytoplankton which creates nuisance bloom conditions are capable of N fixation and are not dependent on dissolved combined forms of N. Nitrogen fixation, however, is inhibited by high cellular ammonia content. Decomposition of organic matter results in release and accumulation of ammonia. Under aerobic conditions, ammonia is oxidized in a two step process called nitrification, first to nitrite, then to nitrate. Under anaerobic conditions nitrification of ammonia to nitrate does not occur, and ammonia accumulates often at the bottom. Nitrate is the first alternate TEA (terminal electron acceptor) used in anaerobic respiration when oxygen is exhausted. As long as nitrate remains available, the redox potential (Eh) remains above that required for iron reduction and subsequent sediment P release from ferric hydroxy-phosphate complexes in the

sediments. Enhancing nitrification of ammonia to nitrate, and subsequent use of nitrate in denitrification can stabilize Eh and reduce internal P loading.

Phosphorus may enter a water body through the inflows, precipitation, and from the sediments, and it may be removed by sedimentation and through the outflow. A certain reduction of P input will generally result in a greater reduction in algal biomass compared with the same reduction of N. Furthermore, the reduction of N input without a proportional reduction in P, creates low N: P ratio which favors N fixing nuisance algae, without any reduction in algal biomass. Even after the external nutrient load has been reduced many rivers and streams may not show reductions in P and N concentrations, as nutrients accumulate in the sediments will be released into the water column. The extent to which sediments will act as a nutrient source depends upon the amount of iron contained in the sediments, the degradability of sedimentary organic matter as an energy source of microorganisms, and the size of the P pool. Even though most organisms utilize P in the form of inorganic phosphate, a major part of the total P in both aquatic and terrestrial ecosystems is often composed of organic P compounds. Organic P occurs in dissolved, particle-associated and colloidal forms, and naturally encompasses a wide variety of organic compounds including phospholipids, nucleic acids, inositol phosphates, phosphoproteins, humic substances, among others. Apart from the strictly organic P compounds, condensed P such as polyphosphates and pyrophosphates may also be highly involved in P cycling in aquatic systems. Humic substances dissolved in water have the ability to bind P and N compounds and metal cations. The nutrients bound to humic substances cannot be directly utilized by phytoplankton due to their high molecular weights and their imperviousness to enzymatic hydrolysis. It has been reported that when both tannins and P were present, high concentrations of tannins inhibited binding of P by alum.

The N: P ratio in particulate organic matter (POM) suspended in rivers is a potentially valuable index of the nutritional status of the phytoplankton or

periphyton. Algae contain approximately 16 atoms of N for every atom of P. Ratios of N to P less than 10 often indicate N deficiency and ratios greater than 20 can indicate P deficiency. In rivers, POM can originate from autochthonous production of phytoplankton and from allochthonous sources like soils, wastewater and atmosphere. It can also be produced in situ from dissolved organic matter (DOM) by physico-chemical and biological processes. The POM is subjected to different processes such as mineralization, disaggregation and sedimentation that determine its role, behavior and fate in the aquatic ecosystem. POM can be divided into a living (i.e. bacteria and plankton) and non-living (detritus) parts. In general, most of the living part is recycled rapidly together with a minor part of the detritus. That part of organic matter which is decomposed is often called labile, and here defined as the fraction of carbohydrates and proteins in POM. Allochthonous inputs are usually dominated by the refractory component while autochthonous inputs are initially labile becoming refractory over time. From an ecological and geochemical point of view it is important to distinguish between labile and refractory components of POM and DOM to provide a general picture of the fate of POM and DOM in the river environment. The labile fraction is an important food source for aquatic organisms. The refractory fraction ultimately ends up in the coastal marine sediments and this is of geochemical significance. A decrease in labile POM is found when the concentration of suspended matter is high. This is probably due to the decreased light penetration in highly turbid waters, which decreases primary production resulting in a low contribution of labile POC (particulate organic carbon). Previous studies indicate that rivers carry 10 times more DOM than POM. However, DOM consists of a complex mixture of organic compounds where the large majorities (80 %) remain unknown and likely resemble the complex humic compounds found in river water. Microbial action not only results in the remineralization of DOM, but also in its transformation in such a way that the DOM pool owes much of its chemical structure to microbial activity. As DOM is very difficult to chemically characterize due to its complexity, often 'bulk' measurements of carbon (DOC),

nitrogen (DON) and phosphorus (DOP) are used. However, the degradation of DOM is also important for the biogeochemical cycles of N and P, as the majority of the fixed N and much of the available P is bound within DOM.

A key component in the cycling of organic matter in aquatic ecosystems is decomposition. In aquatic ecosystems, heterotrophic bacteria are primarily responsible for the bulk of decomposition of organic matter. Decomposition involves the reduction of energy-rich organic matter (detritus), mostly by microorganisms (fungi, bacteria, and protozoa) to CO_2 , H_2O and inorganic nutrients. However, exoenzymatic breakdown, uptake of small molecules, and the eventual intracellular oxidation of organic molecules to CO_2 and inorganic constituents are the principal pathways of organic matter decomposition in aquatic systems. Whether the increase in total nutrient concentrations results in higher available nutrients concentrations, and therefore an immediate increase in growth or productivity, depends upon the original form of the nutrients and physical conditions. However, enzymatic hydrolysis or decomposition is affected by a number of environmental factors, of which temperature, pH and redox potential are the most important. Specifically temperature affects the metabolic activity on the decomposing substrate. If nutrients enter as organic matter that first needs to be decomposed before it can be utilized for growth, temperature becomes important due to its effect on the rate of decomposition. During warmer month, nutrients entering the system as intact organic matter would be decomposed relatively quickly compared to cold, wet-weather months when decomposition is slow. These dynamics are further complicated by the fact that increased growth leads to greater number of organisms that need even more nutrients. So, as nutrients become available they are immediately utilized. In this case, an increase in total nutrients would not be reflected by any measurable increase in available nutrient fractions. However, the clear and simple relationships between increases in organic matter or other sources of nutrients, and resultant increases in either total nutrient concentrations or available nutrient concentrations, become obscure.

Nutritional value of the decomposing structure also affects the time involved in complete breakdown and mineralization. An exoenzyme or extracellular enzyme, that is secreted by a cell and works outside the cell usually used for breaking up large molecules that would not be able to enter the cell otherwise. Alkaline phosphatase, an extracellular enzyme released by microorganisms under conditions of phosphate depletion that cleaves inorganic P from organic matter. Decreases of APA could increase P-stress in low nutrient aquatic environments. Similarly protease enzymes are important in N cycle and function in the breakdown of proteins, resulting in the release of $\text{NH}_4\text{-N}$. Glucosidase catalyzes the hydrolysis of glycoside, resulting in the release of beta-linked monosaccharide. Phenil oxidase is important in the breakdown of lignin-containing compounds. Phosphatases can be produced by algae, but extracellular glycosidases, peptidases, and phenol oxidases generally are produced in quantity only by heterotrophic microorganisms, thus heterotrophic metabolism might be enhanced in the presence of algae. Besides enzymatic breakdown and bacterial decompositions of organic P compounds, abiotic decomposition of organic P compounds into phosphate can occur through hydrolysis and photolysis.

Decomposition rates of organic P and organic N in aquatic environment are important determinants to assess the water quality and predict the effects of P and N for algal growth as well as overall impacts in the river ecosystem. Till now, the decomposition rates of only labile and recalcitrant forms of POM and DOM have been using in modeling the water quality of streams and rivers. According to the Version 3.5 of CE-QUAL-W2 User Manual, the default values of LPOM and LDOM are 0.08 day^{-1} and 0.10 day^{-1} , respectively. In modeling the river water quality, it would therefore be better to introduce more specific decomposition rate coefficients of organic P, organic N and organic C instead of the default values of LPOM and LDOM. Consequently the model predictions related to water quality as well as the management strategies of eutrophication might be more accurate than the existing model predictions. No quantitative studies have been conducted on the

decomposition rates of organic P, organic N, and organic C, and their related constituents of the river ecosystems. In model calculation of decomposition phenomena, expressions are desired that are realistic in terms of both mathematical and biological behavior. Mathematical models are valuable tools to investigate the biogeochemical mechanisms, their interactions and to predict the decomposition rates of organic P, organic N and organic C in river ecosystems. Some interrelated differential model equations have been used to study the decomposition rates of organic P, organic N and organic C in aquatic environment. The differential approach has the advantage that it automatically provides an estimate of the order. To determine the decomposition rate coefficients, the Runge-Kutta method treats every step in a sequence of steps in identical manner. Any point along the trajectory of an ordinary differential equation can serve as an initial input. The fact that all steps are treated identically also makes it easy to incorporate Runge-Kutta into relatively simple 'driver' schemes. The main advantages of Runge-Kutta methods are that they are easy to implement, they are stable, and they are 'self-starting'. The mechanisms involved in these models include decomposition kinetics of various particulate and dissolved organic fractions. These conceptual decay models are useful to determine the decomposition coefficients from the data derived from chemical analyzes. In addition, stoichiometric analyzes of POM and DOM can be used to investigate the linkages between C, N and P cycles and how these linkages influence biogeochemistry at many scales, from components of individual ecosystems up to the biosphere. Ecosystem responses reflect the net sum of processes at the cellular or organismal level and their interaction with abiotic factors in time and space.

Available information on the distributions of particulate and dissolved forms of organic P and organic N in the POM and DOM, and their decomposition processes in river ecosystems are mostly qualitative in nature. The first chapter describes the water quality data especially the distributions of P and N representing the present trophic conditions of the rivers of Korea. It also includes long term ecological

changes and measures compliance with water quality standards for total phosphorus (TP), and total nitrogen (TN). The second chapter describes the decomposition rates of organic P in the POM and DOM of the river systems by microorganisms. And finally, chapter three highlights the changes of P and N content in POM and DOM as well as their rates of changes of their stoichiometric ratios during the enzymatic decomposition processes. Therefore, investigations of these processes will provide a better understanding of the distribution patterns of particulate and dissolved forms of organic P and organic N, and their changing behaviors in the river ecosystems that thereby ultimately influence the water quality of streams and rivers as well as their management practices. The objectives of the study were:

- 1) to measure variations of P and N fractions and their impacts on the river ecology and water quality
- 2) to determine the decomposition rates of organic P in the river water as well as the overall impacts of P in the river ecosystem
- 3) to assess the changes of organic P and organic N and their availabilities for algal growth in rivers and the stoichiometric changes of C:N:P of POM and DOM in the river ecosystem

Chapter I

Spatial and Longitudinal Distribution of Phosphorus and Nitrogen in the Youngsan and the Sumjin River Systems, Korea

ABSTRACT

The spatial and temporal distributions of phosphorus and nitrogen and a number of physical, chemical and biological parameters were analyzed in the Youngsan and the Sumjin River systems, Korea. Substantial amount of P and N was observed in both the rivers all the year round. Mean N:P ratios showed large variations among the sampling sites; highest ratio was observed in most sampling sites during summer. Relative proportions of DOP: TP were fairly constant (0.08-0.09) in both the rivers. In the composition of nitrogen almost all sampling sites of both the rivers were dominated with $\text{NO}_3\text{-N}$ followed by $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$. Variations in dissolved nutrients tended to co-vary with particulate forms (PON and POP), implying that dissolved nutrients are primarily released from the decomposition of particulate forms or dissolved forms are in equilibrium with particulate forms. Chlorophyll *a* levels in the Sumjin River appear to be negatively correlated with the ammonia, implying ammonia is absorbed by algae with preference. While chlorophyll *a* was positively correlated with TP and DIP in the Sumjin River, negative correlations of these parameters was observed in the Youngsan River. The pattern in concentration of nutrients was found to be related with land use and domestic sewage in the study area. Inter-parameter relationships may be strongly influenced by geographical factors relative to temporal factors.

INTRODUCTION

Nutrient concentrations often vary seasonally due to influences of anthropogenic inputs, hydrology, and the growing seasons of algae and macrophytes. Major anthropogenic sources causing freshwater eutrophication are animal farming, urban and agricultural runoff, sewage effluents and industrial wastes. As a result, significant increases in the concentration of nutrients (e.g., N, P) and the abundance of primary producers (e.g., phytoplankton, benthic algae and macrophytes) have occurred around the world's freshwater (Harper, 1992; Biggs, 2000; Wetzel, 2001). In Korea, it is now a recognized problem of water quality deterioration (Kim et al., 1998). Phosphorus and nitrogen are the most important parameters that exhibit the current state of water quality. Elevated P concentrations in rivers have been linked to increasing rates of plant growth, changes in species composition and proliferation of planktonic and epiphytic and epibenthic algae, resulting in shading of higher plants (Mainstone and Parr, 2002). Total P input to surface water has decreased in Korea due to an effective reduction of point sources in recent years. Nevertheless, P input from diffuse sources remains constant or is even increasing. Non-point sources are believed to be the major source of river water pollution, accounting approximately 70 % of total suspended solids (Choi et al., 1994) and 80 % of the TP inputs (Kim and Choi, 1996). In a national P budget analysis of Korea, the discharges from fertilizer, animal excretion and human resources were estimated to contribute 56 %, 31 % and 13 % of total P generation, respectively (Kim, 2002). Intensification of agriculture has increased allochthonous nutrients to farming systems. Although animal wastes are applied to arable land, arable farming is predominantly based on more reliable inorganic nutrients. This has led to a corresponding increase in nutrient loss from the system in the form of discharges to land and water. One of the most common results of agricultural intensification is the increased input of nutrients to streams (Kemp and Dodds, 2001). In most cases, agricultural land use alters the physical structure and chemical

characteristics of streams, which in turn affect the composition of biological communities (Quinn, 2000; Allan, 2004).

The composition and characteristics of water in rivers and streams is determinative and crucial for the structure and function condition of aquatic ecosystems. For example, the concentration level of ammonia in water is an indicator of pollution level. The presence of nitrate and nitrite anions in high concentrations together with high P causes excessive growth of algae. While a moderately high nitrate concentration may help to retain P in the sediment, because of its positive effect on redox and the binding capacity of Fe (Jensen and Andersen, 1992), a high nitrate level may promote P release by stimulating the mineralization of organic matter and thus enhance periphyton and phytoplankton growth. In case of P, $\text{PO}_4\text{-P}$ comprised the largest fraction of total P in water. The relatively high percentage of $\text{PO}_4\text{-P}$ is somewhat unusual compared to most rivers and lakes (Wetzel, 2001) and may be related to the near absence of clay sediments which tend to adsorb $\text{PO}_4\text{-P}$. The P content of DOM is characteristically variable because, unlike N, P is not the integral part of all molecules of dissolved humic substances. Instead, the organic P content is carried by more specific substances that can vary more than other components of the DOM (Qualls and Haines, 1991). Though TP and TN measures may be an overestimate of nutrient bioavailability, these forms are more often measured in monitoring programs than the suite of dissolved inorganic forms. The TP and TN concentrations give a better indication of ultimate bioavailability than dissolved N and P concentrations (Dodds, 1993). Further, TP and TN have been found to relate more strongly to algal biomass than dissolved inorganic P or N (Dodds et al., 1997).

Among the five big rivers in Korea, the River Youngsan and the River Sumjin, the two major rivers run across from the middle to the southern part of the country are being polluted directly or indirectly. Their tributaries contribute to

their pollutions by carrying pollution loads in appreciable quantities. The objectives of this study was to measure variations in important limnological parameters especially on P and N fractions and their impacts on the river ecology and water quality in the Youngsan and the Sumjin River, and highlight some of the key issues facing these aquatic systems.

MATERIALS AND METHODS

Study sites

The river Youngsan and the Sumjin are located in the middle to the southern part of Korea between 35°20' and 35°15'N and between 126° and 127° E. They have watershed area of 3,522 km² and 4,897 km², respectively. Due to natural topography and river regulation the slope of the water surface is low. Although the external nutrient loading decreased in 2000s, the concentrations of P and N are still elevated. The average annual rainfall is 1200 mm year⁻¹ in Korea. Half of the annual precipitation concentrated in the summer monsoon. The regular seasonal front stays in southern Korea in July, and typhoons are common in August. Therefore the ratios of the flow rates between rainy and dry days were very high. In Korea, the river bank erosion is very low due to rocky structure that predominates near the shoreline. The land uses within the river basin largely consists of residential, industrial, commercial, livestock, pasture, row crops and forestry and water. Approximately 70 % of the Korean peninsula is covered by forests. Most of the soils of Korea derive from granite and gneiss. Sandy and brown-colored soils are common, and they are generally well-leached and have little humus content. However, the soils in the watershed areas of the Youngsan River and the Sumjin River belonged primarily to the saline series and were categorized as entisols and inceptisols according to USA comprehensive system of soil classification (Soil Survey Staff, 1975).

Sample collection and analysis

Water samples were collected at 8 sampling sites of each of the Youngsan and the Sumjin River. Out of eight sampling sites of each river, 5 sites were from the main stream and three sites were from their tributaries. Water samples were collected in June, August and December of 2006, and February of 2007.

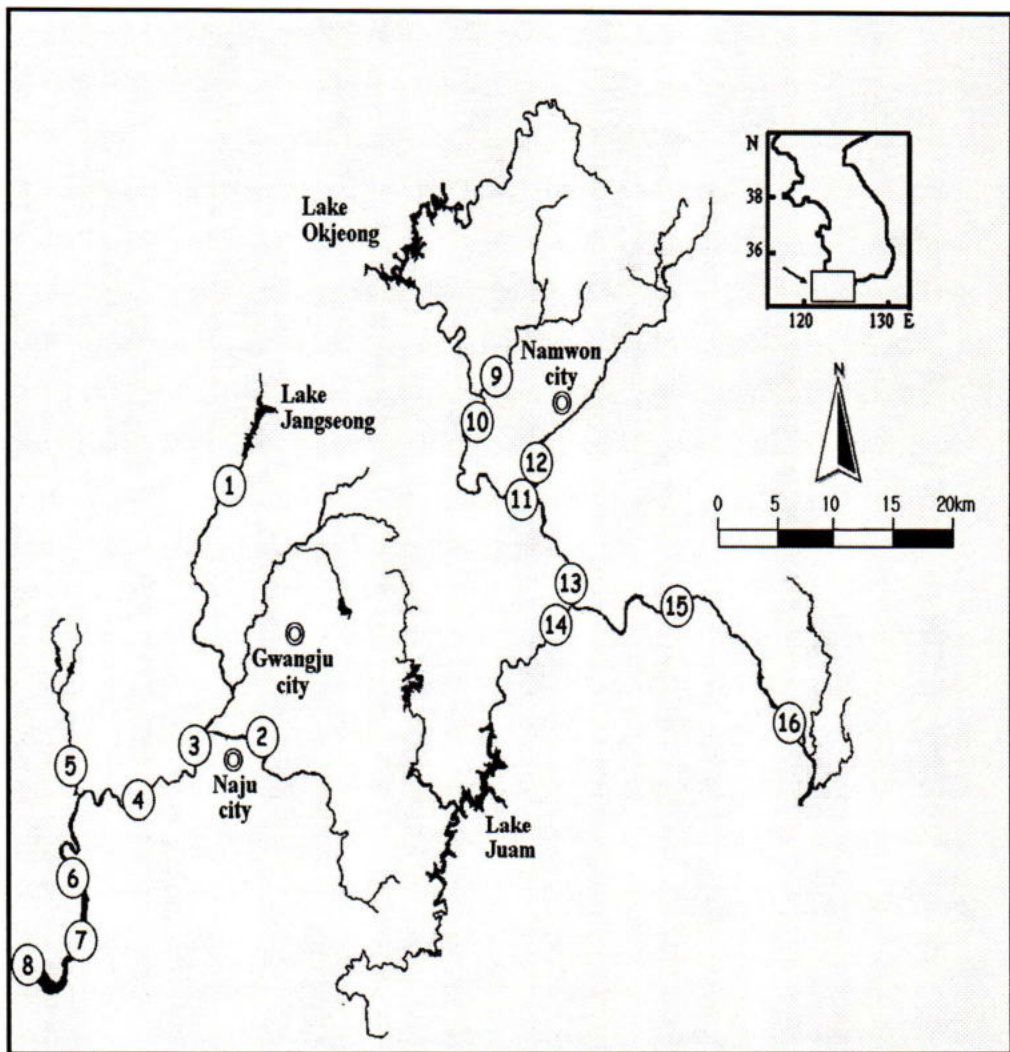


Figure 1. Map of the sampling sites of the Youngsan River (site no. 1-8) and the Sumjin River (site no. 9-16). Different numbers representing the sampling sites are: 1= Hwangryong, 2 = Jiseok, 3 = Naju, 4 = Youngsanpo, 5 = Hampyeong, 6 = Muan, 7 = Lake Youngsan 2, 8 = Lake Youngsan 1, 9 = Osu, 10 = Jeokseong, 11 = Namwon, 12 = Yo, 13 = Gokseong, 14 = Boseong, 15 = Gurye and 16 = Hadong.

used to evaluate the N: P ratio and assess the seasonal (summer and winter) differences and also to relate with other limnological characters.

Temperature, pH and EC were measured in situ with a YSI model 600 multi-parameter water analyzer. Alkalinity (bicarbonate + carbonate) was determined by titrating to pH 4.5 with hydrochloric acid within less than 8 to 10 hr of sample collection. Dissolved oxygen (DO) was measured by DO meter. For the measurements of biological oxygen demand (BOD), sample aliquots were incubated in 300 ml glass BOD bottles at 20°C for 5 days in the dark. For chemical oxygen demand measured by permanganate (COD_{Mn}) method, samples of 30 ml were treated with 5 mN KMnO_4 in 1 % NaOH for 1 hour at 121 °C in an autoclave. Total suspended solids (TSS) were determined gravimetrically by filtration and drying. For analysis of chlorophyll *a*, aliquots of the samples were filtered through

GF/F filters, which were kept frozen. The filters were then ground with a tissue homogenizer in 90 % acetone and centrifuged to remove turbidity. Concentrations of chlorophyll *a* were determined by the spectrophotometric method (UNESCO, 1966). Paired t-test was used to evaluate seasonal differences in the values of some parameters. Correlation coefficients were calculated to establish significant relationships between some physicochemical parameters and some biological variables.

seasonal fluctuation was due to the effect of temperature on the solubility of oxygen to water. Throughout the study period, BOD ranged from 0.70 to 8.9 mg O₂ l⁻¹ and 0.30 to 2.9 mg O₂ l⁻¹ in the River Youngsan and the Sumjin, respectively. The value of COD ranging between 5.3 to 11 mg O₂ l⁻¹ and 3.1 to 7.9 mg O₂ l⁻¹, respectively in the Youngsan and the Sumjin River determined were relatively high. As expected, COD values for all water samples examined were higher than those obtained for BOD, as the latter deals only with the oxidation of biodegradable organic matter.

pH, conductivity and alkalinity

Examined surface waters were within the neutral to alkaline pH range (pH=6.4-9.4 in the Youngsan River and pH= 6.1-8.9 in the Sumjin River). A change in river water pH also affect the portioning of P between dissolved and particulate phases. Since a large fraction of inorganic particulate P in the river is associated with Al (37 %) and Fe (47 %) oxides (Lebo, 1991), the pH dependence of DIP adsorption serves as P partitioning in the aquatic system. In the pH range of natural waters (6-8), DIP adsorption onto iron and aluminum oxides decrease by 15-30 % for an increase of one pH unit (Crosby et al., 1984).

Conductance qualitatively indicates the status of inorganic pollution and is a measure of ionized species in the waters. Throughout the study period, St. 3 and 4 recorded higher EC values (data not shown) than the other 6 sites of the Youngsan River. While the highest value of EC in the Sumjin River was 12225 $\mu\text{S cm}^{-1}$ at St. 12. The high values might be associated either with wastewater discharges from local plants or domestic sewage.

Table 1. Limnological parameters of the Youngsan River and the Sumjin River from June 2006 to February 2007.

Parameters	unit	Youngsan River				Sumjin River			
		Min.	Max.	Mean	SD	Min.	Max.	Mean	SD
pH		6.4	9.4	8.02	0.76	6.1	8.9	7.8	0.7
Temp.	(°C)	3.8	32.5	15.9	10.77	2.1	32.4	13.1	10.31
EC	μScm^{-1}	31	1491	364	397	24	12225	888	2781
TSS	mg l^{-1}	6	55	27.6	41.36	1.5	29.3	8.36	7.59
Alkalinity	$\text{mg CaCO}_3 \text{l}^{-1}$	29	99	52.7	17.61	19	59	39.78	9.87
DO	$\text{mg O}_2 \text{l}^{-1}$	6.3	12.6	9.5	1.75	7	12.5	9.66	1.3
BOD	$\text{mg O}_2 \text{l}^{-1}$	0.7	8.9	3.3	2.2	0.3	2.9	1	0.55
CODMn	$\text{mg O}_2 \text{l}^{-1}$	5.3	11	8.03	1.53	3.1	7.9	5.53	1.38

Total alkalinity was also higher in the effluent receiving water bodies as a result of the contribution of carbonates and bicarbonates. However, the maximum and the minimum values of the Youngsan and the Sumjin River were 99 and 59 mg CaCO₃ l⁻¹ and 29 and 19 mg CaCO₃ l⁻¹ respectively. This buffering capacity is mainly attributable to weak bases such as HCO₃⁻, CO₃²⁻, borates, and to a lesser extent to OH⁻, as well as to species often present in small concentrations such as phosphates, ammonia, silicates (Broecker and Peng, 1982), or organic bases (Cai et al., 1998).

Distributions of phosphorus and P fractionation

DIP concentration was elevated above more pristine temperate rivers, with maximum value clearly associated with municipal inputs into both the Youngsan River and the Sumjin River. As a consequence of these inputs, DIP was the dominant fraction (Table 2) throughout the Youngsan River (57 %) and the Sumjin River (38 %), as it is in other urban rivers (Meybeck et al., 1988; Wulff and Rahm, 1988; Heejun, 2005). The concentrations of PO₄-P in natural surface waters are generally in the range of 0.005-0.020 mg l⁻¹ and the concentration as low as 0.001 mg l⁻¹ may be found in some pristine waters and it may be as high as 200 mg l⁻¹ are in some enclosed saline waters (Chapman and Kinstach, 1996). At St. 3 and 4 of the Youngsan River, there were remarkable variations of DIP concentrations during the study period (Figure 2). In most cases in both the rivers there were a high DIP values during summer, low values during this period might be associated with the increase of flow rate. Possible explanations of DIP increase during winter in some sites could be due to lower river discharges, increase in P inputs, or a change in the portioning of P between dissolved and particulate phases in the river. Increase in agricultural and urban land uses would probably increase discharge of inorganic P and N species due to fertilizer application and / or sewage discharge. However, temporal changes of nutrients were complex and affected by many discharge, transport and transformation

processes. Many site-specific characteristics such as flow, redox and soil features and also forest and wetlands are likely related to the temporal changes of nutrient species. Rainfall variation between seasons was believed to affect flow fluctuation remarkably and thus influence nutrient concentrations. Downstream of low DIP concentrations, POP (particulate organic P) increased to a maximum in the upstream and accounted for 34 % of TP in the Youngsan River and 47 % in the Sumjin River (Table 2). However, the winter decrease in most sampling sites of DIP in both the river could be due to utilization by phytoplankton or low discharge of pollutants in the river water from different point and non-point sources. Some exceptions were at St. 3 and 4 of the Youngsan River and at St. 12 of the Sumjin River.

Variations in water-flow and channel geomorphology may also affect distribution and transport of particulates (Horowitz, 1996). The potential for degradation of samples and the rate of transformations particularly in relation to DIP and DTP are highly variable, and are linked to a variety of factors associated with sample composition, which may include initial P concentrations, matrix chemistry, biological status of the sample and the content of organic matter, sediment and colloids. For one thing, it is a lot easier to measure concentrations in the water than fluxes into a system. If we elect to use this approach to assessing eutrophication status, it is important to measure TP in the surface waters. The concentrations of TP were steeper at St. 3, 4 and 6 of the Youngsan River during winter than the other sampling sites while it was higher at St. 10 and 11 during summer, the mainstreams of the Sumjin River. High TP concentrations can be attributed to P inputs and a high suspended solid concentration, leading to relative peaks in TP. Both these phenomena can be explained by anthropogenic inputs, sedimentation and resuspension of particulate matter. Compared to other sites, St. 3, 4 and 6 of the Youngsan River, and St. 10 and 11 of the Sumjin River are densely populated and potential agricultural productive zones. And elevated concentrations of nutrients from different point and non-point sources could be

minerals and solid carbonates. Dispersion of the finer suspended fraction can be quite extensive while the dissolved fraction follows that of the freshwater plume and may be spatially more extensive. Seasonal variations of DOP concentrations were small compared with DIP. As with average distribution during the study period, DOP was relatively constant. However, surface water DOP concentrations were highest near the mouth of the river and decreased with distance away from the river during both the seasons (Figure 2). In the Sumjin River, St. 10 and 11 showed higher DOP values (above $20 \mu\text{g l}^{-1}$) while the others had the similar concentrations. POP values were also high at the upstream sites which was followed by downstream in both the rivers. Relative proportions of different P fractions varied widely in both the rivers. However, during the study period in the Youngsan River, DIP: TP ratios were relatively high in winter while DOP: TP were fairly constant (0.08-0.09). The POP: TP ratios were relatively high in summer than winter indicating the storm water effect during summer. In case of Sumjin River, DIP: TP ratio was relatively low compared to the ratio of Youngsan River. It is interesting that the POP: TP, DOP: TP and DIP: TP ratios in the Sumjin River were almost constant during summer and winter.

Geology, land use, agriculture and sewage inputs have a major control on river water quality in terms of matrix chemistry, P and suspended sediment concentrations. During high flow conditions, particulate forms of P should dominate while under low river flows the emphasis would be expected to shift towards dissolved P (Hilger et al., 1999). However, it is evident that variation in water temperature, conductivity and loads of particulate matter could explain a substantial part of the total variation in river ecosystem. In both the rivers, concentration levels of P species varied with a large amplitude of a few tenths to a few $\mu\text{g l}^{-1}$ with a decreasing order: TP, POP, DIP and DOP.

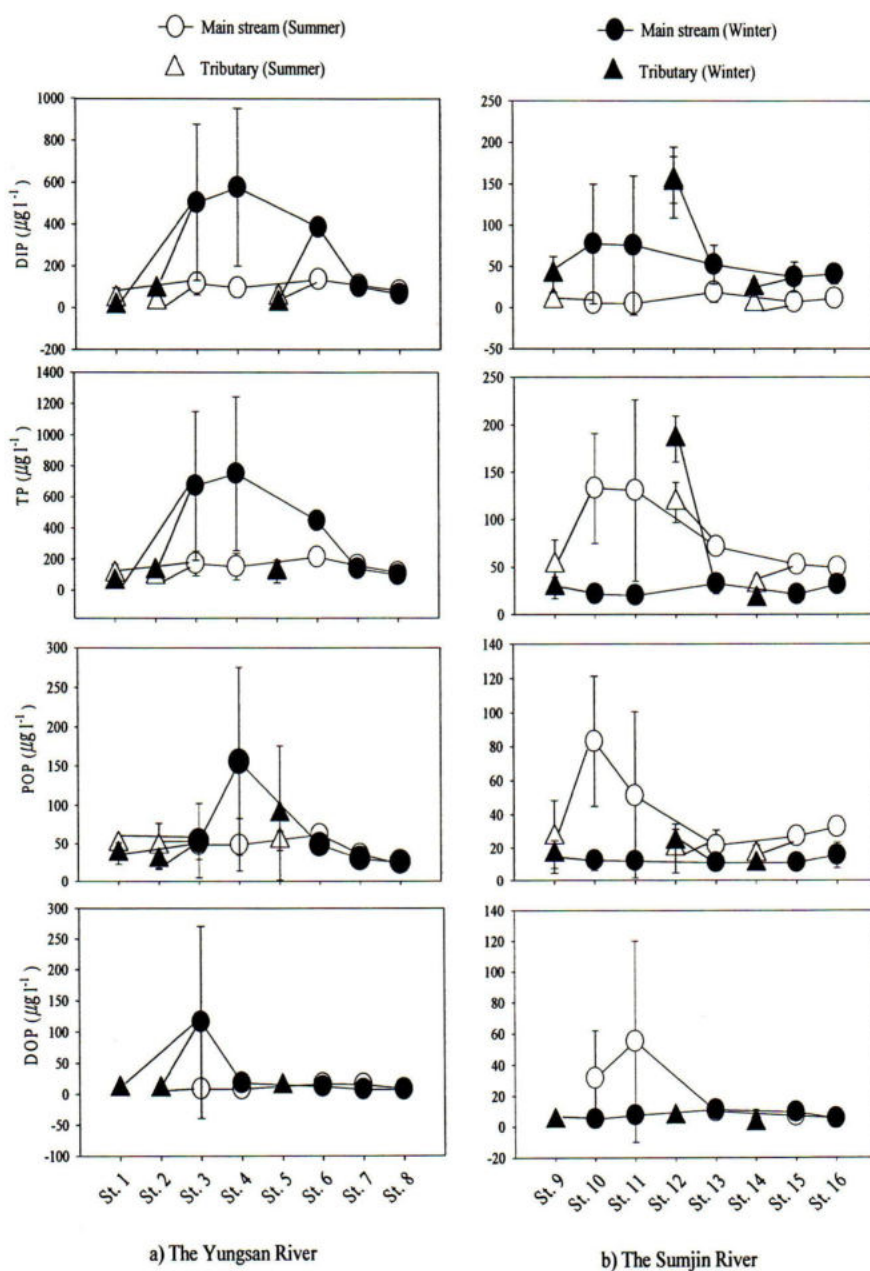


Figure 2. Concentrations of DIP, TP, POP and DOP of the a) Yungsan River and b) Sumjin River during summer and winter seasons in the year of 2006-2007. Bars indicate the standard deviation with mean.

Table 2. Relative proportions of different phosphorus fractions during the study period.

River	Summer		
	POP:TP	DOP:TP	DIP:TP
Youngsan	0.37	0.09	0.54
Sumjin	0.45	0.17	0.39
	Winter		
	POP:TP	DOP:TP	DIP:TP
Youngsan	0.32	0.08	0.60
Sumjin	0.48	0.24	0.38
	Mean value		
	POP:TP	DOP:TP	DIP:TP
Youngsan	0.34	0.09	0.57
Sumjin	0.47	0.20	0.38

Distributions of nitrogen and its fractionations

Total ammonia N was higher in the sampling sites receiving large amounts of city effluents. Total ammonia N (TAN) is composed of unionized $\text{NH}_3\text{-N}$ and $\text{NH}_4^+\text{-N}$ (Cole and Boyd, 1986), and the proportion of $\text{NH}_3\text{-N}$ is known to increase with temperature and pH and this probably accounts for the high values of total ammonia N (TAN) recorded in the dry season although exceptions were there at some sampling sites of the Youngsan River. At St. 3, the concentration of NH_3 was the highest followed by the downstream of the Youngsan River (Figure 3). This means the pollution load in the mouth of this river which was gradually declined. While in the Sumjin River this was at stable condition except the downstream sampling site St. 16. It is well known that $\text{NH}_4^+\text{-N}$ present in the wastewater/water is readily transformed into NO_x species under consumption of oxygen (Wolter, et al., 1985). The reaction rate of nitrification is strongly influenced by water temperature. Moreover, $\text{NH}_4^+\text{-N}$ is the nitrogen species that is first consumed by algae. Negative correlation between chlorophyll *a* and $\text{NO}_3^-\text{-N}$ values suggest that N mineralization due to algal death during the study period in the Youngsan River.

Elevated N levels in rivers are typically associated with agricultural fertilizers, plant and animal wastes or industrial effluents. In both the rivers, the $\text{NO}_3^-\text{-N}$ concentrations were high compared to the freshwater pristine rivers. $\text{NO}_3^-\text{-N}$ concentration was higher in the river Youngsan at St. 3 and 4 during summer, with concentrations exceeding 1.5 mg l^{-1} while in the Sumjin River, the highest concentration was at St. 10 in summer. It has also been reported that when NO_3^- comprises a substantial fraction of dissolved inorganic N, it may indicate diffuse agricultural sources of N (Martinelli et al., 1999). In the Youngsan River, upstream concentration was relatively high which gradually decreased up to the downstream sampling site St. 7 and then a sudden increase at St. 8.

Sudden increase can be attributed to the high concentration of nitrate added some point and non-point sources to this site and/ or low-flow condition and accumulation of nitrate received from different point and non-point sources at the upstream sites. In the Sumjin River, little variation of nitrate concentration was observed in the mainstream while the two tributaries had almost the same nitrate concentrations. Discharge and release of NO_3^- -N from different sources are, however, still within the assimilative capacity of both the rivers. The seasonal variation that was observed in the river basin might originate from land and domestic sewage in response to the natural and anthropogenic activities in the terrestrial ecosystem.

Even though the dilution effect of high discharges during summer, high NO_3^- -N concentration means that storm water runoff may be most important contributing factors of N derived from diffuse sources (e.g., N release from agricultural field). However, the concentrations of N species were typically found at a narrow band of a few mg l^{-1} with a decreasing order: TN, NO_3^- -N, DON, PON and NH_4^+ -N. Nearly all sampling sites, the dominant soluble N form was NO_3^- -N followed by NH_4^+ -N and NO_2^- -N.

Nitrite levels in the mainstream of the Youngsan River were relatively high compared to the tributaries. In tributaries this levels was as little as zero. Concentrations of nitrite in the Sumjin River were also high in the upstream while the two tributaries showed higher than the mainstream. In the winter, its concentration was very low indicating the less or absence of biodegradable organic pollutants in the region. The low concentration of NO_2^- , together with the reduced COD and BOD values indicate that both the rivers are not markedly affected by organic discharges.

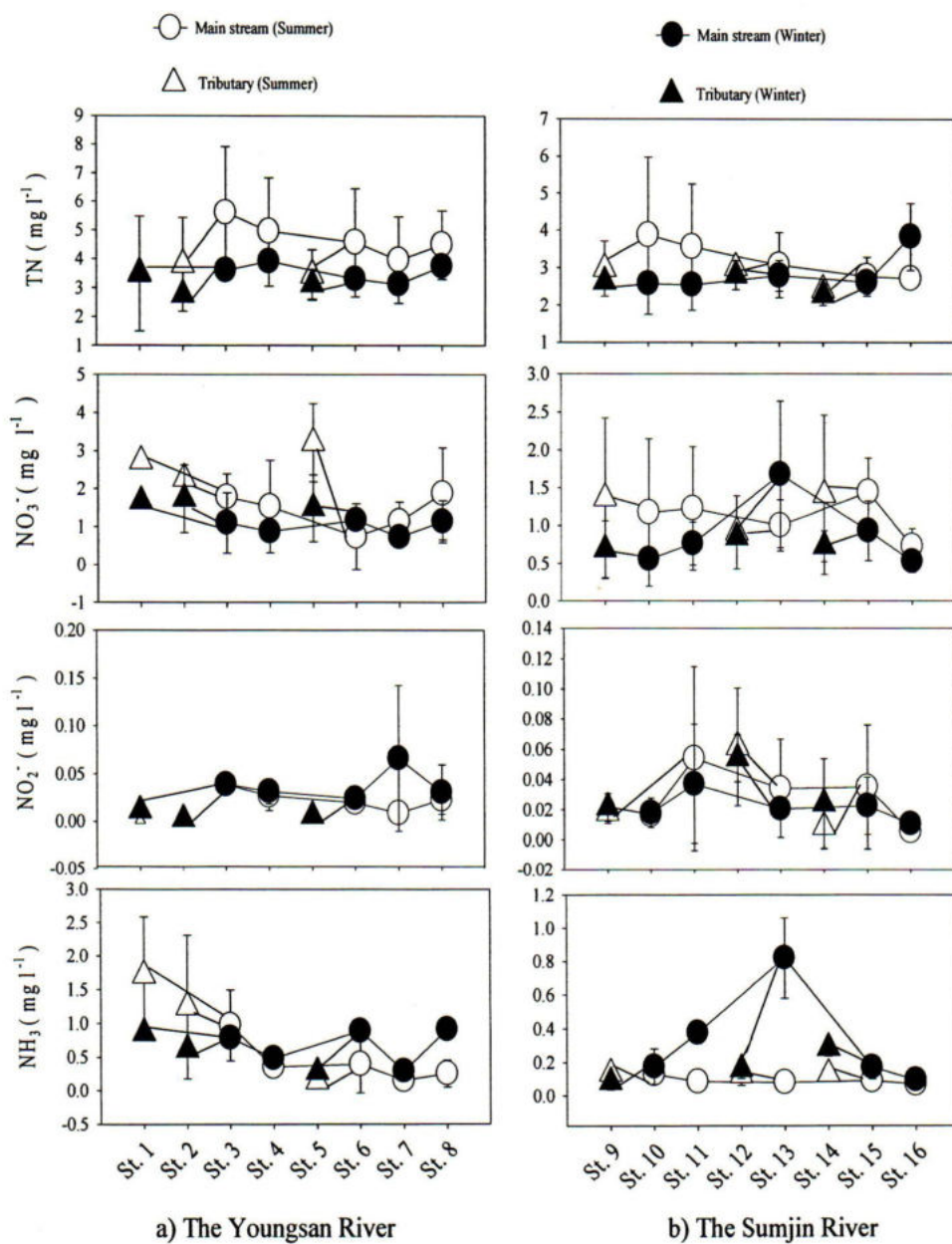


Figure 3. Concentrations of NO_3^- , NO_2^- , NH_3 and TN in the a) Youngsan River and b) Sumjin River during the study period. Bar reflects the standard deviation with mean.

At different sampling sites of both the rivers, TN was also in the similar trends of NO_3^- and NO_2^- concentrations, respectively. During summer, TN content of the Youngsan River was high at the upstream sampling station St. 3 which was followed by St. 4 and other downstream sampling sites. Like TP, the TN concentration at St. 8 was little bit high which could be due to accumulation of the whole river, or low flow condition and/or addition of point or non-point sources of pollutants either with one or combination of all reasons. In both the rivers, TN concentrations of the tributaries were relatively low compared to the mainstream sampling sites.

Evaluation of N: P ratio

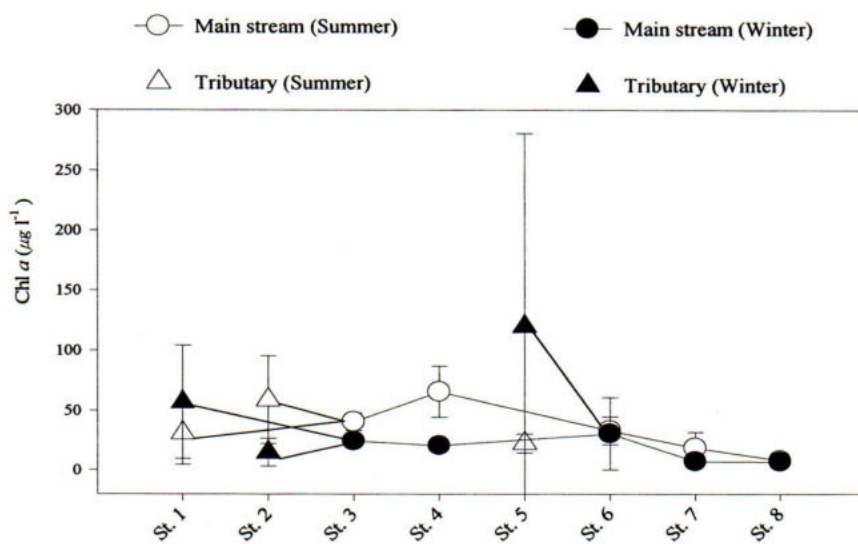
N: P molar ratios were calculated in order to evaluate the relationships between N and P cycling as many researches have been conducted on it (Gardner et al., 1996). In both the rivers, the $(\text{NO}_3^- + \text{NO}_2^-)$: DIP varied considerably with approximately 1/8th with low ratios (Figure 4). In winter, the ratios were all consistently low indicating the possibility of some N stress in the system reflecting N limitation during periods of low flow, when there is more seawater influence in coastal areas (Motazavi et al., 2000; Labry et al., 2002). The consistency of this ratio suggests that there is a strong relation between inorganic P and N, however ratios change with the seasons due to decreased riverine nutrient concentrations during low winter river flows and less bacterial mineralization of refractory DON (Lohrenz et al., 1997). Since the N: P ratios fluctuate widely over time, it is not possible to define N: P descriptive of a given river or even a particular sampling site of a given river. Temporary states of N limitation or P limitation or of approximate balance in N and P may occur over time. This may be due in part to the variability of nutrient concentrations in many rivers and possibly to the different abilities of organisms to make efficient use of the varying concentrations (Jarvie et al., 1998). It should be noticed that the N/P ratio simply shows the likelihood for either P-limitation or N-limitation

conditions, however, it is not indicative of the nutrient concentration levels. There is a clear difference in the N: P ratio among the 16 sampling sites. The molar ratio of TN: TP and DTN: DTP of almost all sampling sites were above the Redfield ratio, although there were some exceptions in both the rivers (Table 3). Most of the sampling stations in both the seasons, the N: P ratio is greater than 16, reflecting the P limitation of phytoplankton growth in both the rivers. Stockner and Shortreed (1988) reported that the development of N-fixing cyanobacterial bloom is dependent on both a low N: P supply ratio and a sufficient P supply. During winter when mean nitrate concentrations at St. 3, 4 and 6 of the Youngsan River are compared with the corresponding DIP values, the average dissolved inorganic ratio of N: P is lower than the Redfield ratio of 16:1 for average plankton biomass. Therefore, it is reflecting that P is not the first nutrient to limit phytoplankton growth during the winter period. It should be mentionable that the waters of streams and rivers are constantly flowing and changing composition as well as flow rate. High inorganic-to-organic ratios of N relative to P appear to be consequences of the general chemical properties of N and P in aqueous phase. It has been documented previously that the dominant portion of aqueous P tends to bound preferentially with particulate phase, while that of N with dissolved phase. Analysis of DTN and DTP composition showed that DON and DOP in both the rivers were relatively low suggesting the dominance and availability of orthophosphate and nitrate and/or ammonium ions. The amount of DON incorporated into DTN was significantly higher than the amount of DOP incorporated into DTP. Therefore, the predominance of DON or DOP could be either the discharge from agricultural practices or domestic sewage or both the two.

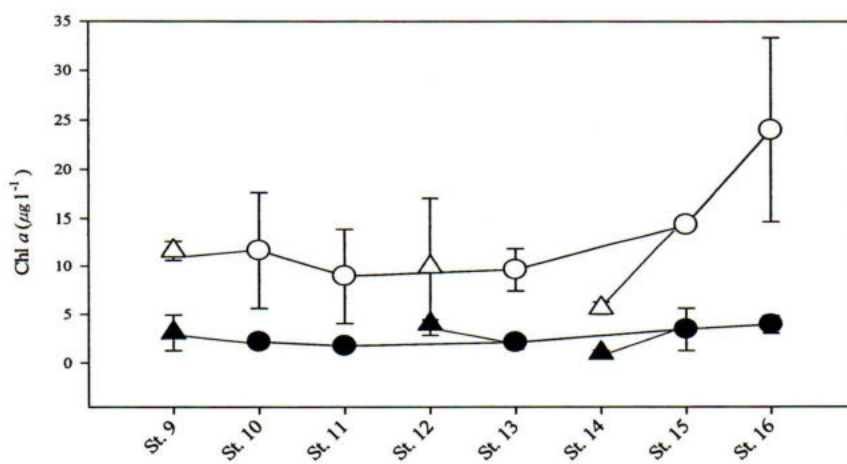
Table 3. The TN: TP ratio (atomic ratio) of the Youngsan River and the Sumjin River during summer and winter seasons.

Rivers		Sites	Summer	Winter	Summer	Winter
			TN:TP	TN:TP	DTN:DTP	DTN:DTP
Youngsan River	Main stream	St. 3	72	12	378	11
		St. 4	73	12	293	11
		St. 6	48	16	255	13
		St. 7	55	51	203	47
		St. 8	89	86	316	87
	Tributaries	St. 1	75	151	162	425
		St. 2	98	50	197	52
		St. 5	68	58	205	179
		St. 10	64	265	190	507
		St. 11	60	281	173	544
Sumjin River	Main stream	St. 13	95	189	172	224
		St. 15	116	275	141	481
		St. 16	121	269	155	415
		St. 9	126	208	184	408
	Tributaries	St. 12	56	33	178	32
		St. 14	171	314	144	314

although the correlation coefficients were weak in both the cases (Table 4). Negative correlations were found between TP and chlorophyll *a*, DIP and chlorophyll *a* in the Youngsan River while the aforementioned correlations were positive in the Sumjin River. Possible explanations could be only the flow rate of the Youngsan River although the overall DIP, DTP and TP concentrations of it were very high compared with the Sumjin River. TN was significantly in positive correlation with BOD, COD and TSS in both the river.



a) The Youngsan River



b) The Sumjin River

Figure 5. Chlorophyll *a* at different sampling sites in the a) Youngsan and the b) Sumjin River water during summer and winter season.

Table 4. Pearson correlation coefficients between nutrient concentrations and limnological parameters in the a) Youngsan River and b) Sumjin River; in each river n=32; units of each parameter are: TSS (mg l⁻¹), Chl *a* (µg l⁻¹), P species (µg l⁻¹), N species (mg l⁻¹) and the units of the rest parameters are in Table 1

a) The Youngsan River.

	Temp	pH	EC	DO	BOD	COD	TSS	Chl <i>a</i>	DIP	TP	TN	NO ₃	TNH ₃
Temp	1												
pH	-0.08	1											
EC	-0.42	0.07	1										
DO	-0.58	0.48	0.20	1									
BOD	-0.13	-0.19	-0.26	0.20	1								
COD	-0.30	-0.45	-0.19	-0.07	0.50	1							
TSS	-0.01	-0.38	-0.26	-0.17	0.54	0.44	1						
Chl <i>a</i>	0.001	0.40	-0.19	0.30	0.54	-0.11	0.06	1					
DIP	-0.29	-0.21	0.15	0.26	0.25	0.21	-0.06	-0.17	1				
TP	-0.27	-0.16	0.13	0.30	0.31	0.20	-0.08	-0.06	0.99	1			
TN	0.02	-0.70	-0.36	-0.32	0.50	0.57	0.67	-0.12	-0.01	-0.02	1		
NO ₃	0.27	-0.40	-0.33	-0.49	0.14	0.18	0.30	-0.19	0.02	-0.02	0.62	1	
TNH ₃	-0.18	-0.37	-0.24	-0.03	0.75	0.68	0.67	0.17	0.09	0.084	0.60	0.28	1

b) The Sumjin River

	Temp	pH	EC	DO	BOD	COD	TSS	Chl <i>a</i>	DIP	TP	TN	NO ₃	TNH ₃
Temp	1												
pH	-0.18	1											
EC	-0.13	-0.02	1										
DO	-0.76	0.30	0.04	1									
BOD	0.09	-0.47	-0.12	0.03	1								
COD	-0.26	-0.08	0.14	0.39	0.64	1							
TSS	0.17	-0.35	0.04	-0.16	0.51	0.43	1						
Chl <i>a</i>	0.61	-0.14	-0.06	-0.56	0.34	-0.04	0.39	1					
DIP	0.01	-0.15	-0.12	-0.11	0.16	0.20	-0.06	0.002	1				
TP	0.19	-0.10	-0.15	-0.36	0.08	0.05	0.07	0.24	0.70	1			
TN	0.09	-0.38	0.33	-0.05	0.74	0.60	0.45	0.17	0.15	0.09	1		
NO ₃	0.17	-0.41	0.32	-0.14	0.72	0.66	0.56	0.26	0.25	0.15	0.87	1	
TNH ₃	-0.32	0.11	0.87	0.22	-0.06	0.25	0.05	-0.26	-0.09	-0.2	0.88	0.35	1

$r \geq 0.42$ means significant at $p = 0.01$; $r \geq 0.33$ means significant at $p = 0.05$;
 Italic values indicate significant relationships.

CONCLUSIONS

A large variability in nutrient fractions for both N and P was found among different sites of both the Youngsan and the Sumjin River. Closer examination of the data at different sampling sites confirms that agricultural activities and domestic sewages could be the major reasons of elevated N and P levels in both the rivers. In most cases, regardless of sampling stations, nutrient levels measured during summer appear to be larger than those during winter. It is noteworthy that TP levels in both the rivers were consistently high during summer relative to winter, with the exception at St. 3, 4, 6 and 2 in the Youngsan River and at St. 12 of the Sumjin River. The TN levels were more variable as a function of season and location. In addition, temporal changes of POP appear to vary in accordance with TP levels. The observations suggest that high POP levels during summer regardless of location and of relative dominance of POP over other dissolved P species suggesting total P budget of both the rivers may be strongly influenced by the input of particulate matters during the summer season. The abundance of DIP and DOP, and $\text{NO}_3^- + \text{NO}_2^-$ varies spatially in both the rivers, with the highest concentrations in upstream and the lowest in downstream in general. Flow-rate and temperature may be the most potential factor regarding to retention and transformation of nutrients. In both rivers, the decrease of N and P in the lower reaches was smaller and the spatial concentrations recorded upstream were steeper than downstream sites. Correlations with chlorophyll *a* and TP were weaker while the DIP was closely related to $\text{NO}_3^- + \text{NO}_2^-$. Pollutants from agricultural activities especially related to field crops and animal production, lower waste treatment capacity and shallow water level which are vulnerable to hydroclimatic variability. Increased inputs into the river systems from such activities emphasize the imbalances and alterations of aquatic communities as well as pollution. Thus the quantity and quality of nutrient input to the rivers need to be monitored to cope with the existing and future changes of land and urban development related to water quality.

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Chapter II

Organic Phosphorus Decomposition Rates in the Youngsan River and the Sumjin River, Korea

ABSTRACT

The variability in phosphorus concentrations and the decomposition rates of organic phosphorus were measured in two rivers, the Youngsan River and the Sumjin River through four surveys in June, August and December of 2006 and February of 2007. Water samples were incubated for 20 days in a dark incubator and the change of forms of phosphorus such as particulate organic phosphorus (POP), dissolved organic phosphorus (DOP) and dissolved inorganic phosphorus (DIP) were analyzed. By fitting the change to four types of models the decomposition rates of organic phosphorus were determined. The mean total organic phosphorus (TOP) decomposition rate coefficients in the Youngsan River and the Sumjin River were 0.036 day^{-1} and 0.035 day^{-1} , respectively. In POP→DIP model, the average decomposition rate coefficients in the Youngsan River and the Sumjin River were 0.049 and 0.035 day^{-1} , respectively. The average POP decomposition rate coefficients of POP→DOP→DIP model were 0.042 day^{-1} and 0.038 day^{-1} in the Youngsan River and Sumjin River respectively while the mean DOP decomposition rate coefficients were 0.255 day^{-1} and 0.244 day^{-1} , respectively. In the Youngsan River, the mean POP→DOP decomposition rate coefficient and POP→DIP decomposition rate coefficient of POP→DOP→DIP, POP→DIP model were 0.039 day^{-1} and 0.007 day^{-1} , respectively. And in the Sumjin River, the above decomposition rate coefficients were 0.031 day^{-1} and 0.004 day^{-1} , respectively. The decomposition rate coefficients measured in this study might be applicable for modeling of river water quality.

INTRODUCTION

The decomposition of organic phosphorus in natural water is determined by a large number of physical driven transformation processes. Many of these processes are known in principle but often the decomposition rate can hardly be measured with a sufficient spatial and temporal resolution. Phosphorus is introduced into the aquatic environment in a number of different forms, and has been described as being present in the dissolved phase as a small fraction of the total and in the particulate phase as a large fraction of the total. Each fraction is made up of a large number of different components, most of which may change between their dissolved or particulate state. POP and DOP forms undergo bacterial decomposition (mineralization) and the P is transferred into the soluble orthophosphate pool. Depending on environmental conditions, stored nutrients could be released from organic matrix via mineralization and recycled through the ecosystems or exported from them.

Phosphorus attached to particles (i.e. PP) is not immediately available for growth and a variety of physical, chemical and biological processes influence the bioavailability of this P fraction. In general, PP is much more variable than dissolved P. Storm events are extremely important for PP dynamics because large portions of annual stream PP loads can be transported attached to sediment and organic matter during only a few major events (Long and Cooke, 1978; Brett et al., 2005a). Decomposition of plant detritus involves stepwise conversion of complex organic molecules to simpler organic and inorganic constituents by processes including abiotic leaching (Harrison and Mann, 1975; Benner et al., 1985), fragmentation (Boulton and Boon, 1991), extracellular enzymatic hydrolysis (Cunningham and Wetzel, 1989; Linkins et al., 1990), and aerobic and anaerobic catabolic activities of microorganisms (Oremland, 1988; Kerner, 1993). As the disintegration of standing dead material proceeds, DOP and associated nutrients including dissolved organic C and dissolved organic N are released and

transported into the water column. On the other hand, water temperature has both economic and ecological significance when considering issues such as water quality and biotic conditions in rivers. Water temperature is one of the parameters that determine the overall health of aquatic ecosystems (Coutant, 1999).

In model calculation of decomposition phenomena, expressions are desired that are realistic in terms of both mathematical and biological behavior. Mathematical models are valuable tools to investigate the biogeochemical mechanisms and their interactions. Models that are primarily used for quantitatively describing processes relevant to P cycling in the environment, it would be beneficial to include more mechanistic detail. Modeling the decrease in organic P concentrations during decomposition process would be of special interest. Interrelationships between different P fractions contain one or more decomposition rate coefficients that are universal in some senses. However, there is little information available concerning the decomposition rate of organic P and its related constituents. A reasonable prediction of water quality for the river requires the decomposition rate of organic P present in the water bodies. The objectives of this study therefore were to assess the decomposition rates of organic P thereby influencing P availability for algal growth in the river water as well as the overall impacts of P in the river ecosystem.

MATERIALS AND METHODS

Study site

The Youngsan River and the Sumjin River are located in the middle to the southern part of Korea between 35°20' and 35°15' north and between 126° and 127° east. They have watershed area of 3,522 km² and 4,897 km², respectively. Although the external nutrient loading decreased in 2000s, the concentrations of P are still elevated. This is mainly due to ongoing emissions from point and non-point sources. However, in the year of 2006, the total precipitation recorded at the Namwon city near to the Sumjin River was 1381 mm and at the Gwangju city near to the Youngsan River, it was 1520 mm. Half of the annual precipitation concentrated in the summer monsoon. The ratios of the flow rates between rainy and dry days were very high. The river bank erosions were very low due to rocky structure predominates near the shoreline in both the rivers. The land uses within the river basin largely consists of residential, industrial, commercial, livestock, pasture, row crops and forestry and water.

Sample collection and analysis

Water samples were collected in 50 liters container at 8 sampling sites of each of the Youngsan River and the Sumjin River. The samples were collected in the month of June, August and December of 2006, and February of 2007. Water samples were filtered with 200µm mesh-sized net and were placed in dark condition at a constant temperature of 20°C for decomposition. In water quality modeling, reaction rates are usually measured at 20°C. Since decay reactions are temperature-dependent, we measured the DIP, DTP and TP concentrations of the water samples after decomposition at this constant temperature. All bottles and glasswares used were cleaned with P-free detergent (Extrans), rinsed three times with ultra-pure water (Milli-Q), soaked in 10% (v/v) HCl for at least 24 h, and finally rinsed three times with ultra-pure water. Aliquots of samples were taken from the containers for DIP, DTP and TP analyses. For the measurement of

organic P decomposition rate coefficient, DIP, DTP and TP concentrations were measured at 0, 1, 2, 3, 5, 7, 10, 15 and 20 days after the beginning of the incubation.

Dissolved and particulate fractions are usually distinguished by filtration through a 0.45 µm membrane filter, which separates most bacteria, algae and mineral particles from the dissolved phase but fails to separate colloidal particles. DIP was analyzed after GF/F filtration (0.45 µm) by applying the molybdenum blue method at 880 nm according to APHA (1998). DTP was estimated from filtered samples by measuring DIP after persulfate digestion (APHA, 1998). DOP was obtained by subtracting the DIP from DTP. TP was analyzed from the unfiltered sample as DIP after persulfate digestion and determined by ascorbic acid method according to APHA (1998). POP was calculated by subtracting the DTP from TP.

Model equations used in determining the decomposition rates of organic P

Various water quality models employ different algorithms for phosphorus cycles and kinetic equations. In this study following four different models were employed for simulating phosphorus cycle in river water. Each decay model was fitted to the data collected from incubation experiment and rate coefficients were determined by optimization. The determinations of coefficients were performed by iterative Runge-Kutta method programmed on EXCEL spreadsheet. The time step for iterative integration was set to 0.1 day.

Model 1; Total organic phosphorus → dissolved inorganic phosphorus (DIP)

$$\frac{d(TOP)}{dt} = -k_{TOP}(TOP) \dots \dots \dots (1)$$

Where, TOP= Total organic phosphorus concentration

k_{TOP} = TOP decomposition rate coefficient [day⁻¹]

t = decomposition time [day]

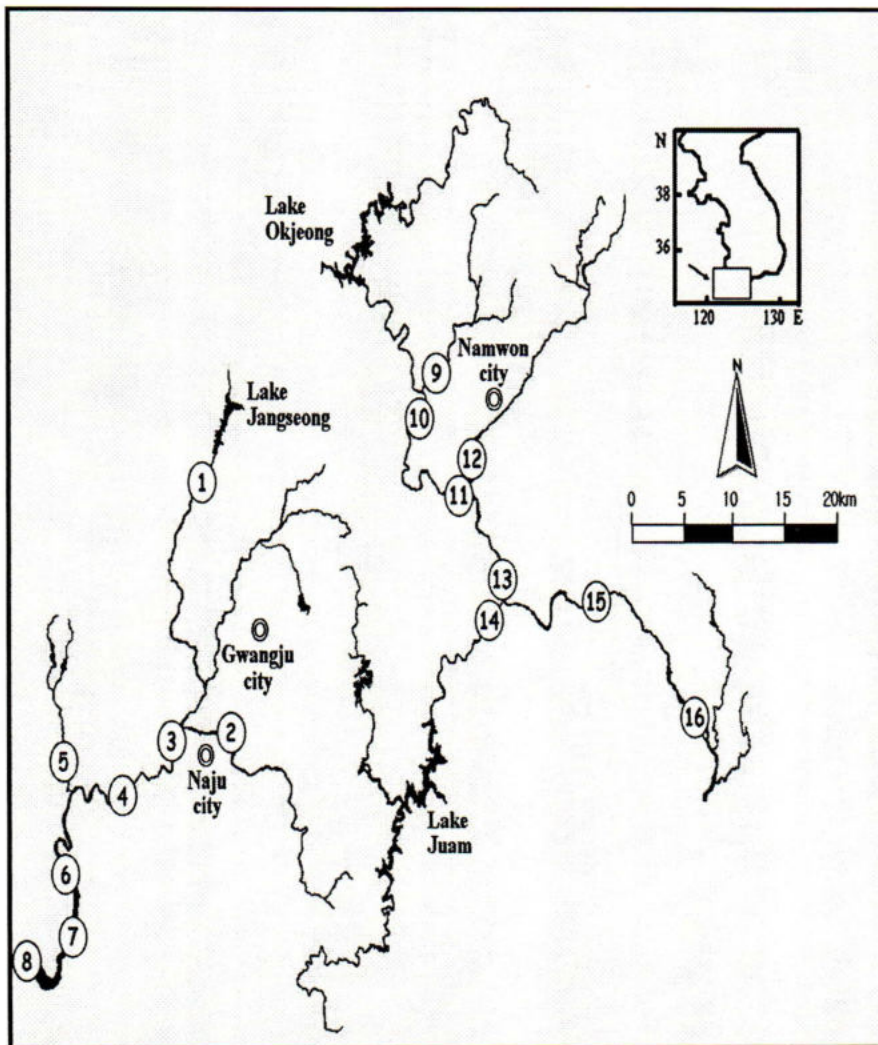
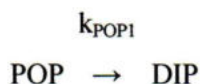


Fig.1. Map of the sampling sites of the Youngsan River (site no. 1-8) and the Sumjin River (site no. 9-16). Different numbers representing the sampling sites which are: 1= Hwangryong, 2 = Jiseok, 3 = Naju, 4 = Youngsanpo, 5 = Hampyeong, 6 = Muan, 7 = Lake Youngsan 2, 8 = Lake Youngsan 1, 9 = Osu, 10 = Jeokseong, 11 = Namwon, 12 = Yo, 13 = Gokseong, 14 = Boseong, 15 = Gurye and 16 = Hadong.

In the Model 1 organic phosphorus is not divided into any forms, and particulate organic phosphorus and dissolved organic phosphorus are assumed to be decomposed at the same rate. All the models employed in this study describe first-order reaction kinetics or exponential decreases. The assumption underlying the single exponential model can be expressed in two ways: either the absolute decomposition rate decreases as the amount of remaining substrate declines, or the relative decomposition rate remains constant. Intuitively, this assumption corresponds well with our experiences of many biological decay reactions including organic phosphorus decomposition.

Model 2; Particulate organic phosphorus (POP) → dissolved inorganic phosphorus (DIP)



$$\frac{d(\text{POP})}{dt} = -k_{\text{POP1}}(\text{POP}) \dots \dots \dots (2)$$

$$\frac{d(\text{DIP})}{dt} = k_{\text{POP1}}(\text{POP}) \dots \dots \dots (3)$$

Some water quality models employ only particulate organic matter and dissolved organic matter is not simulated as a state variable. In the Model 2 only particulate organic phosphorus is modeled and dissolved organic phosphorus is neglected. Particulate organic material such as phytoplankton is assumed to be decomposed directly into DIP.

Model 3; Particulate organic P (POP) → dissolved organic P (DOP) → dissolved inorganic P (DIP)



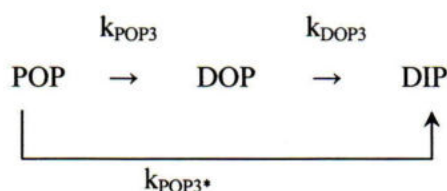
$$\frac{d(\text{POP})}{dt} = -k_{\text{POP2}}(\text{POP}) \dots \dots \dots (4)$$

$$\frac{d(\text{DOP})}{dt} = k_{\text{POP2}}(\text{POP}) - k_{\text{DOP2}}(\text{DOP}) \dots \dots \dots (5)$$

$$\frac{d(\text{DIP})}{dt} = k_{\text{DOP2}}(\text{DOP}) \dots \dots \dots (6)$$

In the Model 3 organic phosphorus was divided into POP and DOP. The basic concept of the model is that during decomposition process POP is first converted into DOP and then DOP is transformed into DIP or SRP (soluble reactive phosphorus).

Model 4; Particulate organic P (POP) → dissolved organic P (DOP) → dissolved inorganic P(DIP)



$$\frac{d(\text{POP})}{dt} = -k_{\text{POP3}}(\text{POP}) - k_{\text{POP3}^*}(\text{POP}) \dots \dots \dots (7)$$

$$\frac{d(\text{DOP})}{dt} = k_{\text{POP3}}(\text{POP}) - k_{\text{DOP3}}(\text{DOP}) \dots \dots \dots (8)$$

$$\frac{d(\text{DIP})}{dt} = k_{\text{DOP3}}(\text{DOP}) + k_{\text{POP3}^*}(\text{POP}) \dots \dots \dots (9)$$

In the Model 4 the pathway from POP to DIP was added to the Model 3. Therefore, POP is decomposed through two pathways; through DOP and directly to DIP.

RESULTS AND DISCUSSION

Distribution of organic P and its decomposition

The concentration of organic P showed high temporal and spatial variations at any station in both the Youngsan and the Sumjin River. During summer, POP was relatively high than winter indicating the storm water effect during summer. The relative fractionations is variable, however, the ratio is influenced strongly by such factors such as rainfall and antecedent soil moisture, in addition to soil type and vegetation cover. A number of studies have demonstrated that riverine P flux is largely attributable to the import of particulate P. In wet seasons nonpoint sources are believed to be the major source of P enrichment in river water, accounting approximately 70 % of total suspended solids (Choi et al., 1994) and 80 % of total P inputs (Kim and Choi, 1996). Changes in the agricultural practices may be a remarkable cause of the recent increase of phosphorus in the freshwater ecosystems.

The decomposition of the TOP, POP and DOP behaved nonlinearly as far as their stabilities in aquatic environment. Differences in overall decomposition rate of organic P were attributed to differences in the relative proportions of the labile and recalcitrant fractions initially present in each water sample. However, the modeled concentrations of DIP, DTP and TP were consistent with the experimental results, although some variation was observed in case of highly polluted water samples.

Decomposition rate coefficients of POP

In the Model 2, decomposition rate coefficient of POP (k_{POP1}) was fastest at St. 3 ($k = 0.068 \text{ day}^{-1}$) followed by St. 2 (0.062 day^{-1}) in the Youngsan River while the lowest decomposition rate coefficient (0.033 day^{-1}) was at St. 1 and St. 5 (Table 1). Despite the high organic and inorganic load at St. 6 of the Youngsan River, the lower POP decomposition rate ($k_{POP1} = 0.044 \text{ day}^{-1}$) was observed in this

site. During the course of decomposition the decrease of POP coincided well with the increase of DIP even though DOP fraction was not incorporated in this model. It implies that POP decomposition into DOP might have been compensated by the decomposition of DOP into DIP. And also it implies that the amount of POP decrease and DIP increase were correctly determined. In the Sumjin River, the highest decomposition rate coefficient was at St. 14 (0.057day^{-1}) and the lowest value was at St. 12 (0.017 day^{-1}).

In the Model 3, highest decomposition rate coefficient of POP ($k_{\text{POP}2}$) was at St. 8 (0.056 day^{-1}) while the lowest decomposition rate coefficient was at St. 5 (0.032 day^{-1}) in the Youngsan River. In the Sumjin River, the highest decomposition rate coefficient of POP was 0.061 day^{-1} at St. 14 while the lowest was 0.007 day^{-1} at St. 9 (Table 2). However, there was no definite trend of the distribution of decomposition rate coefficients observed in this study. In the Model 4, the decomposition rate coefficient of POP ($k_{\text{POP}3}$) varied from 0.027 to 0.059 day^{-1} (Table 4) where the highest value was at St. 2 and the lowest was at St. 5 of the Youngsan River. In case of the Sumjin River, the lowest value of $k_{\text{POP}3}$ was 0.023 day^{-1} at St. 9 while the highest was 0.043 day^{-1} at St. 14. In this model, the POP→DOP decomposition rate coefficient [$k_{\text{POP}3}$] was much higher than POP→DIP decomposition rate coefficient [$k_{\text{POP}3}^*$]. It explains that the direct mineralization of POP does not occur or may occur with a very slower rate. It may also imply that the common stepwise decomposition model of organic matter is plausible; the hydrolysis of particulate polymers to low molecule DOM, and then to DIC.

However, kinetic data suggest that P is regenerated quite rapidly during the initial stages of the decomposition process (De Pinto and Verhoff, 1977; Golterman, 1972). Phosphorus often appears to be released at a more rapid rate than C is mineralized, as shown by changes in the C: P ratio of particulate material during the decomposition process (Motohashi and Matsudaira, 1968). Some of the P released during decomposition appears as free orthophosphate in

the water and probably arises as a result of the release of stored P products during the autolysis process or bacterial lysis (Stewart and Daft, 1976). Although the decomposition rate coefficients of $k_{\text{POP}_3^*}$ of all the analyzed samples were within the range 0.001 day^{-1} to 0.017 day^{-1} , the majority samples showed the lowest decomposition rate coefficient (0.001 day^{-1}). The similar decomposition pattern was also observed in the River Sumjin in this decomposition model.

Several studies on the decomposition of organic matter in sediments reported that aerobic decomposition could be faster (Benner et al., 1985; Lee, 1992) or slower (Sun et al., 1993) than anaerobic decomposition. The hydrolysis and fermentation of POP (complex organic P compounds) to DOP and DIP occurs during initial stages of anaerobic decomposition. Many of these compounds can be directly mineralized to inorganic P by microorganisms using nitrate (NO_3^-) and sulfate (SO_4^{2-}) as electron acceptors. Aerobic decomposition of organic matter involves numerous enzymes most of which are specific to individual groups of compounds (Furlan and Pant, 2005) and each compound could be rapidly and completely metabolized by a single microorganism (Canfield et al., 1994). Anaerobic microorganisms, which are unable to degrade most high molecular weight organic compounds (Jorgensen and Bak, 1991), on the other hand, they may depend on fermentative microorganisms for the supply of metabolizable low molecular weight compounds (Kristensen et al., 1995). In this study only aerobic decomposition was measured and the rates might be different in anaerobic conditions. However, anaerobic condition was not observed in this study and it seems that production of oxygen by photosynthesis may overwhelm oxygen depletion. Light can be another factor affecting decomposition rate of organic matter through photolysis. Enzymes immobilized with humic substances (Pant and Warman, 2000; Burns, 1986) could be regenerated within the ecosystems upon exposure to UV irradiation in photic zone, and that can be an important factor for the decomposition of recalcitrant organic matter.

Table 1. POP decomposition rate coefficient (k_{POP1}) of POP→DIP model
(unit: day⁻¹).

		Sampling	Sampling date				Mean
		site No.	June,2006	Aug.,06	Dec.,06	Feb.,07	
Youngsan River	Main stream	3	0.07	0.078	0.065	0.057	0.068
		4	0.021	0.082	0.065	0.040	0.052
		6	0.029	0.045	0.048	0.053	0.044
		7	0.028	0.063	0.039	0.090	0.055
		8	0.031	0.042	0.066	0.055	0.049
	Tributaries	1	0.023	0.046	0.042	0.022	0.033
		2	0.091	0.047	0.064	0.045	0.062
		5	0.021	0.025	0.044	0.040	0.033
		Mean	0.028	0.054	0.054	0.050	0.049
Sumjin River	Main stream	10	0.018	0.030	0.016	0.015	0.020
		11	0.025	0.029	0.025	0.024	0.026
		13	0.055	0.064	0.017	0.045	0.045
		15	0.067	0.049	0.039	0.028	0.046
		16	0.014	0.043	0.072	0.045	0.044
	Tributaries	9	0.009	0.023	0.055	0.026	0.028
		12	0.013	0.019	0.021	0.016	0.017
		14	0.066	0.075	0.021	0.065	0.057
		Mean	0.033	0.042	0.033	0.033	0.035

Table 2. POP decomposition rate coefficient (k_{POP2}) of POP→DOP→DIP model (unit: day⁻¹).

		Sampling	Sampling date				Mean
		site No.	June,06	Aug.,06	Dec.,06	Feb.,07	
Youngsan River	Main stream	3	0.069	0.064	0.039	0.041	0.053
		4	0.014	0.066	0.059	0.037	0.044
		6	0.025	0.034	0.038	0.048	0.036
		7	0.025	0.026	0.023	0.061	0.034
		8	0.029	0.031	0.085	0.077	0.056
	Tributaries	1	0.025	0.048	0.039	0.027	0.035
		2	0.062	0.065	0.026	0.032	0.046
		5	0.028	0.025	0.035	0.039	0.032
		Mean	0.035	0.045	0.043	0.045	0.042
		10	0.031	0.048	0.021	0.015	0.029
Sumjin River	Main stream	11	0.062	0.052	0.035	0.029	0.045
		13	0.022	0.045	0.035	0.048	0.038
		15	0.049	0.042	0.028	0.023	0.036
		16	0.023	0.061	0.067	0.045	0.049
		9	0.006	0.009	0.005	0.009	0.007
	Tributaries	12	0.035	0.043	0.055	0.037	0.043
		14	0.081	0.090	0.029	0.043	0.061
		Mean	0.039	0.049	0.034	0.031	0.038

Table 3. DOP decomposition rate coefficient (k_{DOP2}) of POP→DOP→DIP model (unit: day⁻¹).

		Sampling	Sampling date				
		site No.	June,06	Aug.,06	Dec.,06	Feb.,07	Mean
Youngsan River	Main stream	3	0.500	0.291	0.415	0.100	0.327
		4	0.225	0.300	0.192	0.100	0.204
		6	0.175	0.430	0.248	0.400	0.313
		7	0.101	0.152	0.181	0.146	0.145
	Tributaries	8	0.118	0.180	0.300	0.223	0.205
		1	0.399	0.245	0.211	0.200	0.264
		2	0.298	0.193	0.416	0.342	0.312
		5	0.133	0.281	0.268	0.387	0.267
		Mean	0.244	0.259	0.279	0.237	0.255
		10	0.254	0.223	0.186	0.216	0.220
Sumjin River	Main stream	11	0.100	0.216	0.182	0.300	0.200
		13	0.239	0.300	0.252	0.291	0.271
		15	0.244	0.224	0.135	0.151	0.189
		16	0.183	0.295	0.144	0.213	0.209
	Tributaries	9	0.104	0.151	0.152	0.15	0.139
		12	0.558	0.146	0.400	0.300	0.351
		14	0.295	0.525	0.291	0.400	0.378
		Mean	0.247	0.260	0.218	0.253	0.244

Decomposition rate coefficients of DOP

Table 3 indicates the DOP decomposition rate coefficient (k_{DOP2}) in Model 2. In this model, decomposition rate coefficient of DOP was the highest at St. 3 ($k=0.327 \text{ day}^{-1}$) in the Youngsan River while the lowest value was at St. 7 (0.145 day^{-1}). Whereas in the River Sumjin, the highest decomposition rate coefficient was 0.378 day^{-1} at St. 14 which was followed by St. 12 (0.351 day^{-1}) and the lowest value was 0.139 day^{-1} at St. 9. DOP decomposition rate coefficient was much higher than that of POP reflecting the simpler biochemical composition of DOP thereby resulting rapid conversion of DOP into DIP. Data from Table 5 shows that in the Model 4, the DOP decomposition rate coefficient (k_{DOP3}) in the Youngsan River was within the range of 0.176 to 0.375 day^{-1} and in the River Sumjin, the lowest decomposition rate coefficient of DOP was 0.173 day^{-1} at St. 15 and the highest value (0.419 day^{-1}) was at St. 14.

Although orthophosphate-P ($\text{PO}_4\text{-P}$) is generally considered to be the most important source of P for microbial metabolism, the pool of DOP, which can equal or exceed $\text{PO}_4\text{-P}$ in certain oligotrophic environments, has been implicated as an important source of P for phytoplankton growth (Jackson and Williams, 1985; Berman, 1988). Through several pathways, DOP can be derived largely from nucleic acids or nucleotides, sugar phosphates, phospholipids and other-P compounds, most of which are well known as essential intracellular intermediates and metabolites having functions as activators and precursors of macromolecular biosynthesis and as regulators of metabolism (Orrett and Karl, 1987; Berman, 1988). DOP consisting of mainly phosphate esters can be biochemically labile to allow active assimilation by bacteria and algae (Orrett and Karl, 1987; Berman, 1988). The results show the highest decomposition rate coefficients of DOP attributing its simpler biochemical composition and labile nature compared to more complex compounds present in POP. Although the dynamics of DOP formation, supply and degradation is very complex because of its heterogeneity coming from their various origins (river supplies, algal

excretion, cell lysis), the largely unknown degradation processes (chemical and enzymatic) of the refractory DOP to easily hydrolysable compounds, and the fast recycling of these compounds.

Alkaline phosphatase has been the subject of several studies on organic P degradation and there is general agreement that only a small proportion of this material (< 10%) can be mineralized by this enzyme (Hino, 1988). DOP is predominantly phosphatase resistant (Peters, 1981) and that high indigenous levels of alkaline phosphatase activity do not correlate with DOP mineralization rates in fresh water lakes (Berman and Moses, 1972; Hino, 1988). This contrasts markedly with the situation in sea water where it has been reported that up to 30 % of organic P is phosphatase degradable (Venkateswaran and Natarajan, 1984). Hydrolysis of phosphate monoester to organic moiety and orthophosphate in seawater is largely dependent on the activity of alkaline phosphatase (Suzumura et al., 1998). Although the enzyme activities were not measured, the basis of the organic P decomposition processes is almost entirely the enzymatic which was excreted by different microorganisms in aquatic environment. Organic P compounds must first be converted to DIP for utilization by bacteria and phytoplankton (Ammerman and Azam, 1985), thus the structural character of DOP influences its bioavailability. Although the phytoplankton is also capable of assimilating P from the POP (Cembella et al., 1984) and DOP (Cotner and Wetzel, 1992), however, the bioavailability of DOP may be reduced if it is associated with humic acids (Reynolds and Davies, 2001).

Decomposition rate coefficients of TOP

Decomposition of total organic P in general is essential for recycling organic and inorganic components in aquatic ecosystems. The TOP decomposition rate coefficient indicates combined gradual decomposition rate coefficients of POP and DOP. Within the models, it is assumed that conversion of POP and DOP to phosphate proceeds through hydrolysis and mineralization. In the Model 1, the

mean TOP decomposition rate coefficient was 0.036 day^{-1} in the Youngsan River while it was 0.035 day^{-1} in the Sumjin River, despite the greater variability of TOP decomposition rate coefficients of different sampling sites of both the rivers.

As decomposition proceeds, soluble components and relatively easily degraded compounds such as sugar, starches and proteins will be rapidly utilized by decomposers, while more recalcitrant materials such as cellulose, fats, tannins and lignins will be decomposed at relatively slower rates. Thus, with time the relative proportion of these recalcitrant materials will progressively increase and the decomposition rate might decrease in the later stage of decomposition. However, in this study labile OP and recalcitrant OP were not discriminated, because it might have increased errors with exponential decrease model.

Comparison of models used in this study

Among the three models simulated in this study, it is apparently clear that Model 3 might be more applicable to the aquatic environment because more complex compounds containing POP will be converted first to relatively simpler compounds containing DOP and the DOP will then be converted to soluble reactive P or DIP. This model also supports the physical changes of most of the naturally occurring substances although there are some exceptions. Model 1 explains a general decomposition rates including both the POP and DOP decomposition phenomena. Model 2 usually represents the special circumstances of organic P conversion. Obviously, special circumstances can consider as limitation step of application of this model. Finally, Model 4 is relatively complex compared to other models used in this study. Thus, the decomposition rate coefficients obtained by Model 3 can be more applicable in modeling the river water quality.

Table 4. POP decomposition rate coefficient (k_{POP3}) of POP→DOP→DIP,
POP→DIP model (unit: day⁻¹).

		Sampling	Sampling		date			
		site No.	June,06	Aug.,06	Dec.,06	Feb.,07	Mean	
Youngsan River	Main	3	0.029	0.048	0.035	0.038	0.038	
	stream	4	0.038	0.054	0.055	0.035	0.046	
		6	0.025	0.044	0.048	0.041	0.040	
		7	0.021	0.048	0.031	0.031	0.033	
		8	0.028	0.039	0.052	0.043	0.041	
		Tributaries	1	0.025	0.026	0.032	0.029	0.028
		2	0.080	0.045	0.040	0.071	0.059	
	5	0.021	0.028	0.030	0.030	0.027		
	Mean		0.033	0.042	0.040	0.040	0.039	
	Sumjin River		10	0.024	0.029	0.031	0.035	0.030
Main		11	0.028	0.036	0.029	0.014	0.027	
		stream	13	0.019	0.025	0.025	0.034	0.026
			15	0.031	0.021	0.028	0.024	0.026
		16	0.032	0.031	0.048	0.047	0.040	
		9	0.010	0.005	0.030	0.048	0.023	
		Tributaries	12	0.025	0.027	0.031	0.038	0.030
14		0.039	0.069	0.035	0.029	0.043		
Mean		0.026	0.030	0.032	0.034	0.031		

Table 6. POP decomposition rate coefficient (k_{POP3}) of POP→DOP→DIP, POP→DIP model (unit: day⁻¹).

		Sampling	Sampling date				
		site No.	June,06	Aug.,06	Dec.,06	Feb.,07	Mean
Youngsan River	Main	3	0.001	0.001	0.009	0.001	0.003
	stream	4	0.001	0.010	0.007	0.001	0.005
		6	0.001	0.002	0.017	0.005	0.006
		7	0.001	0.001	0.002	0.014	0.005
	Tributaries	8	0.001	0.001	0.001	0.090	0.023
		1	0.003	0.020	0.001	0.008	0.008
		2	0.004	0.008	0.001	0.001	0.004
		5	0.001	0.001	0.003	0.008	0.003
		Mean	0.002	0.006	0.005	0.016	0.007
		10	0.007	0.001	0.001	0.001	0.003
Sumjin River	Main	11	0.001	0.009	0.002	0.001	0.003
	stream	13	0.001	0.012	0.001	0.007	0.005
		15	0.008	0.014	0.002	0.002	0.007
		16	0.001	0.015	0.001	0.004	0.005
	Tributaries	9	0.003	0.009	0.001	0.001	0.004
		12	0.005	0.006	0.001	0.003	0.004
		14	0.006	0.009	0.001	0.004	0.005
		Mean	0.004	0.009	0.001	0.003	0.004

Table 7. TOP decomposition rate coefficient (k_{TOP}) in the Youngsan River and the Sumjin River (unit: day⁻¹).

		Sampling	Sampling period				
		site No.	June,06	Aug.,06	Dec.,06	Feb.,07	Mean
Youngsan River	Main	3	0.077	0.038	0.038	0.021	0.044
	stream	4	0.014	0.029	0.047	0.025	0.029
		6	0.033	0.024	0.040	0.052	0.037
		7	0.017	0.019	0.035	0.047	0.030
	Tributaries	8	0.031	0.029	0.028	0.069	0.039
		1	0.061	0.048	0.034	0.020	0.041
		2	0.047	0.033	0.048	0.029	0.039
		5	0.034	0.012	0.028	0.037	0.028
		Mean	0.039	0.029	0.037	0.038	0.036
Sumjin River	Main stream	10	0.021	0.041	0.049	0.016	0.032
		11	0.017	0.025	0.031	0.027	0.025
		13	0.034	0.038	0.013	0.048	0.033
		15	0.044	0.014	0.032	0.027	0.029
		16	0.025	0.036	0.032	0.035	0.032
	Tributaries	9	0.011	0.037	0.054	0.020	0.031
		12	0.028	0.040	0.069	0.031	0.042
		14	0.076	0.053	0.045	0.037	0.053
		Mean	0.032	0.036	0.041	0.030	0.035

Model representations in this study

During chemical analyses, total inorganic and organic P are separated in various ways; these fractions often relate poorly to the way in which P is decomposed (Wetzel, 2001). Obviously errors produced in estimations of parameters can contribute to the uncertainty of predictions. It should be noted that the difference between modeled and measured values may be produced by various factors including sampling and measurements (such as methods, skills, etc.) which will affect the P concentration. These factors are not reflected in the model simulation and a slightly greater variability is expected and reasonable. For example, the release of inorganic PO_4 by particulate seston was reported to be much greater than excretion of soluble organic P by living organisms expressing direct decomposition of POP into DIP (Wetzel, 2001).

There was a difference in the decomposition rates under constant temperature perhaps due to aerobic and anaerobic conditions. Although a more complex model equation including microorganisms, pH, and redox potential may be able to improve the reproduction of real systems, it has been argued that increasing the number of parameters and complexity of the model will lead to an increase in model uncertainty as well as less accurate decomposition coefficient. The results indicate that the calibration results are quite acceptable. Conducting decomposition experiments at constant temperature and pH for a prolonged period would be very helpful to determine the extent of potential mineralization that can be induced by changes in stressors' levels due to hydro-climatic changes. These data should further aid to estimate P stability in rivers that in turn, assist to develop appropriate strategies to reduce the P mobility in the ecosystem.

CONCLUSIONS

Organic P decomposition rate coefficients can provide valuable information for the development of river management strategies. Analyzing only DIP underestimates, and analyzing only TP overestimates, the potential bioavailability of P in the water body. Therefore, it is necessary to know the decomposition rate of organic P and how it varies with time and space to better understanding the P dynamics in any aquatic system. The model equations employed here lend themselves well to determining the rate of decomposition of organic P because it makes no assumption what microorganisms are involved in the decomposition process. This study suggests that the respective decomposition rate coefficients which are fairly constant. Thus, given a uniform environment, the process by which decomposition proceeds may be very similar over a wide range organic P compounds, despite considerable differences in overall decomposition rates. The decomposition coefficients measured in this study would obviously give a guideline to the selection of parameters in modeling the river water quality. The models consisting of nine interrelated differential equations employed here are useful to predict the decomposition rates of organic P in aquatic environment.

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Chapter III

Changes in Phosphorus and Nitrogen Contents in Particulate Organic Matter and Dissolved Organic Matter in Rivers of Korea

ABSTRACT

Changes in the concentrations of major biochemical components of dissolved organic matter (DOM) and particulate organic matter (POM), as well as their proportions, are mainly determined by the biological activity of autotrophic and heterotrophic inhabitants of the aquatic ecosystems. The rates of changes of DOM and POM by microorganisms were measured by the decomposition experiments conducted in dark incubations. Decomposition rates of total organic phosphorus (TOP) and total organic nitrogen (TON), particulate organic phosphorus (POP) and dissolved organic phosphorus (DOP), particulate organic nitrogen (PON) and dissolved organic nitrogen (DON) were measured in six rivers of Korea from October 2005 to October 2008. Water samples were incubated for 20 days in a dark incubator and the different forms of P such as POP, DOP and DIP (dissolved inorganic P) were analyzed. In case of N, the analyzed parameters were PON, DON, NH_3 , NO_2^- , and NO_3^- . Decomposition time courses data were fit in some differential model equations with exponential decay models.

By fitting the changes to four types of models the decomposition rates of organic P were modeled. The mean TOP decomposition rate coefficient (k_{TOP}) was 0.038 day^{-1} . In $\text{POP} \rightarrow \text{DIP}$ model, the average k_{POP1} was 0.048 day^{-1} . In $\text{POP} \rightarrow \text{DOP} \rightarrow \text{DIP}$ model the average k_{POP2} was 0.046 day^{-1} and the mean k_{DOP2} was 0.328 day^{-1} . Based on labile (L) fractions, the mean k_{LPOP} and k_{LDOP} of $\text{LPOP} \rightarrow \text{LDOP} \rightarrow \text{DIP}$ model were 0.149 day^{-1} and 0.718 day^{-1} , respectively. In case of N, the decomposition rates

of N were modeled using three types of models. The mean k_{TON} was 0.026 day^{-1} . In $PON \rightarrow DON \rightarrow NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ model, the k_{PON} , k_{DON} , $k_{NH4(1)}$ and $k_{NO2(1)}$ were 0.028 day^{-1} , 0.191 day^{-1} , 0.520 day^{-1} and 0.890 day^{-1} , respectively. Whereas in $LPON \rightarrow LDON \rightarrow NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ model, the average k_{LPON} , k_{LDON} , $k_{NH4(2)}$ and $k_{NO2(2)}$ were 0.093 day^{-1} , 0.472 day^{-1} , 0.656 day^{-1} and 0.995 day^{-1} , respectively. Our results suggest that the decomposition rates of organic P are faster than organic N. As a result, there were major differences in the relative amount of labile and recalcitrant fractions of POP, DOP, PON and DON. By fitting concentration changes to an exponential model, the rates of changes of PON: POC, POP: PON, DON: DOC and DOP: DON were estimated. There were major differences in the relative amount of labile and recalcitrant fractions of POC, DOC, PON, DON, POP and DOP as a result of preferential remineralization of P over N and N over C. In general, the rate of changes of PON: POC, POP:POC and POP: PON were relatively low compared to the changes of DON: DOC, DOP:DOC and DOP: DON. However, during decomposition the ratios of labile LPON: LPOP increased while the ratios of LDON: LDOP decreased than the initial PON: POP and DON: DOP ratios reflecting faster decomposition of LPOP than LPON. Ratios of N: P and the P and N contents indicate significant modifications in the character of the organic matter. Substantial amounts of the organic matter can contribute to reducing conditions and modify diagenetic processes. The results show that decomposition coefficients of various P and N fractions and changes in the ratios of organic C, N and P measured in this study will be useful for understanding biogeochemical processes affecting river water quality.

INTRODUCTION

Organic matter is present to varying degrees in dissolved and particulate forms in all natural waters, and the term decomposition and degradation of organic matter probably describe the overall sequence of transformations, mediated by enzymes produced by heterotrophic microbes that lead from particulate to dissolved, from large to small molecules, and eventually to inorganic or organic compounds that are resistant to further decomposition. The organic material borne by larger lotic systems is largely terrestrial POM and DOM (Meybeck, 1982; Webster and Meyer, 1997; Raymond and Bauer, 2001) and highly degraded (Ittekkot, 1988; Hedges et al., 1994). The degradation of organic matter is largely dependent on the metabolic activities of bacteria to synthesize the required enzymes and transport systems (Chróst, 1991; Münster and De Haan, 1998).

Decomposition of POM and DOM is one of the essential factors determining the rates of microbial processes in aquatic systems. Microbial extracellular enzymes can cleave the DOM and POM, especially polymeric substances, which are too large to be readily assimilated and must first be transformed into smaller molecules through enzymatic depolymerization. Production of enzymes facilitates the survival of bacteria when easily available energy and nutrient sources become limiting. Enzymatic degradation of large organic molecules is a rate-limiting step, and the degradative activity of microbially derived extracellular enzymes can be considered a direct link between microbial activities and the decomposition and mineralization of organic matter (Sinsabaugh et al., 1993, 1994). Several environmental factors, including temperature, pH, and substrate concentration, influence the activity of extracellular enzymes (Shackle et al., 2000). However, if inorganic nutrients, like nitrate, ammonium or phosphate, become limiting or the allochthonous organic matter is already N- and P-depleted, bacterial growth becomes limited in spite of sufficient organic carbon substrates (Rejas Muylaert and De Meester, 2005). The production of extracellular enzymes by microorganisms is strongly correlated to the

influx of polymeric organic matter and /or the depletion of readily utilizable DOM in the environment (Chróst and Siuda, 2002). Different microorganisms especially bacteria belonging to various physiological groups decompose proteins, cellulose, starch, chitin, lignin and other macromolecular organic matter (Vrba, 1992). However, the intensity and dynamics of the process of decomposition are dependent on the ecological state of the water body (Chróst, 1991; Priest, 1984).

The main biochemical components of POM are proteins. High rates of primary production result in increase carbohydrate content of POM, which approaches that of protein. In addition to protein, particulate and dissolved organic N contains a large portion of nucleic acid, an important source of both organic N and organic P. Dissolved free amino acids are often the main substrates for bacteria (Jørgensen, 1987; Keil and Kirchman, 1991). In contrast, phosphate groups are a basic structural element of nucleic acids, phospholipids and low molecular weight nucleotides (e.g. ATP) participate in energetic and anabolic processes. Humic substances are much more resistant to bacterial degradation especially because of their lower N and P content (Wetzel, 2001). From the biological point of view, the POM and DOM pool can be classified as labile (LPOM) and refractory or recalcitrant particulate organic matter (RPOM), labile (LDOM) and refractory or recalcitrant dissolved organic matter (RDOM). The LDOM pool is comprised mostly of low-molecular weight compounds such as dissolved free amino acids, carbohydrates and fatty acids, vitamins, nucleotides, pigments and steroids (Münster et al., 1999b). Part of the LDOM fraction is produced photosynthetically and excreted as dissolved extracellular organic carbon (EOC), mainly by phytoplankton in pelagic areas and by macrophytes and epiphytic algae in the littoral zone.

Organic P (OP) and organic N (ON) pools are intrinsically linked within the aquatic environment. As for organic C, the OP/ON comprises a range of compounds of different functionality and molecular mass, from small molecules to proteins, in dissolved, colloidal and particulate phases. Because of the differential N and P content of various organic compound classes composing cellular structures and

contents, inherent differences in the decomposition rates of organic N and P compounds and the relative proportions of discrete pools of organic matter might be there as expected. Some studies (Martin et al., 1987; Williams et al., 1980; Hopkinson et al., 1997) have demonstrated the preferential remineralization of N and P relative to C. However, there is very limited information for river ecosystems on the relative pool sizes of N and P containing organic matter of different lability.

In calculation of decomposition phenomena, mathematical models are valuable tools to investigate the biogeochemical mechanisms and their interactions. The modeling of the decrease of different organic P and different organic N concentrations during the decomposition processes, and the interrelationships among different P fractions and different N fractions contain one or more decomposition rate coefficients that are universal in some senses. Qualitative and quantitative changes in the material load are brought about by specialized biological communities and by physical retention processes. The analytical problem is to systematically take into account the dynamics of qualitative and quantitative changes. Understanding the dynamics is an even more difficult task, requiring a long-time series of data collected at various points along the river systems. In order to estimate the rate of changes in the organic P and N cycles and the completeness of metabolic consumption of substances, it is necessary to measure these rates that take part in POM and DOM metabolism. Available information on these processes especially decomposition of organic matter in rivers is mostly qualitative in nature. A reasonable prediction of water quality for the river requires the decomposition rates of organic P and organic N present in the water bodies. However, the objectives of this study therefore were to assess the changes of organic P and organic N and their availabilities for algal growth as well as the overall impacts of P and N in the river and the stoichiometric changes of C:N:P of POM and DOM in the river ecosystem.

MATERIALS AND METHODS

Study area

The Keum River of Korea is located between $35^{\circ} 59' \text{ N}$ and $126^{\circ} 39' \text{ E}$. The Youngsan River and the Sumjin River are located in the middle to the southern part of Korea between $35^{\circ} 20' \text{ N}$ and $35^{\circ} 15' \text{ N}$ and between 126° and 127° E . They have watershed area of $3,522 \text{ km}^2$ and $4,897 \text{ km}^2$, respectively. The Han River, the North Han River and the South Han River of Korea are located between $37^{\circ} 33' \text{ N}$ latitude and $126^{\circ} 59' \text{ E}$ longitude. The Han River in Korea is the largest river based on basin area and river discharge. It has a basin area of $26,018 \text{ km}^2$. The river reaches are short and drainage areas are small in Korea compared with other major continental rivers. The channel slopes are relatively steep upstream because of steep mountains and deep valleys in the uplands. Due to natural topography and river regulation the slope of the water surface is low. Distribution of precipitation is more varied than that of temperature. During the rainy season from June to September, Korea receives about 70 % of its annual precipitation. About 18 % of the total annual precipitation falls during the dry season from October to March. Therefore the ratios of the flow rates between rainy and dry days were very high. The river bank erosion in Korea is relatively low because of the dominance of rocky structure near the shoreline. However, the land uses within the river basin largely consists of residential, industrial, commercial, livestock, pasture, row crops and forestry. Approximately 70 % of the Korean peninsula is under forests. Long stretching rivers with gentle gradients such as the Han River, the Keum River, the Youngsan River and the Sumjin River flow into the Yellow and South Seas in Korea.

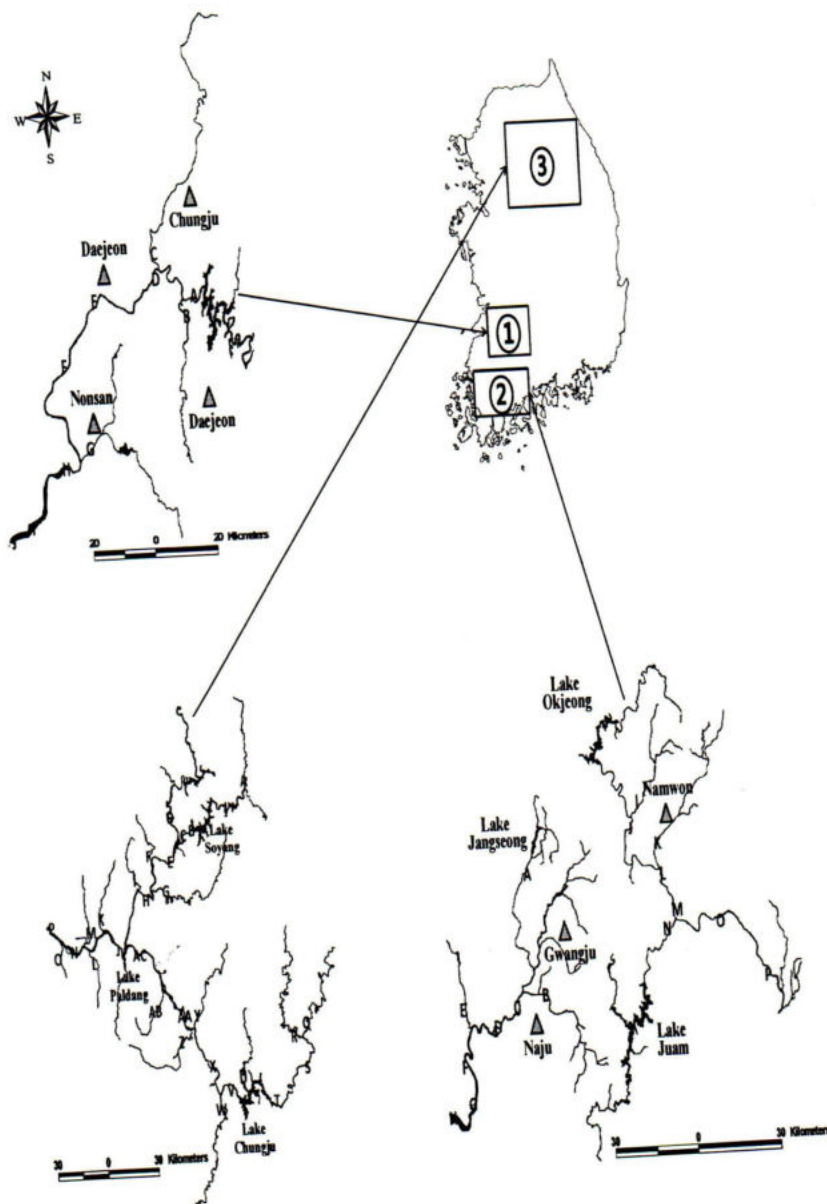


Fig. 1. Map of the sampling sites in six rivers of Korea. Inset 1 shows the Keum River basin (10 sampling sites). Inset 2 shows the Youngsan River and the Sumjin River basins, respectively (8 sampling sites each). Inset 3 shows the Han River basin (25 sampling sites).

Collection of samples and their analyses

Water samples were collected from six rivers of Korea such as the Keum river (10 sites), the Youngsan River (8 sites), the Sumjin River (8 sites), the North Han River (10 sites), the Han River (6 sites) and the South Han River (9 sites). The replication of each sampling site was 3 to 4. Table 2 indicates the sampling period and replication of the samplings. The sampling periods were scheduled in different seasons to encompass the seasonal flow regimes. Sample sites were chosen to represent all areas with consideration given to covering a wide range of parameters such as electrical conductance (EC), nutrients, dissolved (DO), biological oxygen demand (BOD) and chemical oxygen demand (COD). Samples were collected in pre-cleaned polyethylene bottles thoroughly rinsed with surface water and stored in the dark at 4 °C to minimize deterioration prior to analysis. Water samples were filtered with 200µm mesh-sized net and were placed in dark condition at a constant temperature of 20 °C for decomposition. In water quality modeling, reaction rates are usually measured at 20 °C. All bottles and glassware used were cleaned with nutrient P-free detergent (Extrans), rinsed three times with ultra-pure water (Milli-Q), soaked in 10 % (v/v) HCl for at least 24 h, and finally rinsed three times with ultra-pure water.

DIP, DTP (dissolved total P) and TP (total P) concentrations of the water samples were measured for P. Dissolved and particulate fractions are usually distinguished by filtration through a 0.45 µm membrane, that separates most bacteria, algae and mineral particles from the dissolved phase but fails to separate colloidal particles. DIP/soluble reactive P (SRP) is a measure of orthophosphate, the filterable (soluble, inorganic) fraction of P, the form directly taken up by plant cells. DIP was analyzed after GF/F filtration (0.45 µm) by applying the molybdenum blue method at 880 nm according to APHA (1998). DTP was estimated from the filtered sample as DIP after persulfate digestion (APHA, 1998). DOP was obtained by subtracting the DIP from DTP. TP was analyzed from the unfiltered sample as DIP after persulfate digestion and determined after the molybdenum blue method according to

APHA (1998). For the measurement of organic P decomposition rate coefficient, DIP, DTP and TP concentrations were measured at 0, 1, 2, 3, 5, 7, 10, 15 and 20 days after the beginning of the incubation.

Dissolved total N (DTN) and nitrate + nitrite ($\text{NO}_3^- + \text{NO}_2^-$) were sampled using the same procedure as DTP and DIP, respectively. Total N (TN) was determined by cadmium reduction method after persulfate digestion, using flow injection autoanalyzer (SKALAR). Nitrate was determined with an autoanalyzer by the cadmium reduction method. NO_3^- was reduced to nitrite in a cadmium column, after which an acidic sulfanilamide colorimetric reagent was added and measured in a flow injection autoanalyzer. DTN was oxidized to NO_3^- with potassium persulfate and analyzed in a similar manner to NO_3^- . Ammonia was determined by spectrophotometric method and the nitrite was estimated by flow injection autoanalyzer (APHA, 1998). DON was calculated as $\text{DTN} - ([\text{NO}_2^-] + [\text{NO}_3^-] + [\text{NH}_4^+])$. PON was calculated as the difference between TN and DTN. The precisions of the analyzes of both N and P were $\pm 1\%$ of CV based on three replication of each sample. For the measurement of organic N decomposition rate coefficient, PON, DON, NH_4^+ , NO_2^- and NO_3^- concentrations were measured at 0, 1, 2, 3, 5, 7, 10, 15 and 20 days after the beginning of the incubation.

Temperature, pH and EC were measured in situ with a YSI model 600 multi-parameter water analyzer. DO was measured by DO meter. For COD_{Mn} , samples of 30 ml were treated with 5 mN KMnO_4 in 1 % NaOH for 1 hour at 100 °C in an autoclave. The concentration of DOC (dissolved organic carbon) was measured by a TOC analyzer (Shimadzu TOC-5000A) employing high temperature catalytic oxidation method. Analytical precision was $\pm 1\%$ of CV based on three replicates of each sample. After filtering the sample, the filter papers for POC analysis were fumigated in an acidifying desiccator filled with 12N HCl for about 4 hours. After removing DIC, filter papers were wrapped in tin foil and analyzed by a CHN elemental analyzer (VARIO-EL).

Statistics

Correlation coefficients were calculated to establish significant relationships between the organic N and organic P fractions, the different labile and recalcitrant fractions of N and P and their ratios. In contrast, average values of parameters over the whole study period, in most cases, are medians because the data were not normally distributed. A linear regression was significant if $p < 0.05$. Analysis of variance (ANOVA) was used to test for site differences in different rivers as well as the sampling sites in the same river.

Models used in determining decomposition rates of P and N

Some interrelated differential model equations have been used to study the decomposition rates of organic P and N, and inorganic N in aquatic environment. The mechanisms involved in these models include decomposition kinetics of various organic and inorganic fractions. An extensive set of data derived from chemical analyses of the water samples of the six rivers were used for calibration to determine the decomposition rate coefficients. The basic time unit for simulations was the time interval t between iterative solutions of model equations. The choice of the time unit depends on the level of resolution in time needed for the model to address the question of interest. Mostly, the choice of the time unit for simulation depends on the observation interval of available data. Decomposition studies often report simple or complex exponential decay models and show declining mass-loss rates during the decomposition processes (Wieder and Lang, 1982; Moorhead et al., 1996). The remaining recalcitrant material is essentially in the tail end of a declining exponential decay curve. Organic P and N decomposition coefficients were calculated using the above seven models by numerical integration using Runge-Kutta method and the optimum coefficients were determined by the least square method. Computations were carried out under Excel using first order numerical integrations with the integration step set at 0.1 day was chosen. Initial concentrations of DIP, DOP, POP TOP, TON, DON NH_4^+ , and NO_2^- are required to start numerical

computations. They were determined as arbitrary values that were set according to experimental results during simulation periods. The values were reset until the results simulated during the commencing simulation periods are stable.

In case of P, the TOP decomposition was modeled by the model:

Model 1; Total organic P (TOP) → dissolved inorganic phosphorus (DIP)

$$\frac{d(\text{TOP})}{dt} = -k_{\text{TOP}}(\text{TOP}) \dots \dots \dots (1)$$

Where, TOP = total organic phosphorus concentration

k_{TOP} = TOP decomposition rate coefficient [day⁻¹]

t = decomposition time [day]

This model specifies an exponential depletion; that is the concentration halves per unit time. The assumption underlying the single exponential model can be expressed in two ways: either the absolute decomposition rate decreases as the amount of remaining substrate declines, or the relative decomposition rate remains constant. Intuitively, this assumption corresponds well with our knowledge and understanding of organic P decomposition. As decomposition proceeds, soluble components and relatively easily degraded compounds such as sugar, starches and proteins will be rapidly utilized by decomposers, while more recalcitrant materials such as cellulose, fats, tannins and lignins will be decomposed at relatively slower rates. Thus, with time the relative proportion of these recalcitrant materials will progressively increase and the absolute decomposition rate should decrease.

In model 1 organic P is not divided into any forms, and particulate organic P and dissolved organic P are assumed to be decomposed at the same rate. All the models employed in this study describe first-order reaction kinetics or exponential decreases.

Model 2; Particulate organic P (POP) → dissolved inorganic phosphorus (DIP)

k_{POP1}

POP → DIP

$$\frac{d(\text{POP})}{dt} = -k_{\text{POP1}}(\text{POP}) \dots \dots \dots (2)$$

$$\frac{d(\text{DIP})}{dt} = k_{\text{POP1}}(\text{POP}) \dots \dots \dots (3)$$

Some water quality models employ only POM and DOM is not simulated as a state variable. In model 2, only POP is modeled neglecting DOP. Particulate organic material such as phytoplankton is assumed to be decomposed directly into DIP.

Model 3; Particulate organic P (POP) → dissolved organic P (DOP) → dissolved inorganic P (DIP)



$$\frac{d(\text{POP})}{dt} = -k_{\text{POP2}}(\text{POP}) \dots \dots \dots (4)$$

$$\frac{d(\text{DOP})}{dt} = k_{\text{POP2}}(\text{POP}) - k_{\text{DOP2}}(\text{DOP}) \dots \dots \dots (5)$$

$$\frac{d(\text{DIP})}{dt} = k_{\text{DOP2}}(\text{DOP}) \dots \dots \dots (6)$$

In model 3 organic P was divided into POP and DOP. The basic concept of the model is that during decomposition process POP is first converted into DOP and then DOP is transformed into DIP or SRP (soluble reactive phosphorus).

Model 4; Labile particulate organic P (LPOP) → Labile dissolved organic P (LDOP) → dissolved inorganic P (DIP)



$$\frac{d(\text{LPOP})}{dt} = -k_{\text{LPOP}}(\text{LPOP}) \dots \dots \dots (7)$$

$$\frac{d(\text{LDOP})}{dt} = k_{\text{LPOP}}(\text{LPOP}) - k_{\text{LDOP}}(\text{LDOP}) \dots \dots \dots (8)$$

$$\frac{d(\text{DIP})}{dt} = k_{\text{LDOP}}(\text{LDOP}) \dots \dots \dots (9)$$

These model equations imply that during decomposition the labile POP will be first converted into labile DOP and the labile DOP will then be transformed into DIP or SRP (soluble reactive P).

Model 5; Total organic N → dissolved inorganic N (NH_4^+ , NH_3 , NO_2^- , NO_3^-)

$$\frac{d(\text{TON})}{dt} = -k_{\text{TON}}(\text{TON}) \dots \dots \dots (10)$$

Where, TON= total organic N concentration

k_{TON} = TON decomposition rate coefficient [day⁻¹]

t = decomposition time [day]

In model 5 organic N is also not divided into any forms, and PON and DON are assumed to be decomposed at the same rate. The assumption underlying the single exponential model is as like as P. Obviously, this assumption corresponds well with our experiences of many biological decay reactions including organic N decomposition.

Model 6; $\text{PON} \rightarrow \text{DON} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$

$$\frac{d(\text{PON})}{dt} = -k_{\text{PON}}(\text{PON}) \dots \dots \dots (11)$$

$$\frac{d(\text{DON})}{dt} = k_{\text{PON}}(\text{PON}) - k_{\text{DON}}(\text{DON}) \dots \dots \dots (12)$$

$$\frac{d(\text{NH}_4^+)}{dt} = k_{\text{DON}}(\text{DON}) - k_{\text{NH}_4^+(1)}(\text{NH}_4^+) \dots \dots \dots (13)$$

$$\frac{d(\text{NO}_2^-)}{dt} = k_{\text{NH}_4^+(1)}(\text{NH}_4^+) - k_{\text{NO}_2^-(1)}(\text{NO}_2^-) \dots \dots \dots (14)$$

$$\frac{d(\text{NO}_3^-)}{dt} = k_{\text{NO}_2^-(1)}(\text{NO}_2^-) \dots \dots \dots (15)$$

In model 6 organic N was divided into PON and DON. During decomposition processes, PON is first converted into DON and then DON is transformed into $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$.

Model 7; $\text{LPON} \rightarrow \text{LDON} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$

$$\frac{d(\text{LPON})}{dt} = -k_{\text{LPON}}(\text{LPON}) \dots \dots \dots (16)$$

$$\frac{d(\text{LDON})}{dt} = k_{\text{LPON}}(\text{LPON}) - k_{\text{LDON}}(\text{LDON}) \dots \dots \dots (17)$$

$$\frac{d(\text{NH}_4^+)}{dt} = k_{\text{LDON}}(\text{LDON}) - k_{\text{NH}_4^+(2)}(\text{NH}_4^+) \dots \dots \dots (18)$$

$$\frac{d(\text{NO}_2^-)}{dt} = k_{\text{NH}_4^+(2)}(\text{NH}_4^+) - k_{\text{NO}_2^-(2)}(\text{NO}_2^-) \dots \dots \dots (19)$$

$$\frac{d(\text{NO}_3^-)}{dt} = k_{\text{NO}_2^-(2)}(\text{NO}_2^-) \dots \dots \dots (20)$$

In model 7, we considered only the labile PON will be decomposed into labile DON and then only labile DON will be transformed into $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$. The organic form of N can be converted NO_3^- through nitrification. Ammonium, a primary decomposition product from organic matter, is first transformed by microbes to nitrite (NO_2^-) and then nitrate (NO_3^-) under oxic condition (nitrification). Nitrification is a two-step process performed by two different functional bacterial groups. *Nitrosomonas* and *Nitrobacter* are assumed to be the major players in the oxidation of $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ and $\text{NO}_2^- \rightarrow \text{NO}_3^-$, respectively. The decomposition values of carbon were also modeled using some C decomposition models which are similar to P decomposition models of model 1, model 3 and model 4.

RESULTS AND DISCUSSION

Basic water characteristics during sampling periods

The variances in the magnitudes of the quality indices such as pH, EC, DO, CODMn are summarized in Table 1. The pH of all the rivers ranged from 7.1 to 8.2 with a mean of 7.7. As the river flowed downstream, the average pH increased from about 7.1 at the upstream of the North Han River to about 8.2 at the downstream of the South Han River. However, the differences of pH among the samples collected at each site were relatively small. Differences in the decomposition rates could be due to differences in water chemistry (pH, alkalinity, nutrient concentrations). Higher breakdown rates have been described before in alkaline systems in comparison with more acidic ones (Chamier, 1992). The effects of pH are complex and may be due to combined effects of low buffering capacity and the direct effects of low pH on the microorganisms and their enzyme activities (Jenkins and Suberkropp, 1995). In reflective of the extent of ion strengths, EC increased by several folds along the river line, with its values being obviously smaller for samples at lower flow rate and water levels. However, the median value of EC of all the rivers was $240 \mu\text{S cm}^{-1}$.

Oxygen is consumed during decomposition and respiration. Respiration and decomposition occur 24 hours a day accounting large daily variations in DO concentrations. Low DO contents indicate the presence of substances liable to oxidation, such as biodegradable organic matter and ions in lower oxidation state. DO values increased in winter and showed a relative decrease in summer. Chemical oxygen demand (COD), an index of BOD is inversely proportional to DO. COD is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. Consequently, the higher the value of DO, the lower the level of COD and BOD were observed in the waters. COD was relatively low in North Han and South Han Rivers compared to the other studied rivers.

Table 1. Limnological characteristics of the six rivers of Korea during the study period from October 2005 to October 2008.

Parameters		Keum	Yongsan	Sumjin	North Han	Han	South Han	Mean
pH	Mean	7.6	8.0	7.8	7.2	7.4	8.2	7.7
	Median	7.5	8.1	7.9	7.1	7.3	8.1	7.7
	SD	0.4	0.8	0.7	0.3	0.2	0.4	0.5
EC ($\mu\text{S cm}^{-1}$)	Mean	334	364	888	104	365	226	380
	Median	318	262	135	89	411	225	240
	SD	139	397	2781	49	153	44	594
DO ($\text{mg O}_2 \text{ L}^{-1}$)	Mean	11.1	9.5	9.7	10.0	6.5	10.1	9.5
	Median	11.5	9.5	9.7	10.2	6.8	9.8	9.6
	SD	2.1	1.8	1.3	1.2	2.3	1.8	1.8
COD($\text{mgO}_2 \text{ L}^{-1}$)	Mean	7.2	8.0	5.5	3.4	10.1	3.2	6.2
	Median	7.1	7.9	5.4	3.1	11.9	2.7	6.3
	SD	2.2	1.5	1.4	0.9	4.1	1.5	1.9
DIP($\mu\text{g L}^{-1}$)	Mean	132	149	28	11	508	5.4	139
	Median	50	88	13	6	358	3.0	86
	SD	179	198	40	14	398	5.8	139
NH_4^+ (mg L^{-1})	Mean	1.326	0.646	0.188	0.066	1.313	0.042	0.597
	Median	0.587	0.530	0.115	0.043	1.189	0.047	0.419
	SD	1.827	0.515	0.192	0.067	0.927	0.028	0.593
NO_3^- (mg L^{-1})	Mean	2.584	1.574	0.996	1.071	1.839	1.543	1.601
	Median	2.347	1.425	0.845	1.099	1.815	1.500	1.505
	SD	1.243	0.855	0.551	0.398	0.680	0.253	0.663

Actual nutrients and energy requirement strongly affects the synthesis rates, structure and efficiency of microbial ectoenzymes. The resultant activity of ectoenzymes determines the sequence and rates of utilization of various DOM and POM constituents by microorganisms (Siuda and Chróst, 2002). NO_3^- generally dominated in the rivers, with NH_4^+ contributing a small fraction. The concentrations of NO_3^- of the Keum River had significantly higher than the Youngsan River and the Sumjin River ($p < 0.05$) while there were no significant differences between the Sumjin River and the North Han River, the North Han and the Han River, and the North Han and the South Han River. DIP concentrations were generally low except in the Youngsan River and the Han River.

Initial concentrations of POP, DOP, PON and DON

Concentrations of dissolved and particulate forms of organic P and N and their stoichiometric ratios in different rivers are summarized in Table 2. There were large differences in ambient concentrations of POP, DOP, PON and DON in different rivers. Discharge largely determines the temporal variation in allochthonous POM and DOM inputs into rivers which may in turn reflect the quality and quantity of organic matter in the river water. There was no specific pattern in the concentrations of POM and DOM, however, there were seasonal trends. For example, due to the storm of rain, the concentration of suspended solids (SS) and DOM in the river water changed and were different in different rivers. Similar to the trend of SS, remarkable changes in the TN and TP were also confirmed. Mean concentration of PON was $812 \mu\text{g L}^{-1}$ with the highest in the Han River followed by the Youngsan and the Keum River and lowest in the South Han River, while the concentrations of POP were from $8 \mu\text{g L}^{-1}$ to $118 \mu\text{g L}^{-1}$ with the highest value also in the Han River and lowest in the North Han River (Table 2). As expected, POP and PON were not significantly correlated ($r = 0.27$, $n = 167$, $p < 0.05$) due to the different origin of POM. However, the mean stoichiometric ratio of PON: POP was 17 with 75 percentile. Both DON and DOP concentrations were higher in Han River than the

Table 2. Median values of initial POP, DOP, PON and DON and their molar ratios; concentration units are in $\mu\text{g L}^{-1}$; n = 152.

River	Sampling dates	PON	POP	Molar N:P	DON	DOP	Molar N:P
Keum	2005-10-15	746	49	34	468	10	104
	2005-11-19	752	72	23	499	8	147
	2006-03-10	368	94	9	811	21	86
	2006-06-09	654	80	18	781	14	128
Yongsan	2006-06-14	1555	44	78	985	10	218
	2006-08-14	520	46	25	945	13	161
	2006-12-02	525	37	32	655	8	193
	2007-02-03	895	32	63	725	14	119
Sumjin	2006-06-14	720	29	56	915	8	270
	2006-08-14	535	28	43	1190	8	329
	2006-12-02	590	13	105	1140	4	631
	2007-02-03	530	12	102	1165	3	860
North Han	2007-04-23	640	8	185	1108	4	656
	2007-08-28	350	27	29	665	10	147
	2007-10-01	300	16	42	785	5	348
Han	2007-04-23	815	105	17	1194	6	459
	2007-08-28	2540	118	48	444	47	21
	2007-10-01	2305	50	103	690	8	191
South Han	2008-05-20	940	23	93	206	4	114
	2008-07-15	440	20	49	35	3	26
	2008-10-08	340	11	72	89	3	79
Mean		812	43	58	738	10	252
Median		647	34	48	759	8	176
75 percentile		815	50	78	985	10	329

others. DON and DOP contributed significantly to the total dissolved N and P pools, respectively (Table 2). The ratio of DON and DOP varied widely, however, with 75 percentile it was 149. These ratios differed considerably from those of POM, being on average about 3-5 times higher. In case of DON, highest value recorded in the Sumjin River and lowest in the North Han River with a median value of $759 \mu\text{g L}^{-1}$. The average DOP value of the studied rivers was $10 \mu\text{g L}^{-1}$ with 75 percentile. The correlation between DON and DOP was not significant ($r = 0.14$, $n = 168$, $p < 0.05$), which could explain the sources of their origins. In aquatic environment, the easily oxidizable compounds in the DOM can act as chemical- and biological-oxygen demand compounds, thereby capable of depleting the O_2 concentration in water and influencing aquatic biota.

Origin and distribution of organic matter, and decomposition of TOP and TON

Riverine organic matter is generally derived more from soil and plant material and less from phytoplankton (Meybeck, 1982; Hedges et al., 1992). POM includes both living organisms (bacteria, phytoplankton, protozoa and metazoans) and particulate detritus. Depending on riparian vegetation, stream size, and discharge, autochthonous microbial production may also contribute significant portions to riverine organic matter (Vannote, 1980). The influx and presence of these different sources vary along longitudinal transport and also with seasons, mainly due to large spatial-temporal variations in physical and chemical characteristics. The POM is subjected to different processes such as decomposition, disaggregation and sedimentation that determine its role, behavior and fate in the aquatic ecosystem. The organic P pool present in the river could originate from soil catchment and weathering. In particular, monoester phosphates are usually considered the dominant form of organic P in most soils and inositol phosphates are predominant particularly phytic acid (myo-inositol hexakisphosphate), whereas sugar phosphates, mononucleotides and phosphoproteins are only generally present at trace

concentrations (Condrón et al., 2005).

Using model 1 and model 5, we modeled the decomposition coefficients of TOP and TON respectively. The average k_{TOP} in Table 3 was 0.038 day^{-1} while its median value was 0.036 day^{-1} . Similarly, the mean and median k_{TON} values were 0.026 and 0.025 day^{-1} respectively (Table 4). These decomposition patterns of TOP and TON clearly demonstrate that the decomposition rate of organic P is faster than the decomposition rate of organic N compounds. The prevailing view of decomposition is that organic matter becomes progressively more recalcitrant as decomposition progresses because microorganisms consume the more labile material early in the decay process. The source of organic material and its biochemical composition is likely to be important in determining the structure and activity of microbial communities associated with particles. From a trophic view point, DOM and POM might have different nutritional value and might serve as food sources for different organisms. Because enzyme production is N and energy intensive, microbes should only produce enzymes at the expense of growth and metabolism if available nutrients are scarce (Koch, 1985). In contrast, when assimilable resources are available, microbes may decrease the production of enzymes that is consistent with the hypothesis that abundant labile nutrients inhibit the decomposition of more recalcitrant compounds (Schimel et al., 1992; Moorhead and Linkins, 1997). Concentrations of available nutrients are often negatively correlated with the activities of nutrient-releasing enzymes (Chróst, 1991; Sinsabaugh and Moorhead, 1994).

Decomposition of POM

It is now well known that microheterotrophs associated in the aquatic community with the fraction of particulate material, occupy the central position in organic matter decomposition. In addition, particulate material may adsorb dissolved enzymatic proteins and give rise to catalytic aggregates taking part in the transformation of organic matter and in regeneration of nutrient elements. When the

concentrations of P and N containing compounds in DOM pool did not fulfill bacterial demand, microorganisms intensified enzymatic mechanisms to utilize substrates from the POM pool (Siuda and Chróst, 2002). Within the P models, it is assumed that conversion of POP to orthophosphate proceeds through hydrolysis and mineralization. In model 2 ($\text{POP} \rightarrow \text{DIP}$), mean and median values of k_{POP1} were 0.048 day^{-1} and 0.042 day^{-1} , respectively (Table 3). But in model 3 ($\text{POP} \rightarrow \text{DOP} \rightarrow \text{DIP}$), when POP converts to DOP, the mean k_{POP2} was relatively slightly low (0.046 day^{-1}), compared to the mean decomposition value of model 2. This implies that the decomposition rates would be relatively low when the decomposition pathway encompasses more steps. However, in model 4 ($\text{LPOP} \rightarrow \text{LDOP} \rightarrow \text{DIP}$), the decomposition pathway considers only the labile form of organic P, both the mean and median values of k_{LPOP} were 0.149 day^{-1} . This decomposition rate was almost 3 times higher than k_{POP} calculated using the model 2 and model 3.

POM was mainly composed of proteins (about 50 %), polysaccharides (25 %) and chemicelluloses (25 %) whereas the chitin, uric acid and lipids were generally less abundant (Riley, 1970). Particle attached bacteria exhibited higher enzymatic activity in comparison to free-living bacteria (Siuda and Chróst, 2002). The hydrolysis and fermentation of POP (complex organic P compounds) to DOP and DIP occurs during initial stages of anaerobic decomposition. Many of these compounds can be directly mineralized to inorganic P by microorganisms using NO_3^- and SO_4^{2-} as electron acceptors. Aerobic decomposition of organic matter involves numerous enzymes most of which are specific to individual groups of compounds (Furlan and Pant, 2005) and each compound could be rapidly and completely metabolized by a single microorganism (Canfield et al., 1994). In this study only aerobic decomposition was measured and the rates might be different in anaerobic conditions. However, anaerobic condition was not observed in this study and it seems that production of oxygen by photosynthesis may overwhelm oxygen depletion. Since so far there were no information on the bacterial community composition in the study river, it cannot be concluded that in times of external

forcing e.g., temperature changes, the community is completely restructured and does not respond to substrate availability. Changes in substrate composition itself can also affect bacterial community composition (Besemer et al., 2005; Kirchman et al., 2004). However, phosphatase activity showed a more erratic pattern, not depending on site or particle size as has been observed before (Sinsabaugh and Moorhead, 1994). There are also several reports of the inhibitory effect of polyphenolic and humic compounds on decomposition, which typically affect enzymes by enhancing their stability and reducing their activity (Wetzel, 1991).

In model 6 ($\text{PON} \rightarrow \text{DON} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$), the mean k_{PON} of the study river was 0.028 day^{-1} (Table 4). On the other hand, model 7 ($\text{LPON} \rightarrow \text{LDON} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$) determines the k_{LPON} with a mean value of 0.093 day^{-1} that was also 3 times higher than the k_{PON} using the model 6. Utilization of labile organic N is known to be fast, usually within the order of days, from decomposing woody material (Kaushik and Hynes, 1971). In case of P, the k_{POP} were also recorded high considering only the labile, and both the labile and recalcitrant forms in combination. The PON fraction comprises mainly proteinaceous compounds (Pantoja and Lee, 1999). Organic matter chemical composition is crucial for nutrient mineralization, especially reactive components in PON are responsible for replenishing dissolved organic and inorganic N pools. However, the role of free-living and particle-attached bacteria in organic matter decomposition processes is the question of whether the POM or the DOM concentration induces the selection of bacterial populations that utilize preferentially POM or seston or DOM adsorbed on large colloidal particles as the major nutrient source. It is not completely clear whether bacteria are mostly free living or attached to the surface of solid particles.

Decomposition of DOM

In model 3 ($\text{POP} \rightarrow \text{DOP} \rightarrow \text{DIP}$), mean and median k_{DOP} were 0.328 day^{-1} and 0.294 day^{-1} , respectively (Table 3) while the mean and median k_{LDOP} in model 4

(LPOP $\rightarrow$ LDOP $\rightarrow$ DIP) were 0.718day^{-1} and 0.643 day^{-1} , respectively. The k_{LDOP} was almost 3 times higher than k_{DOP} . However, the k_{DOP} was much higher than that of k_{POP} reflecting the simpler biochemical composition of DOP thereby resulting rapid conversion of DOP into DIP. Higher decomposition rates for the DOM suggest that microbial decomposition of DOM was more efficient than POM; i.e., DOM was more labile than POM. In reality, DOM is composed of an unknown number of individual compounds, each with a different lability. Thus DOM represents a continuum of biological lability from recalcitrant material turning over on time scales of millennia to very labile material turning over on time scales of minutes (Carlson, 2002). Increased influx of DOM to the environment increases the number of heterotrophic bacteria, whereas the presence of POM and colloidal DOM intensify commonly bacterial respiration, and thus the overall organic matter decomposition rates in aquatic environments (Siuda and Chróst, 2002). The most likely source is DOM production associated with primary production through direct exudation from phytoplankton, from viral-mediated cell lysis, from sloppy zooplankton feeding or from particle solubilization. Rivers are a potential source of labile DOM. All of the sources of decomposable DOM are also likely sources of recalcitrant DOM.

There is considerable evidence that a sizable fraction of DOP in natural water is readily amenable to hydrolysis by microbial populations, phytoplankton and /or zooplankton (Dyhrman et al., 2006). In freshwater and marine systems, DOP can be a bioavailable nutrient source (Cotner and Wetzel, 1992; Nicholson et al., 2006). In particular, several studies have shown that P from DOP can be taken up by bacteria and phytoplankton in the presence of DIP, via enzymatic hydrolysis, depending on their strengths, substrate concentrations, saturation, storage capacity and the availability of other nutrients such as organic C (Cotner and Wetzel, 1992; Cotner et al., 1997; Labry et al., 2005). The lability of the DOP fraction is of primary importance. This study shows that most of the organic fraction among the rivers was labile with an average of 68 % of DOP preferentially amenable to hydrolysis by

enzymatic processes (data not shown). The decomposition rate was higher in summer than the other seasons. Others also reported that the hydrolysis was highest during summer and autumn, when P demand is presumably at its highest due to the prevalence of algal blooms at this time of year (Jackson et al., 1987). In winter, half of the DOP pool appeared to be refractory while in spring the degree of lability of DOP was more pronounced (data not shown). The dynamics of DOP formation, supply and degradation is very complex because of its heterogeneity coming from their various origins (river supplies, algal excretion, cell lysis), the largely unknown degradation processes (chemical and enzymatic) of the refractory DOP to easily hydrolysable compounds, and the fast recycling of these compounds. However, through several pathways, DOP can be derived largely from nucleic acids or nucleotides, sugar phosphates, phospholipids and other-P compounds, most of which are well known as essential intracellular intermediates and metabolites having functions as activators and precursors of macromolecular biosynthesis and as regulators of metabolism (Orrett and Karl, 1987; Berman, 1988). DOP consisting of mainly phosphate esters can be biochemically labile to allow active assimilation by bacteria and algae (Orrett and Karl, 1987; Berman, 1988).

Although the enzyme activities were not measured, the basis of the organic P decomposition processes is almost entirely the enzymatic which was excreted by different microorganisms in aquatic environment. Organic P compounds must first be converted to DIP for utilization by bacteria and phytoplankton (Ammerman and Azam, 1985), thus the structural character of DOP influences its bioavailability. Although the phytoplankton is also capable of assimilating P from the POP (Cembella et al., 1984) and DOP (Cotner and Wetzel, 1992), however, the bioavailability of DOP may be reduced if it is associated with humic acids (Reynolds and Davies, 2001). The P content of DOM is characteristically variable because, unlike N, P is not the integral part of all molecules of dissolved humic substances. Instead, the organic P content is carried by more specific substances that can vary more than other components of the DOM (Qualls and Haines, 1991).

Table 3. Mean and median values of the decomposition rates of the various organic P fractions using different P decomposition models; unit of decomposition rates is day^{-1} ; n = 152.

Decomposition.			Rivers						
Model	rate					North		South	Mean
			Keum	Youngsan	Sumjin	Han	Han	Han	
TOP-DIP	k_{TOP}	Mean	0.034	0.036	0.035	0.034	0.05	0.038	0.038
		Median	0.037	0.034	0.033	0.034	0.048	0.032	0.036
POP-DIP	k_{POP1}	Mean	0.046	0.049	0.035	0.031	0.071	0.056	0.048
		Median	0.04	0.026	0.027	0.032	0.073	0.052	0.042
POP-DOP-DIP	k_{POP2}	Mean	0.043	0.042	0.038	0.031	0.063	0.057	0.046
		Median	0.038	0.038	0.036	0.032	0.065	0.053	0.044
	k_{DOP2}	Mean	0.294	0.255	0.244	0.302	0.448	0.426	0.328
		Median	0.223	0.235	0.224	0.258	0.433	0.389	0.294
LPOP-LDOP-DIP	k_{LPOP}	Mean	0.146	0.174	0.143	0.123	0.178	0.13	0.149
		Median	0.135	0.17	0.14	0.14	0.19	0.12	0.149
	k_{LDOP}	Mean	0.818	0.67	0.622	0.485	0.68	1.035	0.718
		Median	0.825	0.5	0.56	0.47	0.61	0.89	0.643

In model 6 ($\text{PON} \rightarrow \text{DON} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$), mean k_{DON} was 0.191 day^{-1} (Table 4) while the mean and median k_{LDON} in model 7 ($\text{LPON} \rightarrow \text{LDON} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$) were 0.474 day^{-1} and 0.466 day^{-1} , respectively. This decomposition coefficient was also more than double compared with the decomposition coefficients of combined labile and recalcitrant DON. However, likewise P, the k_{DON} was much higher than that of k_{PON} reflecting the simpler biochemical composition of DON thereby resulting rapid conversion of DON into DIN (dissolved inorganic N). Higher decomposition rates of DON again suggest that DOM was more labile than POM.

A significant portion of DON may be remineralized by microbes depending upon ambient nutrient status, C: N: P ratios of source materials (Tezuka, 1990), and the chemical stability and bioavailability of DOM (Amon and Benner, 1996). As for microbial loop energetics, DON is very important especially in oligotrophic environment where most of the N is in the dissolved organic form (Boyer et al., 1997; Bronk, 2002). Preferential utilization of DON over ammonium, urea, or nitrate is energetically advantageous since bacteria conserve energy by avoiding biosynthesis of amino acids and other nitrogenous biosynthetic precursors (Payne and Wiebe, 1978). Nevertheless, probably a more important pathway for DON utilization by phytoplankton in nature is the release of NH_4^+ from DON compounds as a result of bacterially mediated, enzymatic breakdown and deamination (Pantoja et al., 1997). Subsequently the released NH_4^+ would be available for bacterial and phytoplankton uptake or might be transformed to nitrate via nitrifying bacteria. It is generally believed that the low molecular weight organic compounds (i.e., amino acids, short chain peptides, fatty acids, monosaccharides) can be directly assimilated (without their primary decomposition outside the cell) and metabolized by bacteria. Protein and their constituents in living and dead phytoplankton are among the most labile fractions of bulk organic matter, and their degradations support both microbial production and regeneration of nitrogenous nutrients such as NO_3^- , NO_2^- and NH_4^+ (Stepanauskas and Leonardson, 1999).

Table 4. Mean and median values of the decomposition rates of the various N fractions using different N decomposition models; unit of decomposition rates is day⁻¹; n = 152.

Decomposition.			Rivers						
Model	rate					North		South	Mean
			Keum	Yongsan	Sumjin	Han	Han	Han	
TON-DIN	k _{TON}	Mean	0.027	0.026	0.032	0.024	0.022	0.026	0.026
		Median	0.025	0.025	0.031	0.022	0.020	0.025	0.025
PON-DON- NH ₄ ⁺ - NO ₂ ⁻ -NO ₃ ⁻	k _{PON}	Mean	0.028	0.027	0.027	0.025	0.028	0.030	0.028
		Median	0.029	0.025	0.027	0.025	0.029	0.030	0.028
	k _{DON}	Mean	0.161	0.194	0.204	0.187	0.168	0.234	0.191
		Median	0.148	0.205	0.210	0.185	0.150	0.240	0.190
	k _{NH4(1)}	Mean	0.364	0.428	0.510	0.651	0.593	0.571	0.520
		Median	0.360	0.410	0.470	0.665	0.580	0.550	0.506
	k _{NO2(1)}	Mean	0.564	1.033	1.009	0.853	1.090	0.793	0.890
		Median	0.564	1.050	1.050	0.855	0.975	0.760	0.876
LPON- LDON- NH ₄ ⁺ - NO ₂ ⁻ -NO ₃ ⁻	k _{LPON}	Mean	0.120	0.080	0.095	0.083	0.089	0.093	0.093
		Median	0.120	0.080	0.086	0.080	0.086	0.090	0.090
	k _{LDON}	Mean	0.373	0.433	0.497	0.444	0.565	0.521	0.472
		Median	0.355	0.450	0.470	0.500	0.565	0.450	0.465
	k _{NH4(2)}	Mean	0.551	0.600	0.663	0.824	0.768	0.532	0.656
		Median	0.580	0.645	0.655	0.850	0.760	0.450	0.657
	k _{NO2(2)}	Mean	0.726	1.136	1.110	1.092	0.990	0.916	0.995
		Median	0.735	1.200	1.100	1.050	0.955	0.880	0.987

Despite considerable variability, the results of these experiments clearly indicate the potential for degradation of DON to NH_4^+ by microorganisms or free dissolved enzymes. In model 6 ($\text{PON} \rightarrow \text{DON} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$) the mean and median $k_{\text{NH}_4(1)}$ were 0.520 day^{-1} and 0.506 day^{-1} , respectively. Whereas in model 7 ($\text{LPON} \rightarrow \text{LDON} \rightarrow \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$), these decomposition rates were 0.656 day^{-1} and 0.657 day^{-1} , respectively. The decomposition rates of NO_2^- were faster than NH_4^+ decomposition rates. It is well known that during nitrification, NO_2^- is an intermediate step for conversion into NO_3^- . In both the models (model 6 and model 7), the transformation rates of NO_2^- to NO_3^- was approximately twice than the transformation of NH_4^+ to NO_2^- . However, it seems reasonable to assume that there was a constant flux of NH_4^+ and /or urea from suitable DON pool components to phytoplankton and bacteria (Berman, 1997), especially when the ambient levels of NH_4^+ or NO_3^- are low.

Spatial variability of the decomposition rates

There were no significant variations of k_{TOP} among the 5 rivers except the Keum River (one-way ANOVA, $p < 0.05$). In $\text{POP} \rightarrow \text{DIP}$ model, significant variations of k_{POP1} recorded in the Sumjin, the North Han and the South Han Rivers whereas in $\text{POP} \rightarrow \text{DOP} \rightarrow \text{DIP}$ model significant variations of k_{POP2} was in the Sumjin and the Han River (one-way ANOVA, $p < 0.05$). In $\text{LPOP} \rightarrow \text{LDOP} \rightarrow \text{DIP}$ model, there were no significant variations of k_{LPOP} and k_{LDOP} in the studied rivers except the Youngsan River. Significant variations in the decomposition rates of P components might be the representation of the high initial DIP concentration in different rivers and/or in different sampling sites even in the same river. In case of N, there was no significant differences in the studied rivers except the k_{PON} and $k_{\text{NH}_4(1)}$ of the Han River and k_{TON} of the Sumjin River (one-way ANOVA, $p < 0.05$). This variation might be the attributable to high initial DIN (NH_4^+ , NO_2^- , and NO_3^-) of this river than the others.

Temporal variation of the decomposition rates

In cases of all P components, relatively low decomposition value obtained in November, with gradual increase in March and June in the Keum River (Fig. 2). In the Youngsan and the Sumjin River, decomposition rates were high in August that gradually declined in the month of December and February. However, the low decomposition value of June compared to August recorded in both the rivers. In the North Han River and the Han River, decomposition rates of all P components were slightly high in May compared to the end of August while in the South Han River highest value obtained in the month of July than May and October.

Except the North Han River, no significant variations of k_{TOP} were observed among the 5 rivers. Based on model 2 and model 3, significant variations of k_{POP1} and k_{POP2} were only found in the Keum River (one-way ANOVA, $p < 0.05$). No significant differences of k_{LPOP} recorded in the studied rivers while significant variations of k_{LDOP} were found in the Keum River and the South Han River (one-way ANOVA, $p < 0.05$). Variations in the rates of decompositions were mainly due to the availability of nutrients, origin of substrates and temporal activity of microorganisms. However, it is not clear why the significant variations of k_{TOP} and k_{LDOP} in the respective North Han and the South Han River were observed although the initial DIP of these rivers was relatively low compared to others.

In the Keum River, the decomposition rates of all the N components were high during October followed by June and November. The low k_{TON} in June gradually increased up to February in the Youngsan River while in the Sumjin River relatively low values recorded in August compared to other periods (Fig. 3). In both the Youngsan and Sumjin Rivers, k_{PON} and k_{LDON} gradually increased from June to August and then slightly declined in December and relatively stable up to February. The k_{LPON} values in both the rivers were high in June that declined in August and relatively stable up to December and then slightly increased in February. The k_{DON} values of all the rivers were relatively stable (0.16-0.22) in all seasons. In all N components of the North Han and the Han River, the decomposition values in April

were same or slightly high than October. But in the South Han River, high decomposition values of all N components obtained in July compared to May and October except the k_{LDON} . There were little differences between the $k_{NH4(1)}$ and $k_{NO2(1)}$ while the $k_{NH4(2)}$ was far below the $k_{NO2(2)}$ in the Youngsan River (Fig. 4). In the Sumjin River, the decomposition pattern of NH_4^+ and NO_2^- were similar in both the models. Both NH_4^+ and NO_2^- decomposition rates of two models were relatively low in April than October in the North Han River. But in the Han River, the $k_{NH4(1)}$ was high in October than April while the $k_{NO2(1)}$ was relatively low in October than April reflecting the more reduced conditions in October. While the both $k_{NH4(1)}$ and $k_{NO2(1)}$ were similar in May, July and October, there was an increased decomposition rates of both the $k_{NH4(2)}$ and $k_{NO2(2)}$ from May to October. Except the Keum River, there were significant differences in the decomposition rates of different N components of above 1/3rd of the total 45 decomposition rates of the rest 5 study rivers (one-way ANOVA, $p < 0.05$). While there have been a number of decomposition studies conducted over the past 60 years, decomposition rate constants were seldom reported. Those few studies reported rate constants that did not differentiate between labile and recalcitrant pools. This is not to imply that other investigations have conceptualized DOM and POM as having pools of varying lability.

Relative proportions of labile and refractory fractions of P and N

The relative content of an individual component in the POM and DOM is a more important biological characteristic than its concentration. The ratios of major biochemical compounds in DOM and POM as labile and recalcitrant forms allow one to hypothesize not only about the origin of the OM and the paths of its transformation, but also about its food value at higher trophic levels in river ecosystems. The relative proportions of labile and recalcitrant forms of N varied widely from station to station and from river to river (Fig. 5). The LPON varied from 40-75 % in the studied rivers. The higher the available inorganic N concentrations, the lower percentage of LPON were observed in the studied rivers

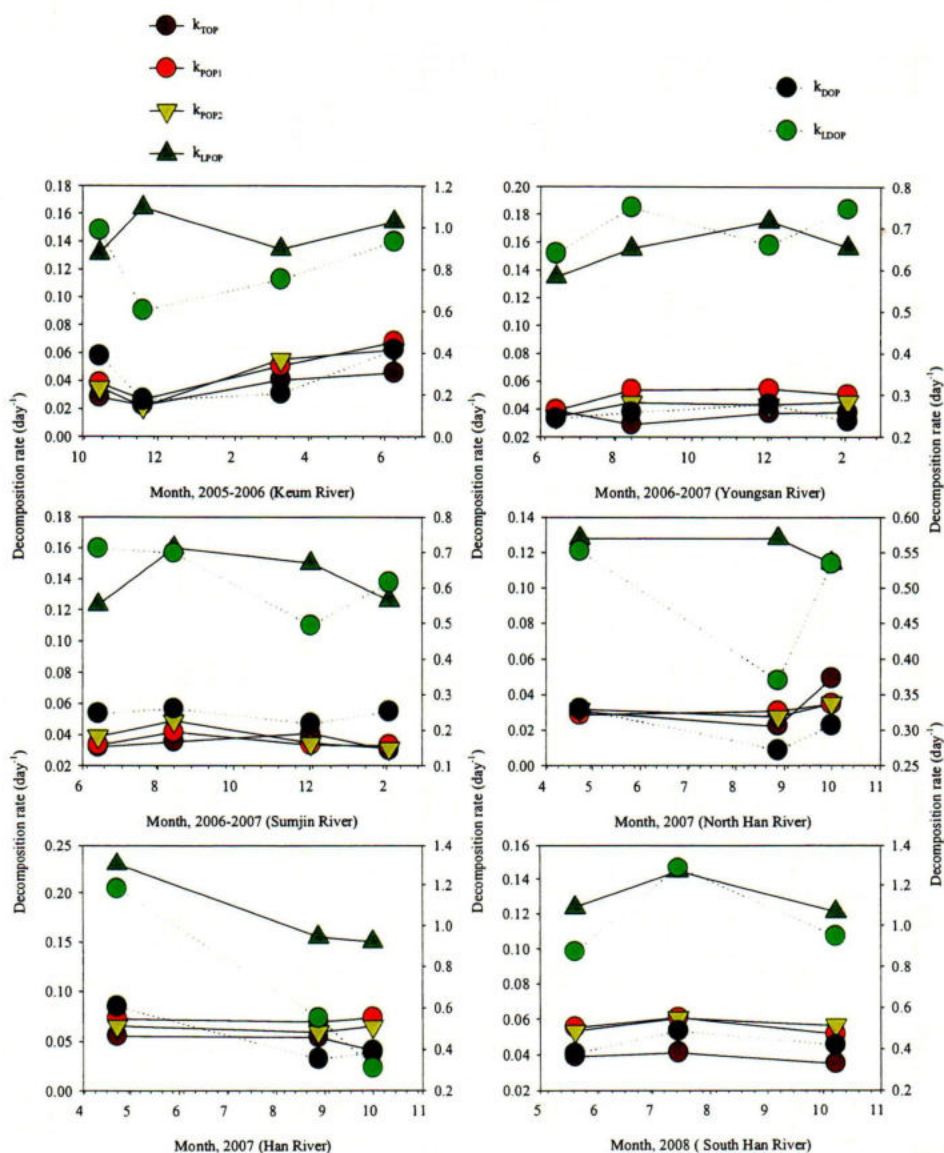


Fig. 2. Temporal variation of the decomposition rates of various P fractions. Decomposition mean values were plotted for each of the sampling dates in each river. Left side scales are for k_{TOP} , k_{POP1} , k_{POP2} and k_{LPOP} while the right side scales are for k_{DOP} and k_{LDOP} . In X-axis, numbers indicate the month of sampling and incubation periods for the decomposition of organic P components of the respective years.

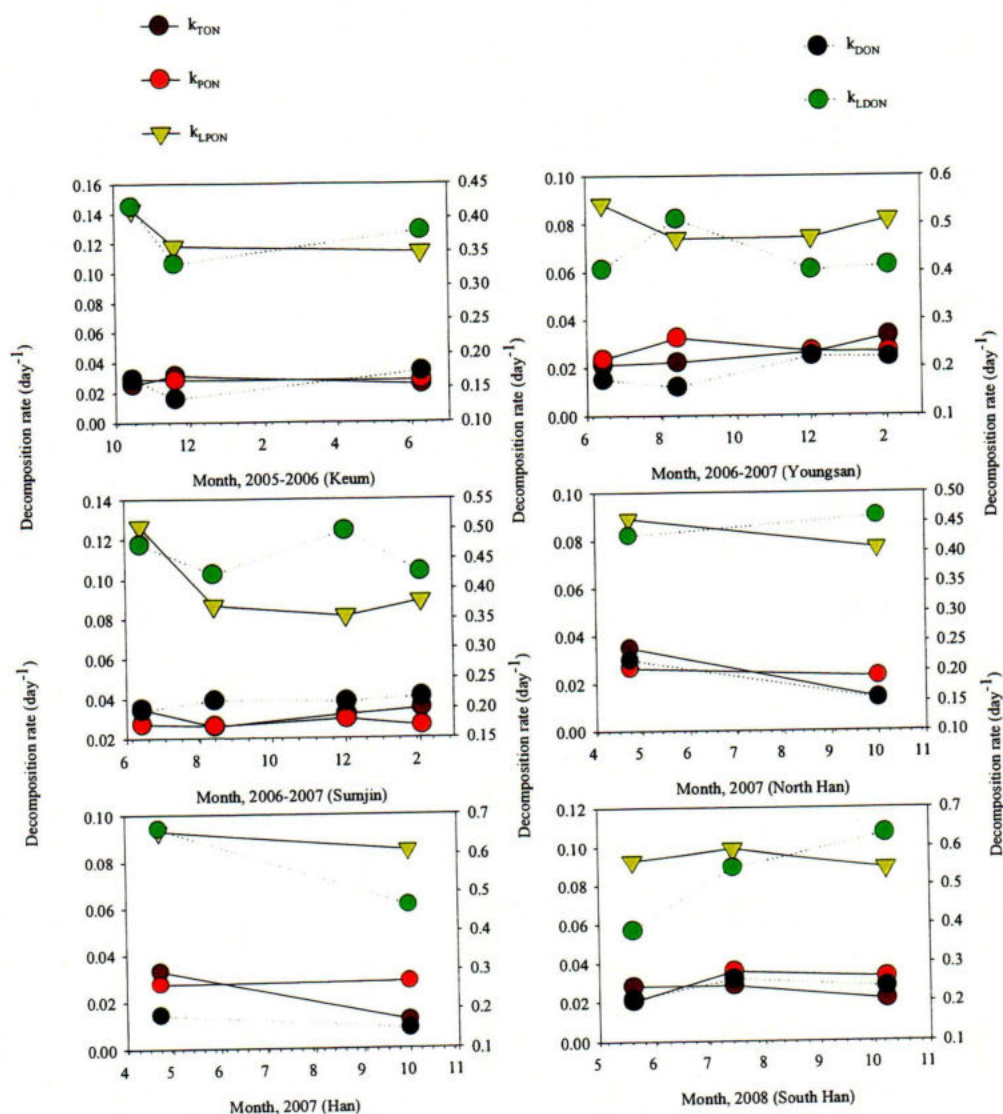


Fig. 3. Temporal variation of the decomposition rates of various organic N fractions.

Decomposition mean values were plotted for each of the sampling dates in each river. Left side scales are for the k_{TON} , k_{PON} and k_{LPON} while the right side scales are for k_{DON} and k_{LDON} . In X-axis, numbers indicate the month of sampling and incubation periods for decomposition of organic N components of the respective years.

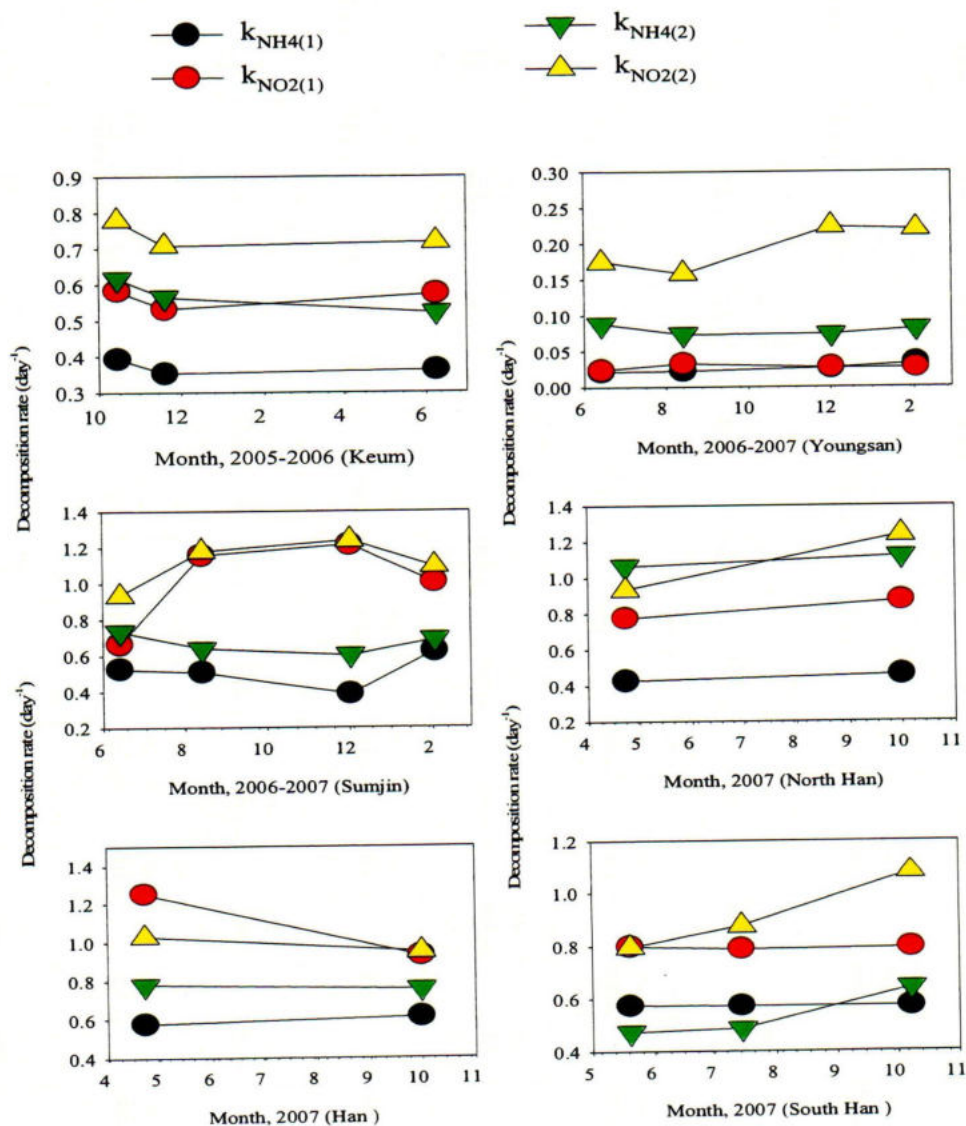


Fig. 4. Temporal variation of the decomposition rates of NH_4^+ and NO_2^- fractions.

Decomposition mean values were plotted for each of the sampling dates in each river. On the X-axis, numbers indicate the month of sampling and incubation periods for the decomposition of NH_4^+ and NO_2^- fractions of the respective years in each river.

also supporting the inhibitory effect of extracellular enzymes. In case of DON fractionations, the LDON varied from 14-54 %. But in the South Han River, it was above 74 %, perhaps due to the scarce of available inorganic N species. In case of RDOP and RDON, although their percentages were relatively high, those should not consider as real recalcitrant compounds. The median value of LPON and LDON of all the study rivers were 57 % and 42 %, respectively. As the DOP and DON are the available forms of organic P and N, and as the phytoplankton and bacteria prefer the most available form of orthophosphate for P and NH_4^+ for N, these RDOP and RDON forms can be considered as relatively slightly recalcitrant forms of DOP and DON, respectively. Indeed, they are not recalcitrant.

Besides the induction and/or suppression of hydrolytic activity by its organic substrates (Hoch and Bronk, 2007), organic matter lability has been suggested as one of the regulating factors (Hoppe and Ullrich, 1999). Other studies have suggested that the ratio of proteins to carbohydrates should be an adequate evaluation tool, as proteins have high lability than such refractory carbohydrates as cellulose or chitin remnants (Cividanes et al., 2002). However, the protein ageing (Keil and Kichman, 1994) and the tendency of proteins to combine with refractory carbohydrate and phenolic radicals may actually sequester these compounds in refractory pools. Therefore, increases in protein: carbohydrate ratio values do not necessarily mean an increase in food quality (Covazzi Harriague et al., 2007).

The relative proportions of different labile and recalcitrant forms of P also varied widely from river to rivers even in different sampling sites of the same river. However, likewise N, the higher the DIP concentrations, the lower the percentage of labile POP were observed in the rivers supporting the inhibitory effect of extracellular enzymes in presence of excess available PO_4^{3-} . Based on this hypothesis, the recalcitrant POP also varied amongst the studied rivers. In case of DOP fractionations, the LDOP varied from 35-50%. But in the South Han River, it was above 82 %, perhaps due to the scarcity of available inorganic P species (Fig. 6). Extracellular enzymatic activities of the study sites of this river might be

pronounced due to the scarcity of available nutrients. Consequently, the labile fractions of POP and DOP were relatively very high than others. However, the median value of the LPOP and LDOP of the studied rivers were 41% and 50 % respectively (Fig. 7). A relatively similar proportion of labile and refractory DOP coexists along the rivers and across the seasons, implying that processes such as production and remineralization that affect the distribution of the different P compounds in the organic fraction are ubiquitous and have approximately the same timescales. The refractory fraction of DOP is likely to consist of inositol phosphates, phosphonates and possibly phospholipids (Kolowitz et al., 2001). Labile monoesters are readily hydrolysable by alkaline phosphatase (Monbet et al., 2007). Other organic P compounds such as P diesters and even phytic acid are potentially bioavailable because enzymes such as phosphodiesterase and even phytase are found in aquatic systems (Chen and Lim, 2006) either on cell surface or dissolved in the water after cell lysis or excretion (Paytan and McLaughlin, 2007). However, the phosphate diester, which includes nucleic acids, phospholipids, teichoic acids and some aromatic compounds, generally represent only a small fraction of the organic P pool, when compared with the monoester phosphates (Condrón et al., 2005).

Atomic ratios of labile and recalcitrant forms of P and N

Relationship between the C, N and P contents of river samples offer an informative look at organic matter dynamics. Before and after decomposition, the atomic ratio of the labile and recalcitrant forms of P and N are the indicatives of their chemical structure of both the dissolved and particulate forms of organic P and N. The molar ratios of labile and recalcitrant P and N fractions in different seasons at different sampling sites varied widely. This variation was reasonable as because of different sampling locations varied with respect to urban and industrial discharges and runoff, agricultural activities and the bathymetric consequences. The average ratio of LPON:LPOP in the studied rivers was 84 while its 75 percentile was 107. But in case of dissolved fractions, the mean LDON:LDOP ratio was 190 while the

75 percentile was 219 (Table 5). In contrast, the mean ratio of RPON:RPOP was 189 while the 75 percentile was 71. Similarly, the average ratio of RDON:RDOP was 416 and the 75 percentile was 282 (Table 6). However, the mean initial atomic ratio of PON:POP and DON:DOP were 58 (median value 48, 75 percentile 78) and 252 (median value 176, 75 percentile 329). The ratios of labile LPON: LPOP increased during decomposition while the ratios of LDON:LDOP decreased than the initial PON:POP and DON:DOP ratios reflecting faster decomposition of LPOP than LPON. The correlation studies indicate the positive correlations between the labile and recalcitrant PON and POP (RPOP-RPON, $r = 0.24$, $n = 143$, $p < 0.05$; LPOP-LPON, $r = 0.42$, $n = 155$, $p < 0.05$).

The spatial and temporal changes in the C:N:P composition of POM could be due to variations in the proportions of the four major groups of biomolecules (carbohydrates, lipids, proteins, and P-compounds) than the variations in the molecular formula of each group. In case of dissolved fractions, the negative correlation values in both the labile and recalcitrant fractions of P and N suggests the release of both DON and DOP through excretion or cell lysis. But the initial DON and DOP was positively correlated ($r = 0.23$, $n = 167$, $p < 0.05$). However, the correlation coefficient between the initial PON and POP ($r = 0.27$, $n = 167$, $p < 0.05$) was almost similar with the correlation coefficient of recalcitrant PON and POP suggesting the decrease of particulate P and N was relatively proportional during the decomposition period (Fig. 8). The ratio of PON:POP and RPON:RPOP correlated significantly and positively ($r = 0.65$, $p < 0.0001$, $n = 133$) (Fig. 9). A significantly positive correlation also found between the ratio of DON:DOP and the ratio of RDON:RDOP ($r = 0.45$, $p < 0.0001$, $n = 125$). The N: P stoichiometry of DOM in the unpolluted rivers is 30-170:1 (Meybeck, 1982). In this study, there were also significant differences in the N: P stoichiometry of the POM and DOM. In general, the organic matter at the North Han River presents a larger N: P ratio than the other rivers, a clear indication of the higher lability of the organic matter. In fact, the average N:P molar ratio of POM (Table 2) in the Keum River throughout the study

Table 5. Median values of LPOP, LDOP, LPON and LDON and their molar ratios; concentration units are in μgL^{-1} ; n = 152.

River	Sampling dates	LPON	LPOP	Molar N:P	LDON	LDOP	Molar N:P
Keum	2005-10-15	37	0.61	61	12	0.11	109
	2005-11-19	47	0.44	107	11	0.15	73
	2006-3-10	19	1.5	13	13	0.23	57
	2006-6-9	40	1.4	29	20	0.18	111
Youngsan	2006-6-14	66	0.36	183	35	0.16	219
	2006-8-14	26	0.31	84	39	0.19	205
	2006-12-2	27	0.63	43	35	0.16	219
	2007-2-3	52	0.71	73	25	0.27	93
Sumjin	2006-6-14	33	0.19	174	47	0.097	485
	2006-8-14	18	0.29	62	45	0.13	346
	2006-12-2	24	0.13	185	41	0.065	631
	2007-2-3	19	0.16	119	52	0.065	800
North Han	2007-4-23	12	0.081	148	8	0.065	123
	2007-8-28	11	0.13	85	8	0.081	99
	2007-10-1	13	0.13	100	8	0.032	250
Han	2007-4-23	22	0.74	30	8	0.16	50
	2007-8-28	18	0.24	75	8	0.56	14
	2007-10-1	20	0.36	56	9	0	56
South Han	2008-5-20	7	0.32	22	5	0.35	14
	2008-7-15	14	0.23	61	6	0.61	10
	2008-10-8	13	0.26	50	3	0.13	23
Mean		26	0.44	84	21	0.19	190
Median		21	0.32	74	13	0.16	110
75percentile		33	0.61	107	35	0.19	219

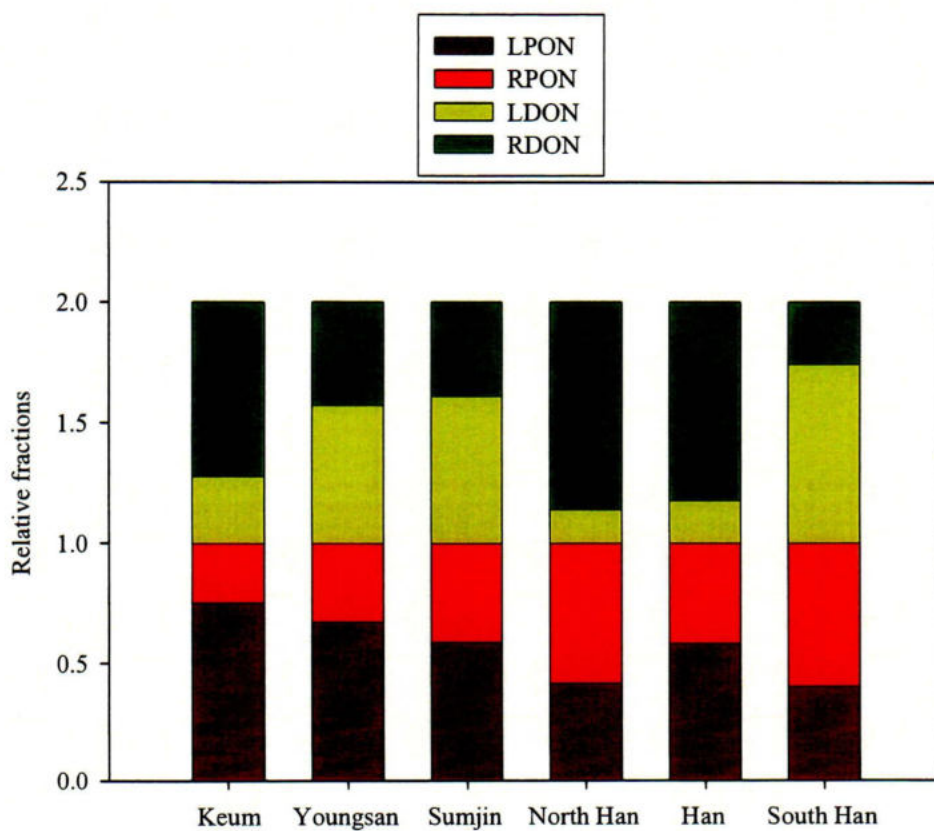


Fig. 5. Median values of the relative proportions of labile (LPON, LDON) and refractory (RPON, RDON) fractions of the particulate organic nitrogen (PON) and the dissolved organic nitrogen (DON) in the study rivers.

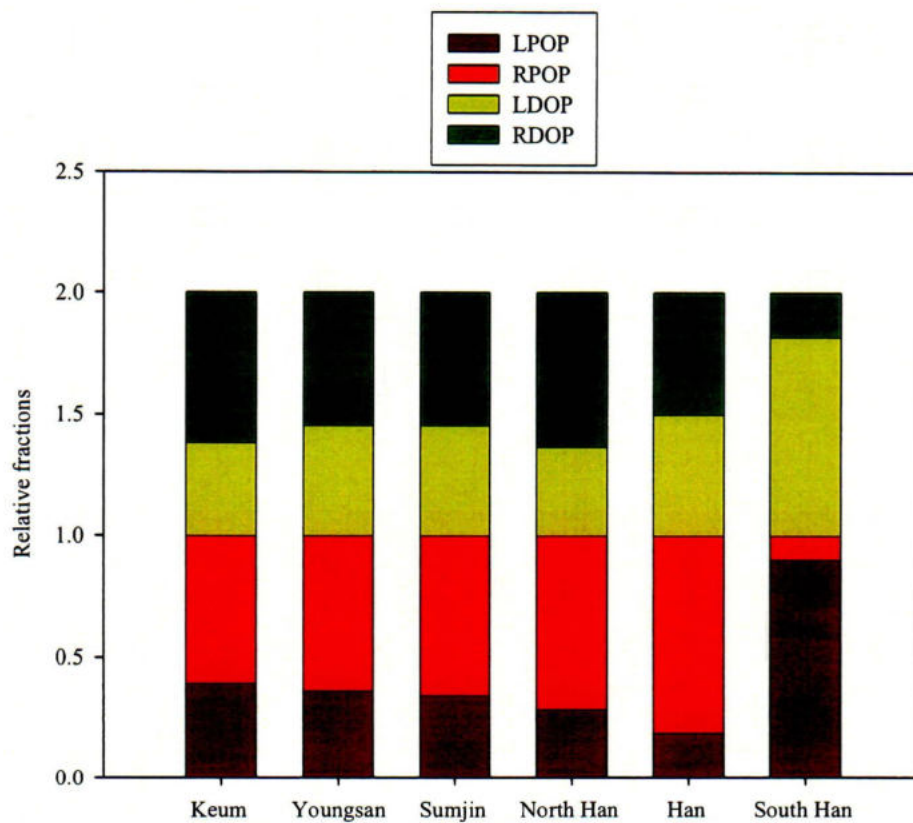


Fig. 6. Median values of the relative proportions of labile (LPOP, LDOP) and refractory (RPOP, RDOP) fractions of the particulate organic phosphorus (POP) and the dissolved organic phosphorus (DOP) in the study rivers.

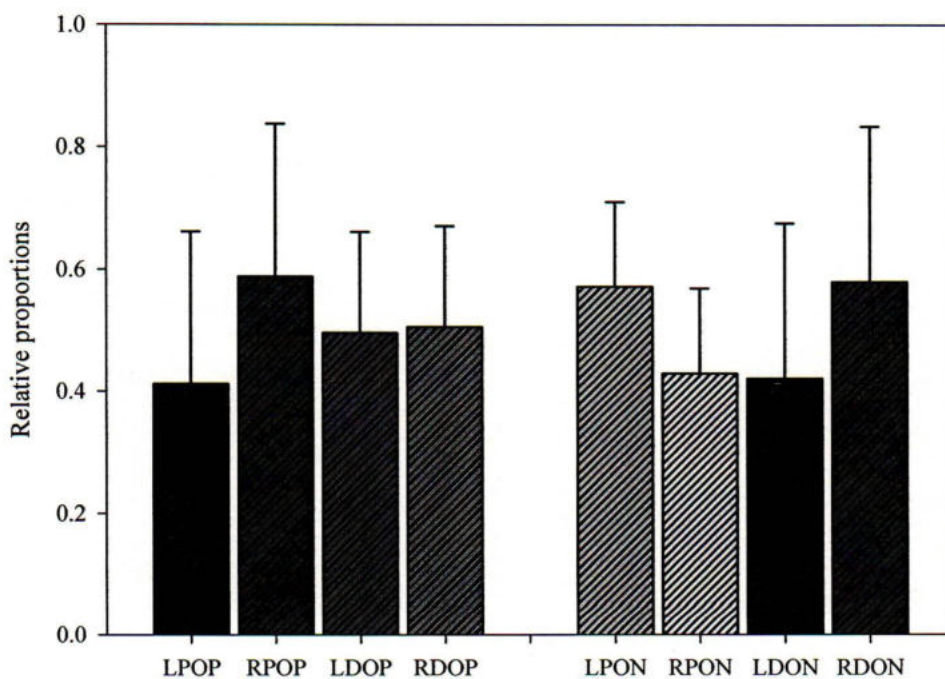


Fig. 7. Average values of the labile (L) and the recalcitrant (R) fractions of particulate organic phosphorus (POP), dissolved organic phosphorus (DOP), particulate organic nitrogen (PON) and dissolved organic nitrogen (DOP) in the study rivers.

Table 6. Median values of RPOP, RDOP, RPON and RDON, and their atomic ratios; concentration units are in μgL^{-1} ; n=152.

River	Sampling date	RPON	RPOP	Molar N:P	RDON	RDOP	Molar N:P
Keum	2005-10-15	16	1.07	15	21	0.13	162
	2005-11-19	20	1.55	13	23	0.21	110
	2006-3-10	6	1.52	4	43	0.39	110
	2006-6-9	9	0.98	9	26	0.19	137
Yongsan	2006-6-14	44	1.45	30	32	0.27	119
	2006-8-14	7	1.05	7	24	0.18	133
	2006-12-2	11	0.69	16	13	0.065	200
	2007-2-3	19	0.61	31	31	0.23	135
Sumjin	2006-6-14	14	0.83	17	16	0.18	89
	2006-8-14	21	0.42	50	31	0.11	282
	2006-12-2	17	0.24	71	32	0.065	492
	2007-2-3	9	0.26	35	32	0.016	2000
North Han	2007-4-23	36	0.26	138	73	0.051	1431
	2007-8-28	14	0.47	30	39	0.2	195
	2007-10-1	8	0.34	24	49	0.13	377
Han	2007-4-23	36	2.63	14	78	0.032	2438
	2007-8-28	164	3.55	46	24	0.9	27
	2007-10-1	145	1.26	115	40	0	211
South Han	2008-5-20	64	0.03	2133	5	0.1	50
	2008-7-15	17	0.03	567	1	0.06	17
	2008-10-8	18	0.03	600	1	0.03	33
Mean		33	0.92	189	30	0.18	416
Median		18	0.69	31	31	0.15	149
75 percentile		36	1.26	71	39	0.20	282

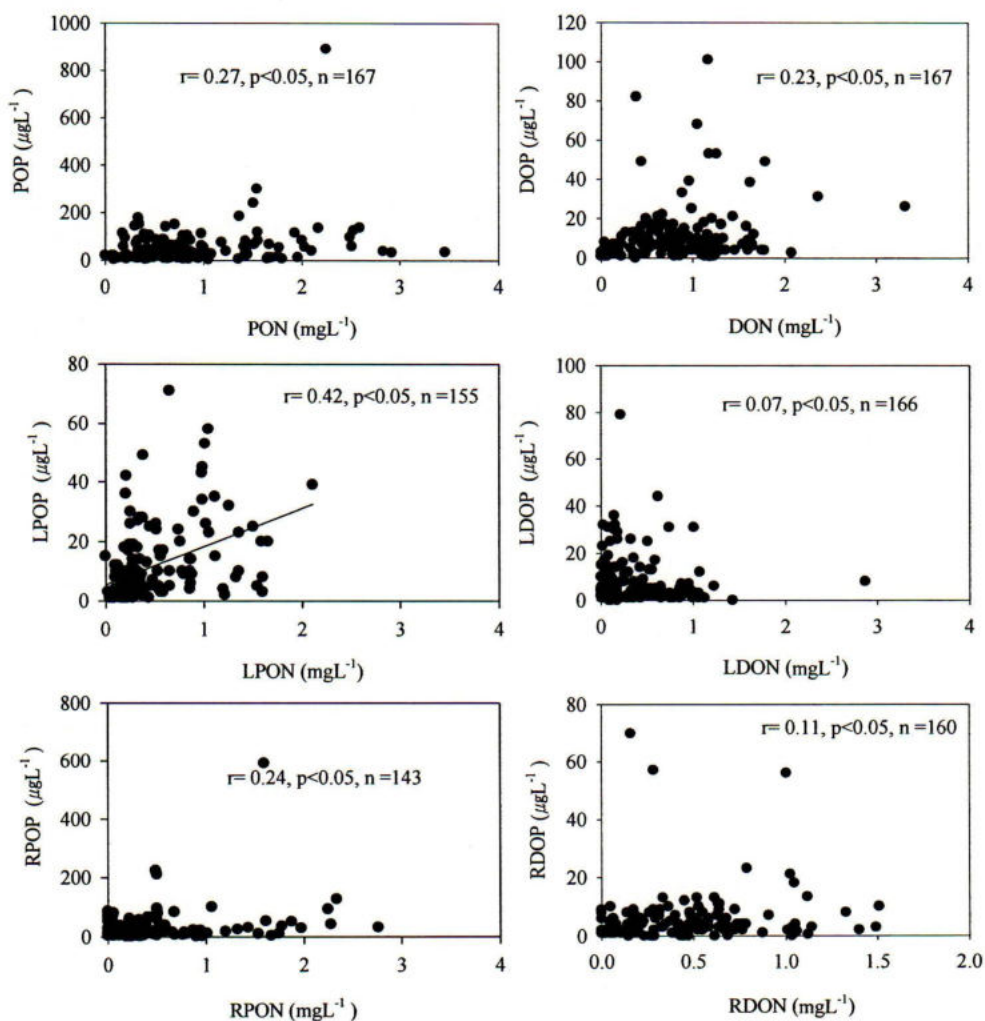


Fig. 8. Correlations between the fractions of POP and PON, LPOP and LPON, RPOP and RPON, DOP and DON, LDOP and LDON, and RDOP and RDON of the study rivers.

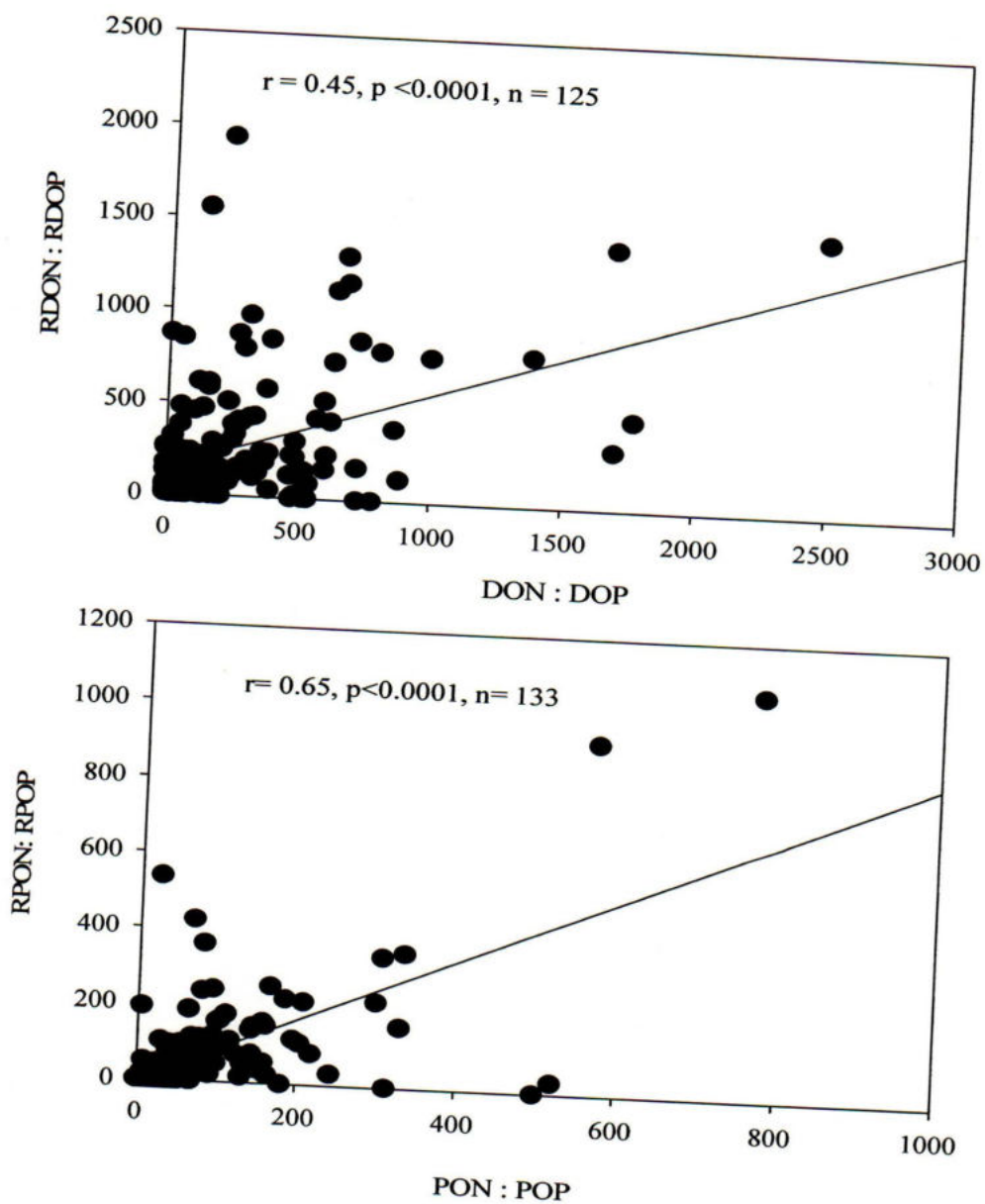


Fig. 9. Scatter charts between the atomic ratios of PON:POP with its refractory counterpart RPON: RPOP, and DON:DOP with RDON:RDOP of the study rivers.

period, in the Youngsan River during August and in the Han River during April was close to the Redfield ratio (16:1), typical of detrital organic matter derived from aquatic plants and phytoplankton (Anderson, 1995; Fraga et al., 1998). On the other hand, N:P ratio of other rivers was away from the Redfield ratio perhaps due to the marked increase in the proportion of particulate carbohydrates at the expenses of proteins and P-compounds. Depending on the type of vegetation, such as plants with soft tissues vs. woody tissues, terrestrial organic matter shows a wide range of N:P values. In general, terrestrial plants are relatively poor in P and N content with N: P ratio ranging 10-100 for soft tissues and 100-1000 for woody tissues (Ruttenberg and Goni, 1997).

Changes in the stoichiometric ratios during decomposition

Spatial and temporal changes in the concentrations of major nutrients in DOM and POM, as well as their proportions, are mainly determined by autotrophic and heterotrophic biological activity. The changes in various ratios of particulate and dissolved organic fractions of C, N and P were modeled. Variations were found in initial concentrations of POC, DOC, PON, DON, POP and DOP, and their ratios (PON:POC, DON:DOC, POP:PON and DOP:DON) among the sampling sites. In general, patterns in organic decomposition followed an exponential decrease during the incubation period. A typical example of the changes in different particulate and dissolved fractions of C, N and P is shown in Fig. 10. When one of the inorganic fractions was found at very low concentrations, the rate of exponential decrease was very high. For example, at very low DIP concentration, the rate of changes of DOP:DON was very high compared to high DIP concentrations. In contrast, when DIP concentrations were higher, the decrease in the ratio of POP: PON was low. The average values of the rate of changes of the ratios of PON:POC, DON:DOC, POP:PON, DOP:DON, POP:POC and DOP:DOC were 0.036, 0.078, 0.069, 0.140, 0.041 and 0.086 day⁻¹ (Table 7). The rate of changes of PON:POC, POP:PON and POP:POC were, however, relatively low compared to the changes of DON:DOC,

DOP:DON and DOP:DOC.

Low concentrations of DIP and NO_3^- indicate rapid changes in the rate of changes of the PON:POC, POP:PON and POP:POC compared to the changes of DON:DOC, DOP:DON and DOP:DOC implying that low concentrations of inorganic N and P accelerates the activity in decomposing particulate phases of organic matter. In contrast, high concentrations of inorganic N and P suppress the activity of enzymes responsible for decomposing dissolved organic matter. Previous work showed that DOP is predominantly phosphatase resistant (Peters, 1981) and high indigenous levels of alkaline phosphatase activity do not correlate with DOP mineralization rates (Hino, 1988). Preferential hydrolysis of POP relative to PON and PON relative to POC when overall organic matter mineralization rates were high appear to drive the observed patterns in PON:POC, DON:DOC, POP:PON DOP:DON, POP:POC and DOP:DOC ratios.

The stoichiometric approach explicitly recognizes that the relative abundances of elements can control rates of nutrient cycling and energy flow within and across ecosystem compartments. Table 8 indicates the stoichiometric ratios of C, N and P at 0 day and 20 days after incubation. The median value of initial TOC:TON:TOP was 259:52:1 while the 20 days median value was 371:110:1. Changes of TON:TOP supports the notion that preferential decomposition of P over N where the 20 days ratios were approximately two times higher than the initial ratios. In case of TOC:TON, the pattern did not follow the preferential mineralization of N over C, implying the rapid decomposition of DOC to dissolved inorganic C during incubation. As a result, the concentration of TOC decreases, resulting in decreased ratios of TOC:TON. Inorganic C is abundant in water, and so any increase in concentration resulting from decomposition of organic matter and anthropogenic CO_2 emissions might be expected on first glance to have little or no impact on phytoplankton growth and subsequent food-web dynamics. If photosynthesis is not limited by C, then it seems that the biological pump cannot sequester CO_2 . It should

however be noted that sequestration of anthropogenic CO₂ does occur as a result of the 'solubility pump' which is the uptake of C by air-sea exchange driven by undersaturation of pCO₂ (partial pressure of CO₂) with respect to the atmosphere and subsequent transport of C-enriched waters to depth by physical processes (Follows et al., 1996).

During incubation, calculated C:N, C:P and N:P molar ratios (Table 9 & Table 10) were found to increase from particulate phase to dissolved phase. Lower C:N, C:P and N:P molar ratios in the particulate phase indicates that the POM was relatively fresh and contained less altered organic materials while the higher ratios in DOM suggested to a more degraded recalcitrant organic material. Higher ratios in DOM seemed to suggest a direction for the degradation, decomposition and transformation of riverine organic matter from particulate to dissolved phases. However, this is consistent with other observations for estuarine and marine organic matter, which showed similar decomposition or diagenetic pathways from particulate to dissolved phases (Guo and Santschi, 1997).

Ecological stoichiometry theory has developed rapidly in recent years (Sterner and Elser, 2002) to integrate energy flow and nutrient cycling concepts. The relationships between C and N cycling are fundamental biochemical links in the biosphere (Turner, 2002). For example, increased atmospheric CO₂ can lead to greater rates of C fixation (photosynthesis) and higher C:N in terrestrial primary producers. Primary producers in aquatic and terrestrial environments have more environmentally induced phenotypic variation in C:N than consumers because of their ability to vary structural C; even single-celled primary producers can alter their C:N widely in response to nutrient limitation, whereas metazoans are more narrowly constrained (Elser et al., 2000). Systems dominated by autotrophs with low C:element ratios and fast turnover rates such as phytoplankton communities are effectively grazed and little C is sequestered to recalcitrant detrital pools, while terrestrial systems dominated by high C:element ratios and low turnover sequester

Table 7. Rate of changes of the ratios of different organic fractions of POM and DOM during the decomposition (units are shown as day⁻¹); n = 152.

Rivers	PON:POC	DON:DOC	POP:PON	DOP:DON	POP:POC	DOP:DOC
Keum	0.042	0.076	0.084	0.110	0.044	0.054
Youngsan	0.048	0.103	0.081	0.147	0.048	0.078
Sumjin	0.049	0.097	0.076	0.116	0.055	0.086
North Han	0.027	0.075	0.065	0.124	0.036	0.077
Han	0.023	0.028	0.059	0.205	0.029	0.130
South Han	0.029	0.089	0.050	0.139	0.035	0.091
Mean	0.036	0.078	0.069	0.140	0.041	0.086
SD	0.011	0.027	0.013	0.035	0.010	0.025

Table 8. Changes in the ratios of organic C, N and P (TOC:TON:TOP) during decomposition of natural riverine organic matter; n = 152.

Rivers	Mean		Median	
	0 day	20 days	0 day	20 days
Keum	136:20:01	182:42:01	105:09:01	120:19:01
Youngsan	267:61:01	488:122:01	241:53:01	346:110:01
Sumjin	298:128:01	626:228:01	271:118:01	402:197:01
North Han	361:62:01	528:174:01	387:40:01	508:135:01
Han	156:39:01	318:94:01	154:30:01	316:68:01
South Han	394:71:01	588:144:01	397:59:01	535:132:01
Mean	269:64:01	455:134:01	259:52:01	371:110:01

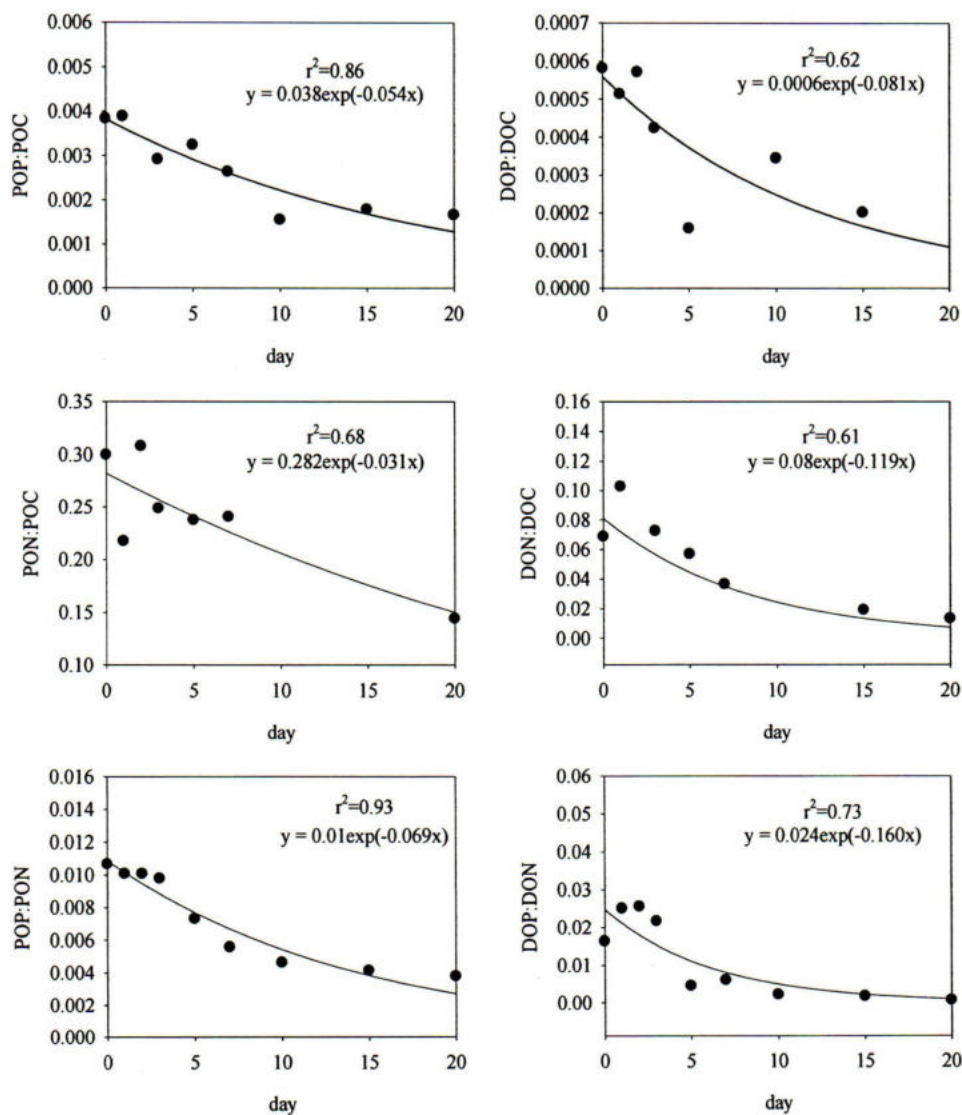


Fig. 10. Typical changes in ratios of POP:POC, DOP:DOC, PON:POC, DON:DOC, POP:PON and DOP:DON during the decomposition period.

most of the fixed C as detritus (Hessen et al., 2004). However, much aquatic detritus is derived from terrestrial plant material, and C:N of detritus is on average 4 times higher in terrestrial than aquatic habitats (Dodds et al., 2004). This may be due to the derivation of aquatic detritus from aquatic producers in part with a lower C:N than terrestrial detritus.

After 20 days, the changes of POC:PON were twice than the initial ones (Table 9). POM of streams, shallow lakes, and reservoirs with short residence times have C:P ratios <350 and N:P ratios <26 , whereas lakes with longer residence times differentiate from their inflows typically with C:P >400 and N:P >30 (Wetzel, 2001). Appreciable loadings of POM from the structural tissues of terrestrial and littoral plants, however, can result in seston relatively rich in C and lesser amounts of N and lead to high C:N, C:P and N:P ratios. When P availability is low, C:P ratios of POM will tend to be low and the photosynthetic productivity low. The mean values of the changes of the ratios of PON:POP, POC:POP and POC:PON at 0 day and 20 days were 35 to 63, 106 to 176 and 2.7 to 3.9, respectively. However, the initial and 20 days ratios of PON:POP and POC:POP were lower than the respective POC:PON ratios (Table 9). The ratios of PON:POP, POC:POP and POC:PON at 20 days were 2.7, 1.7 and 1.4 times higher than their respective initial ratios. Similarly, in case of DOM, the initial and 20 days ratios of DOC:DON were lower than the DON:DOP and DOC:DOP ratios. The ratios of DON:DOP and DOC:DOP at 20 days were at least 2.5 times higher than their initial values while the ratios of DOC:DON at 20 days were approximately 2 times higher than the initial ratios. (Table 10). The C:N ratio of DOM may often be significantly higher than the Redfield ratio (Søndergaard et al., 2000).

In both the POM and DOM, the changes of the ratios of different organic C, organic N and organic P support the preferential mineralization of P over N and N over C. Freshwater systems exhibit greater variability of seston C:N:P ratios (Elser et al., 2000), variation that has been shown to affect patterns of nutrient cycling,

secondary production, and community structure (Sterner and Elser, 2002; Hessen, 2005). Systematic increases in nutrient content (i.e., lower C:P and C:N) with increasing productivity or biomass have been reported before in the context of changing nutrient use efficiency in ecosystems, particularly in terrestrial systems (Vitousek, 1982), but also more recently in aquatic systems (Sterner and Elser, 2002). Reduced nutrient use efficiency could arise because of the introduction of other limiting factors (light or other nutrients) when any given nutrient becomes high in concentration.

It should be mentioned that the natural organic matter consists approximately 90 % organic C, 8-9 % organic N and 1 % organic P. The results of this study support the compositional pattern of organic C, organic N and organic P of natural riverine organic matter. The amount of changes of PON and POP based on POC were calculated before and after incubation. The initial mean value of PON:POC and POP:POC were 0.18 and 0.011, respectively while after 20 days the respective above-mentioned values were reduced to 0.12 and 0.0063 (Table 11). The percent reduction ratios of PON:POC and POP:POC were 33 % and 40 % suggesting the faster decomposition of POP over PON. In contrast, the changes of mean DON:DOC and DOP:DOC were decreased from 0.096 to 0.052 and 0.0013 to 0.0005, respectively during the initial and 20 days incubation periods (Table 12). These changes of the DON:DOC and DOP:DOC in DOM reflects the preferential mineralization of DOP over DON, and also the faster decomposition rates of DOM than that of POM.

The effects of changing nutrient supply on C cycling are commonly associated with freshwater systems because of their close proximity to human activity. Adding more P (and subsequently N) leads to eutrophication; primary production will draw CO_2 dissolved in water, hence more atmospheric CO_2 will enter the aquatic system for conversion to algal biomass, potentially sedimenting and thus being sequestered into a C sink. In fact, freshwater sediments may be a globally significant, yet

neglected organic C-sink (Dean and Gorham, 1998). While CO_2 fluxes to some extent are governed by the pCO_2 gradients across the water-air boundary layer, biological processes and stoichiometric balance will also be major determinants of net CO_2 balance. Freshwater systems are prone to large variations in CO_2 , and even a moderate increase in CO_2 could yield increased C:P ratios in algae (Urabe et al., 2003). Thus, major changes in fluxes of C to and from the atmosphere may be induced by relatively subtle shifts in the C: nutrient ratios of particular pools or in the relative importance of different pools having different C: nutrient ratios.

The ratios of the median values of TON:TOC and TOP:TOC at 0 day and 20 days are 0.25 to 0.18 and 0.0048 to 0.0026, respectively. Reduction rates of the ratios of TON:TOC and TOP:TOC were 28 % and 40 % during this incubation period (Table 13). Both N:C and P:C ratios increase when relative growth rate of an autotroph is increasing, in relative terms, a larger relative allocation to active N- and P-based compounds than C-based structural compounds (Vrede et al., 2004). This variability in stoichiometry is characteristic of the overall plasticity of autotrophic organisms and has its physiological base in the ability of autotrophs to maintain a balance between the types of compounds required for growth (Droop, 1974). Another cause of variability in stoichiometry comes from excess uptake of elements, i.e., autotrophs have considerable capacity to accumulate elements in excess of what is not immediately needed for growth. In contrast to the great physiological plasticity in growth form, tissue allocation, and thus biochemical and elemental composition exhibited by autotrophic organisms, metazoans exhibit far less intraspecific plasticity with a relatively narrow range of interspecific variation in C:N:P ratios, and a generally nutrient-rich biomass compared with autotrophs (Sturner and Elser, 2002).

Nutrients like N or P will be recycled and reused by autotrophs, while excess C may either be oxidized to inorganic forms by the organisms themselves or heterotrophic decomposers, or be more permanently buried in sediments or soils.

Table 11. Median values of the changes of PON and POP based on POC (PON:POC and POP:POC molar ratios) during decomposition of natural riverine organic matter; n = 152.

Rivers	PON:POC	PON:POC	POP:POC	POP:POC
	0 day	20day	0 day	20day
Keum	0.10	0.09	0.014	0.009
Youngsan	0.14	0.09	0.010	0.007
Sumjin	0.20	0.11	0.011	0.006
North Han	0.11	0.06	0.008	0.005
Han	0.26	0.20	0.014	0.007
South Han	0.26	0.20	0.006	0.004
Mean	0.18	0.12	0.011	0.0063
Median	0.17	0.10	0.011	0.0063
SD	0.07	0.06	0.003	0.0017

Table 12. Median values of the changes of DON and DOP based on DOC (DON:DOC and DOP:DOC molar ratios) during decomposition of natural riverine organic matter; n = 152.

Rivers	DON:DOC	DON:DOC	DOP:DOC	DOP:DOC
	0 day	20day	0 day	20day
Keum	0.07	0.041	0.0015	0.0008
Youngsan	0.11	0.070	0.0015	0.0005
Sumjin	0.10	0.040	0.0014	0.0005
North Han	0.11	0.062	0.0011	0.0004
Han	0.12	0.070	0.0011	0.0003
South Han	0.06	0.027	0.0009	0.0003
Mean	0.096	0.052	0.0013	0.0005
Median	0.105	0.052	0.0013	0.0005
SD	0.023	0.018	0.0003	0.0002

These similarities in feedbacks arise not because ecosystems mimic organismal allocation rules for C, N, or P, but because the interacting biota themselves that comprise ecosystems must obey stoichiometric rules at the level of their individual cells and bodies that greatly constrain the range of values that ecosystem level pools and process can attain. Geider and La Roche (2002) concluded that, both on the basis of laboratory C:N:P data and theoretical approaches to biochemical composition, there was little evidence to support the contention that the Redfield ratio reflects a physiological or biochemical constraint on the elemental composition of primary production, a conclusion also reinforced by Sterner and Elser (2002). Thus, the fate or sequestration of C will be determined by the absolute and relative demands for C, N and P of each organism relative to its resources.

Relations between stoichiometric ratios of organic matter and phytoplankton

The C:N:P ratios of phytoplankton collected from these rivers were measured during the study period. A small number of C:N, N:P, and C:P ratios of POM and DOM showed significant relationships (at $p = 0.05$) with C:N, N:P, and C:P ratios of phytoplankton of the study rivers. Nutrient stress will increase the C:N and C:P ratios of primary production, but not necessarily of the standing crop because much of the excess C may be lost as exudates (Carlson, 2002). In this study, the C:N:P ratios of POM and DOM were measured under dark conditions i.e., only enzymatic decompositions were determined. Other factors of natural environment are to be photodecomposition or variation of temperature that might have significant influences on the decomposition of POM and DOM as well as the uptake pattern of nutrient elements. Also, the flow rates of the rivers may be the most important reason for explaining the above phenomena. Under conditions of saturating light and limiting N, certain photoautotrophs can store C as lipid or carbohydrate, thereby increasing their C:N and C:P ratios (David et al., 2001). Likewise, if P is present in excess of cellular demands, it can be taken up and stored as polyphosphate, causing a decrease in the bulk C:P and N:P ratios. Conversely, when the bioavailable N:P

Table 13. Median values of the changes of TON:TOC and TOP:TOC molar ratios during decomposition of natural riverine organic matter; n = 152.

Rivers	TON:TOC	TON:TOC	TOP:TOC	TOP:TOC
	0 day	20days	0 day	20days
Keum	0.09	0.07	0.0051	0.0034
Yongsan	0.28	0.20	0.0052	0.0030
Sumjin	0.41	0.29	0.0046	0.0021
North Han	0.23	0.16	0.0032	0.0014
Han	0.31	0.27	0.0078	0.0041
South Han	0.16	0.11	0.0026	0.0018
Mean	0.25	0.18	0.0047	0.0026
Median	0.25	0.18	0.0048	0.0026
SD	0.11	0.08	0.0018	0.0010

Table 14. Pearson correlation coefficients between the C:N, N:P and C:P ratios of POM and DOM with C:N, N:P and C:P ratios of phytoplankton. Numbers in parentheses indicate n (number of observation). Bold numbers indicate significant relationships (at $p = 0.05$) between the C:N, N:P and C:P ratios of organic matter and phytoplankton.

Ratios	Keum	Youngsan	Sumjin	North Han	Han	South Han	All rivers
POC:PON	0.50	-0.37	-0.45	-0.32	-0.47	0.45	-0.26
DOC:DON	0.20	-0.09	0.11	0.70(13)	0.36	0.23	-0.21
PON:POP	-0.26	-0.14	0.12	0.53(20)	-0.46	0.59(19)	0.06
DON:DOP	0.22	0.12	-0.18	-0.37	0.66	0.08	-0.32
POC:POP	-0.04	-0.12	-0.17	0.52(11)	-0.37	0.28	0.16
DOC:DOP	0.30	-0.33	-0.33	-0.17	0.84	0.02	-0.07
TOC:TON	-0.20	-0.24	-0.12	-0.20	-0.08	0.58(24)	-0.17
TON:TOP	-0.07	-0.08	-0.30	0.53(13)	-0.26	0.71(24)	-0.004
TOC:TOP	-0.03	0.41	0.13	0.81(13)	-0.34	0.57(24)	0.05

ratio is greater than what is present in 'average' organic matter (i.e., >16N:1P by atoms) selected groups of microorganisms can exhibit a metabolic 'P-sparing' effect and produce biomass with C:P and N:P ratios significantly greater than the hypothesized Redfield ratios of 106:1 and 16:1, respectively (David et al., 2001). However, in laboratory studies, the Redfield stoichiometry is achieved only during maximum cell growth rate in nutrient-sufficient culture (Goldman et al., 1979). When either energy (including light energy) or nutrient limitation is imposed on prokaryotic and eukaryotic microbial population there are systematic and therefore predictable offsets in the C:N, N:P and C:P ratios that also affect cellular functions. The fact that POM and DOM, is not in 'Redfield equilibrium' implies limitation, or at least control, of cell growth by exogenous energy or nutrient supplies.

Model representations of these decomposition studies

During chemical analyses, total inorganic and organic P and N are separated in various ways; for example, the fractions of P often relate poorly to the way in which P is decomposed (Wetzel, 2001). Measurement of inorganic species (DIP, NH_3 , NO_2^- , NO_3^-) play a key role in quantifying dissolved fractions of N and P. The fractionation of P and N components within the total P and N pools in aquatic systems is usually determined by applying operationally defined approaches. DOP and DON are estimated as the difference between total dissolved fractions and dissolved inorganic fractions of P and N respectively. Thus the precision of DOP and DON pool estimations are tied directly to those of the respective inorganic P and N analyses. One of the problems with the most commonly used protocol, which employs a reagent containing sulfuric acid, is that of the potential acid hydrolysis of DOP compounds leading to an overestimation of the DIP pool. Obviously errors produced in estimations of parameters can contribute to the uncertainty of predictions. It should be noted that the difference between modeled and measured values may be produced by various factors including sampling and measurements (such as methods, skills, etc.) which will affect the P and N concentrations. These

factors are not reflected in the model simulation and a slightly greater variability is expected and reasonable. For example, the release of inorganic PO_4 by particulate seston was reported to be much greater than excretion of soluble organic P by living organisms expressing direct decomposition of POP into DIP (Wetzel, 2001). Incubations were conducted at 20°C temperature, and the extended incubations may undoubtedly result in extensive modifications of the biotic community. Light can be another factor affecting decomposition rate of organic matter through photolysis. Enzymes immobilized with humic substances (Pant and Warman, 2000) could be regenerated within the ecosystems upon exposure to UV irradiation in photic zone, and that can be an important factor for the decomposition of recalcitrant organic matter. Although humic substances are highly resistant against microbial decomposition, bacteria are mainly able to metabolize such refractory materials mostly to a lower extent of 15 % (Tranvik, 1988). The use of enzymatic techniques for qualitative and quantitative descriptions of transformation and decomposition of various POM and DOM components in aquatic environment is also difficult.

Even though there was a difference in the decomposition rates under constant temperature perhaps due to aerobic and anaerobic conditions; in most cases, the data were well fitted with the model simulation. I believe that every model-whether it relies on a simple conceptual or a fully mechanistic approach will certainly run into the limits if other factors of decomposition go down to a level where distinct changes in the overall structure of the ecosystem appear. Although a more complex model equation including microorganisms, pH, and redox potential may be able to improve the reproduction of real systems, it has been argued that increasing the number of parameters and complexity of the model will lead to an increase in model uncertainty as well as less accurate decomposition coefficient. The results indicate the general trend of simulated P and N concentrations agree well with the measured data. In some points, there were indeed some differences between the measured and simulated data sets. In spite of the differences between measured and simulated data sets, the calibration results are quite acceptable.

CONCLUSIONS

As microbial decomposition progresses, the extent of degradation that organic matter has experienced (i.e. its diagenetic state) is a predictor of its further reactivity and value as a substrate for microbial utilization. Organic P and organic N decomposition rate coefficients can provide valuable information for the development of river management strategies. The model equations employed here lend themselves well to determining the rate of decomposition of organic P and organic N because those make no assumption what microorganisms are involved in the decomposition processes. There was a great variability in decay rates from station to station and from the river to river during the different study periods. Most of the variability was attributable to a smaller number samples of the total sample analyzed. The high variability was not explained by any of the variables we measured, including N: P stoichiometry or inorganic nutrient concentrations. Variations in the decomposition rates of different P and N fractions might be responsible for the respective initial DIP and inorganic N concentrations in different rivers and/or in different sampling sites even in the same river. The changing pattern of the ratios of different organic fraction such as PON:POC, DON:DOC, POP:PON, DOP:DON, POP:POC and DOP:DOC were exponentially decreased supporting the preferential mineralization of P over N and N over C. Our study suggests that the respective decomposition rate coefficients can be considered as constant for modeling of river water quality. Thus, given a uniform environment, the process by which decomposition proceeds may be very similar over a wide range organic P compounds and organic N compounds, despite considerable differences in overall decomposition rates. A relatively similar proportion of labile and refractory DOP coexists in different seasons, implying that processes of production and remineralization that affect the distribution of the different P compounds have approximately the same timescales. Concentrations of the labile and recalcitrant fractions of P and N and their ratios varied widely in different rivers even in different sampling sites of the same river.

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SUMMARY

Eutrophication from nitrogen and phosphorus causes proliferation of algal masses, some of which may be toxic. Often the limiting nutrient is reduced to very low concentrations, while nutrients less in demand have higher concentrations. However, nutrients are present in different forms, which vary in their relevance to assessing eutrophication. Although availability of P is most often limiting to freshwater aquatic organisms, quantities and forms of N can influence P availability and the type of biotic response to a given P level. In the headwater reaches of streams and rivers, external sources such as forests and soils are particularly important sources of organic material for organisms and decomposition of microscopic particles occurs very rapidly. The bacteria and fungi modify the organic material through decomposition and make it an important food source for invertebrate and vertebrate detritivores.

Temporal distributions of N and P of both the Youngsan and the Sumjin River varied widely especially during summer and winter seasons. A large variability in nutrient fractions for both N and P was found among different sites of both the rivers. Closer examination of the data at different sampling sites confirms that agricultural activities and domestic sewages could be the major reasons of elevated N and P levels in both the rivers. In most cases, regardless of sampling stations, nutrient levels measured during summer appear to be larger than those during winter. It is noteworthy that TP levels in both the rivers were consistently high during summer relative to winter with some exceptions. The TN levels were more variable as a function of season and location. In addition, temporal changes of POP appear to vary in accordance with TP levels. The observations suggest that high POP levels during summer regardless of location and of relative dominance of POP over other dissolved P species suggesting total P budget of both the rivers may be strongly influenced by the input of particulate matters during summer season. The abundance of DIP and DOP, and $\text{NO}_3^- + \text{NO}_2^-$ varies spatially in both the rivers, with the highest

concentrations in the upstream and lowest in the downstream in general. Flow-rate and temperature may be the most potential factor regarding to retention and transformation of nutrients. In both the rivers, the decrease of N and P in the lower reaches was smaller and the spatial concentrations recorded upstream were steeper than downstream sites. Correlations with chlorophyll *a* and TP were weaker while the DIP was closely related to $\text{NO}_3^- + \text{NO}_2^-$. Pollutants from agricultural activities especially related to field crops and animal production, lower waste treatment capacity and shallow water level which are vulnerable to hydroclimatic variability. Increased inputs into the river systems from such activities emphasize the imbalances and alterations of aquatic communities as well as pollution. Thus the quantity and quality of nutrient input to the rivers need to be monitored to cope with the existing and future changes of land and urban development related to water quality.

Seasonal variations of water temperature are important determinants for the distribution of aquatic species, as pointed out in the River Continuum Concept. Decomposition of POM and DOM is influenced by temperature, exposure, type of microbial substrate, etc. For the sake of simplicity the labile part of POM is defined as the sum of carbohydrates and proteins. In chapter II, the decomposition rates of organic P were measured. However, organic P decomposition rate coefficients can provide valuable information for the development of river management strategies. Analyzing only DIP underestimates, and analyzing only TP overestimates, the potential bioavailability of P in the water body. Therefore, it is necessary to know the decomposition rate of organic P and how it varies with time and space to better understanding the P dynamics in any aquatic system. The model equations employed here lend themselves well to determining the rate of decomposition of organic P because it makes no assumption what microorganisms are involved in the decomposition process. This study suggests that the respective decomposition rate coefficients which are fairly constant. Thus, given a uniform environment, the process by which decomposition proceeds may be very similar over a wide range

organic P compounds, despite considerable differences in overall decomposition rates. The decomposition coefficients measured in this study would obviously give a guideline to the selection of parameters in modeling the river water quality. The models consisting of nine interrelated differential equations employed here are useful to predict the decomposition rates of organic P in aquatic environment.

As microbial decomposition progresses, the extent of degradation that organic matter has experienced (i.e. its diagenetic state) is a predictor of its further reactivity and value as a substrate for microbial utilization. Organic P and organic N decomposition rate coefficients can provide valuable information for the development of river management strategies. The model equations employed here lend themselves well to determining the rate of decomposition of organic P and organic N because those make no assumption what microorganisms are involved in the decomposition processes. There was a great variability in decay rates from station to station and from the river to river during the different study periods. There were variations among different labile and recalcitrant fractions of organic N and organic P. However, the median values of the LPOP, LDOP, LPON and LDON of the six rivers were 41 %, 50 %, 57 % and 42 %, respectively. The rate of changes of different organic fractions such as PON: POC, DON: DOC, POP: PON and DOP: DON varied in accordance with the decomposition rates of organic C, N and P fractions with time. In general, the rates of changes of the above-mentioned ratios are exponentially decreased with time. Although the variations in the rates of changes were observed, most of the variability was attributable to a smaller number samples of the total sample analyzed. The high variability was not explained by any of the variables we measured, including N: P stoichiometry or inorganic nutrient concentrations. Given a uniform environment, decomposition rates may vary over a wide range organic P and organic N compounds. Despite these variations, the decomposition rates measured for different organic phosphorus, and organic and inorganic nitrogen in this study might be applicable for modeling the river water quality. Concentrations of the labile and recalcitrant fractions of P and N and their

ratios varied widely in different rivers even in different sampling sites of the same river. In river ecosystems, the inorganic nutrient concentrations as well as the activities of microorganisms plays the dominant role on stoichiometric variability of the C, N and P of organic matter among other influential factors. The decomposition rate coefficients of various organic P, and organic and inorganic N fractions, and changes in the C:N:P ratios of POM of DOM measured in this study will be useful for modeling the river water quality and for better understanding the biogeochemical processes affecting river water quality.

한국, 강 생태계에서의 유기인과 유기질소의 분포 및 분해 연구

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요약

인과 질소에 의한 부영양화는 조류대발생을 일으키고, 이들 조류의 몇몇은 독성을 가지고 있다. 제한 영양염은 수중에 매우 낮은 농도로 감소하지만, 다른 영양염은 더 높은 농도로 존재하게 된다. 그러나 영양염류는 여러형태로 존재하고 이들은 부영양화의 평가와 관련되어 있다. 비록 인의 농도가 담수에서 주로 제한영양염류가 되지만, 질소의 양과 형태는 인의 이용가능성에 영향을 줄 수 있고, 현재의 인 수준과 관련하여 생물의 종류에 영향을 미칠 수 있다. 하천과 강의 상류에서는 숲이나 토양과 같은 외부기원이 특히 유기물의 주요기원이 되며, 이들 유기물 입자는 빠르게 분해된다. 박테리아와 세균이 유기물질을 분해하며 분해된 유기물은 무척추동물이나 척추동물의 중요한 먹이원이 된다.

영산강과 섬진강 수계에서 인과 질소의 시간적 분포는 특히 여름과 겨울시기에 편차가 매우 크다. 두 수계에서 질소와 인의 형태에 있어서의 큰 변동은 지점에 의해서 나타났다. 서로 다른 조사

지점에서 얻어진 데이터는 농업활동과 도시하수가 두 수계의 인과 질소의 수준을 높이는 주요 원인일 수 있음을 말하는 것이다. 대부분의 경우에 조사지점에 상관없이 영양염류는 여름이 겨울보다 더 높게 나타났다. 총인 수준이 몇몇 경우를 제외하면 겨울에 비해 여름에 높았다는 것은 주목할 만 한다. 총인 수준은 계절과 지점에 따라서 변동이 컸다. POP의 시간적 변동은 총인과 마찬가지로 변동하였다. 여름 동안의 높은 POP 농도와 상대적으로 높은 POP 함량은 여름 계절 동안 유입된 입자성 유기물에 의한 영향으로 사료된다. DIP, DOP, $\text{NO}_3^- + \text{NO}_2^-$ 농도는 두 수계에서 공간에 따라 다른 농도 수준을 보였는데, 상류는 가장 높은 농도를 나타냈고, 하류는 가장 낮은 농도를 나타냈다. 유량과 온도는 영양염류의 이동과 체류시간을 알 수 있는 잠재적인 요인일 것이다. 두 수계에서, 하류에서 인과 질소의 감소는 더 작았고, 알려진 상류의 공간적 농도는 하류지점보다 더 급격히 변하였다. 엽록소와 총인의 상관관계는 DIP와 $\text{NO}_3^- + \text{NO}_2^-$ 와의 상관관계보다 더 낮은 값을 나타냈다. (특히, 기후의 다변성은 농업활동에 의해 야기되는 농작물과 관련이 있는 오염원과 동물로부터 발생하는 오염물질, 낮은 하수처리능력과 낮은 수위 등에 영향을 줄 수 있다.) 그와 같은 활동에 의한 하천으로의 유입량의 증가는 오염물질의 유입 뿐만 아니라 수계균집을 변화시키고 균형을 깨지게 한다. 그래서 계속적인 토지와 도시 개발에 따라서 수질이 변동할 것이기 때문에 하천으로 유입되는 영양염류의 질과 양은 계속적으로 모니터링 할 필요가 있다.

수온의 계절적 변동은 River Continuum Concept의 개념에서 보면

수중에서 종의 분포를 결정하는데 중요하다. POM과 DOM의 분해는 온도, 노출시간, 미생물 기질의 종류 등에 의해서 영향을 받는다. 단순화시켜서 POM의 생분해성 부분은 탄수화물과 단백질의 합으로 정의된다. 본 논문의 2장에서 유기인의 분해속도를 측정했다. 유기인 분해속도계수는 하천관리를 위한 가치 있는 정보를 줄 수 있다. 단지 DIP를 분석하는 것은 수체내에서 잠재적인 인의 생물학적 이용가능성을 과소평가하는 것이고, 단지 TP를 분석하는 것은 수체내에서 잠재적인 인의 생물학적 이용가능성을 과대평가하는 것이다. 그러므로 수계에서 인의 동적변동을 더 잘 이해하기 위해서는 유기인의 분해과정을 아는 것이 필요하고 어떻게 시간과 공간에 따라서 변하는가를 알 필요가 있다. 여기에서 적용된 모델식은 어떠한 박테리아도 분해과정 중에 포함되지 않는다고 가정하였기 때문에 유기인의 분해속도를 잘 모의하였다. 본 연구는 믿을만한 분해속도계수가 얼마인지를 제안하였다. 그래서 주어진 특수한 환경에서, 어떤 분해 과정은 넓은 범위의 유기인 분해속도와 매우 유사할 수 있다. 본 연구에서 측정된 분해속도계수는 확실히 하천수질모델에서 계수를 선택하는데 가이드라인이 될 것이다. 서로 관련있는 9개의 다른 식으로 구성된 이 모델은 수계에서 유기인의 분해속도를 예측하는데 매우 유용하다.

일반적으로 위에 언급한 비의 변화는 시간에 따라 지수적인 감소를 보인다. 비록 변화비에서의 변동이 관측되었지만 대부분의 변동은 분석한 총 시료 중 적은 부분에서만 보였다. 유기인과 유기질소의 분해속도계수는 하천을 관리하는데 가치있는 정보를 제공할 것이다. 여기에서 적용된 모델식은 어떠한 박테리아도 분해과정 중

에 포함되지 않는다고 가정하였기 때문에 유기인의 분해속도를 잘 모의하였다. 지점에 따라서 하천에 따라서 조사시기에 따라서 분해속도는 편차가 컸다. 유기인과 유기질소의 난분해성과 생분해성 비율은 차이가 컸다. 그러나 6개 하천의 LPOP, LDOP, LPON, LDON의 중앙 값은 각각 41%, 50%, 57%, 42%였다. PON:POC, DON:DOC, POP:PON, DOP:DON의 비는 시간에 따른 유기탄소, 질소, 인의 분해속도에 따라 달랐다. 일반적으로 위에 언급된 비율의 변화속도는 지수적으로 감소한다. 그러나 만약 이들 비 중의 하나가 부족하거나 매우 낮다면 또한 지수적으로 증가한다. DON:DOP 변화패턴은 일반적으로 시간에 따라서 증가한다. 이들 변화의 대부분은 분석된 총 샘플 중에서 더 작은 수의 샘플이 분석되었기 때문이었다. 더 큰 편차는 우리가 측정한 어떠한 매개변수(무기영양염 농도 혹은 N:P 화학양론을 포함)로도 설명되지 않았다. 주어진 특수환경에서, 분해속도는 다양한 유기인과 유기질소 화합물에 따라서 다양할 수 있다. 이들 편차에도 불구하고 본 연구에서는 각각의 유기인, 유기질소, 무기질소를 위한 분해속도가 측정되었고, 이들은 하천수질을 모의하는 데 적용될 수 있을 것이다. 인과 질소의 생분해성과 난분해성 부분의 농도와 비는 수계에 따라서 변화가 컸고, 심지어는 같은 수계의 다른 정점들에서도 차이가 컸다. 하천생태계에서, 미생물의 활동뿐만 아니라 무기영양염도 유기물질 중의 탄소, 질소, 인의 화학양론의 변화에 중요한 역할을 한다. 본 연구에서 측정한 POM과 DOM의 C:N:P비의 변화, 다양한 유기인의 분해계수 그리고 유기 및 무기 질소 fraction은 강의 수질에 미치는 생지화화적인 과정을 더욱 이해하고 강의 수질을 모델하기 위해 유용할 것이다.

RESUME

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