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Chlorophyll-*a* and its Degradation Products of the Sediment in the Downstream of the Nakdong River

Ha-Young Jung and Kyung-Je Cho*

School of Environmental Science and Engineering, and Nakdong River Environmental Research Center,
Inje University, Gimhae 621-749, Korea

Abstract - Chlorophyll-*a* and its degradation products (pheopigment) contained in the sediment were determined to evaluate the eutrophication status in the downstream of Nakdong River. The chlorophyll-*a* and pheopigment concentrations of sediment ranged 11-646 mg m^{-2} (mean 172 mg m^{-2}) and 48-1,564 mg m^{-2} (mean 454 mg m^{-2}) over 11 sampling stations of the Nakdong River. The chloropigment concentrations in this local area were higher than other values reported previously and this river waters showed hypertrophic status in view of sedimentary chloropigment. Total chloropigment standing crops of sediment, which are the residuals after the longterm degradation, were 2.2-3.6 fold higher than chlorophyll-*a* contents of overlying water. The amounts of chloropigments of sediment suggest a large contribution of phytoplankton to the sediment. While chloropigment standing crops are evaluated with organic-C and nitrogen contents, the algal contribution to the carbon and nitrogen pool of the sediment were estimated to be approximately 30% and 40%, respectively.

Key words : sediment, chlorophyll-*a*, pheopigment, degradation, eutrophication

INTRODUCTION

Freshwater zone from surface to the euphotic zone are especially referred to productive area to make organic matter through the photosynthesis activity of phytoplankton. Suspended particles or organics including microplankton would finally settle down on the bottom of lakes and rivers, and in part flow towards the lower regions of the river. The sediment acts as a reservoir or repository for organic matters and suspended organisms in the overlying water column. Settlement of particulate organic matters is the primary process to connect water column with bottom sediments. The fertility of the water body and deposition rate of pigment products are generally strongly correlated and sediment pigments would give useful informations about paleoproduction and paleoenvironment (Wetzel 1970).

Chlorophyll pigments in photosynthetic tissues are relatively stable but may be changed by chemical, photochemical and biological process. As chlorophyll pigments in freshwater and marine water may be turned over about more 40 times a year than that originated from the terrestrial because of the shorter life spans of algae, global chlorophyll degradation about 75% occurs in oceans, lakes and rivers (Porra *et al.* 1997). Chlorophyll derivatives and degradation products can be made by grazing and digestion by herbivores, and also by cell senescence and microbial degradation. Cyclic tertrapyrrole compounds of chlorophyll degrade rapidly in the water column and on the surface sediments. The products of biological degradation are classified into two categories-cyclic tetrapyrrole products by enzyme catalysis and linear tetrapyrrole products by oxdative cleav-

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* Corresponding author: Kyung-Je Cho, Tel. 055-320-3216, Fax. 055-334-7092, E-mail. kjcho@ijnc.inje.ac.kr

age (Brown *et al.* 1991). Pheophytin as Mg and phytol free molecules and pheophorbides as Mg-free chlorophyll molecules are collectively called as pheopigments and usually abundant in the water column and sediments. Chloropigments in this literature are referred to the sum of the active chlorophyll and the unactive pheopigment. Tetrapyrrole derivatives as degradation products of chlorophyll pigment can be preserved for long times in sediments. Anoxic conditions may be critical for the chlorophyll preservation. In contrast to the peripheral compounds of chlorophyll molecule, the macrocycles such as tetrapyrroles are remarkably stable when oxygen and light are excluded. Some metal complexes of five-ring macrocycles have survived chemical modification over a long geochemical time scale (diagenesis) and molecular fossils in a wide range of sediments dating back to the Precambrian period (Porra *et al.* 1997).

This investigations were conducted in the estuarine water system of the Nakdong River, in which three rivers flow over the delta plain-the Nakdong River as the main river, the Seonakdong River as the downward tributary of the main river and the Joman River as the upward tributary of the Seonakdong River. Sediments for pigment determination were collected at 11 sampling stations in three river system. Sampling locations and their topography were in detail presented in Jung and Cho (2003). Seawater intrusion up to 30 km inland from the river mouth in the Nakdong River became the primary nuisance in water supply for drinking, agriculture and industrial complex. The estuarine dam or watergates were constructed at the river mouth in 1987 to solve these problem. River-like lake was made in the estuary extending 60 km from dam up to Samrangjin. Two watergates in both upstream and downstream of the river were already constructed in 1930s for agricultural water supply in the Seonakdong River. There were no altitude and inclination in these estuarine delta plain. Water quality was deteriorated with phytoplankton blooms and cultural eutrophication, which provoked the social problems in this local area. Sediments were collected in the freshwater zone above the estuarine dams at six stations-Samranjin Bridge (SAM), Mulgeum (MUL), Gupo Bridge (GUP), Nakdong Bridge (NAK) and the estuarine dam (HAG)-in the Nakdong River, two stations-Gimhae Bridge (GIM) and Seonakdong Bridge (SON)-in the Seonakdong River and three stations-Machal Bridge (MAC), the confluence of Haeban River and Joman River (HAE), Joman Bridge (JOM)-in the Joman River.

This studies focus on the photosynthetic pigments in the sediment of the lower parts of the Nakdong River in April and September of 2000. Pigment contents or concentrations can be used to estimate algal contribution to the organic matter of sediment and to evaluate the eutrophication status of the river water.

MATERIALS AND METHODS

Surface sediments at eleven stations were collected with a Petersen grab sampler on April 12-16, 2000. In addition, profile materials along sediment depth were sampled using a small plastic core (inner diameter 3.0 cm and 25 cm length) inserted into a long core on September 6-8, 2000. Long sediment cylinders were cut by 3 cm interval and pore waters were removed by centri-

Table 1. Comparison of sediment pigment extraction efficiency through some conditions. Sediment were collected at station JOM of Joman River (n = 3)

Solvent	Sediment water	Extraction method	Chlorophyll-*a* (μg fw g^{-1})	Pheopigment (μg fw g^{-1})	Total pigment (μg fw g^{-1})
Acetone	Absent	Sonication	0.98	9.23	10.21
		Vortex mix	1.79	17.95	19.74
	Present	Sonication	0.76	6.16	6.92
		Vortex mix	0.32	4.91	5.23
Ethanol	Absent	Sonication	1.31	7.96	9.27
		Vortex mix	0.57	7.06	7.63
	Present	Sonication	0.55	4.17	4.72
		Vortex mix	0.35	3.82	4.17

fuging (approximately 3,000 rpm) before pigment extraction (Jung and Cho 2003). Pigment extraction efficiency was tested according to two solvent kinds (acetone and ethanol), water content, cell break (sonication and vortex mix) (Table 1). When waters were removed from sediment, efficiency by acetone extraction increased to 2.5 fold in comparison with control and to 1.9 fold by ethanol boiling extraction (Nusch 1980), and efficiency by vortex mixing was better than sonication treatment. After sediment waters were removed by centrifuging, pigments were extracted by using acetone and vortex mixing. Unactive or nonreactive pheopigment were determined by HCl acidification (1 N HCl 1-2 drops) when absorbances were measured (Lorenzen 1967). Extraction of sediment pigment repeated three times for same materials and significant amounts of pigment were extracted in third determination process. Pigment concentrations were expressed as the sum of three determinations.

RESULTS AND DISCUSSION

Pigments in sediment were monitored over the sediment surface and along the sediment depth in the downstream of the Nakdong River. Chlorophyll-*a* concentration of sediment ranged from 1-25 μg fw g^{-1} (average 12 μg fw g^{-1}) and pheopigment from 6-63 μg fw g^{-1} (average 30 μg fw g^{-1}) (Fig. 1). Pigment concentrations were high in the Seonakdong River regions (GIM and SON station). Sediments were collected at three stations to determine pigments profiles along the depth (Fig. 2). Average pigment concentrations from surface to 20 cm depth at three stations (GUP, GIM and JOM) were 1.5 μg fw g^{-1}, 6.5 μg fw g^{-1} and 5.1 μg fw g^{-1} of chlorophyll-*a*, and 5.6 μg fw g^{-1}, 37.1 μg fw g^{-1} and 23.4 μg fw g^{-1} of pheopigment. Unactive pigments as pheopigment in sediment comprised over 80% of the total pigments through three stations. Though chloropigment concentrations gradually increase towards top sediment, however, depth profiles didn't show the clear trends to have little variations (Fig. 2). Water depths at sediment sampling stations were between 2 m and 5 m and irradiance didn't penetrate to the sediment surface as river waters were strongly turbid or productive. Benthic algae would cover the submerged surfaces of sediment if enough irradiance is received. Phytoplanktonic algae of the water column are the most contributor to the chloropigments of sediment. Euphotic depths of this river waters ranged from 1.4 m to 2.1 m (Jeon *et al.* 2003). In contrast to our data, chloropigments of the sediment showed an exponential decline with sediment depth in the marine coastal zone as high concentrations of pigment were contained in the top centimeter (Chung *et al.* 1999; Hansen and Josefson 2001). Frequent sediment disturbance by fisheries and aquaculture activity, and sedimentation or erosion would keep the sediment from clear depth profiles of chloropigments. If the ratio of surface to depth averaged chlorophyll approaches unity, the mixing is intense (DiToro 2001).

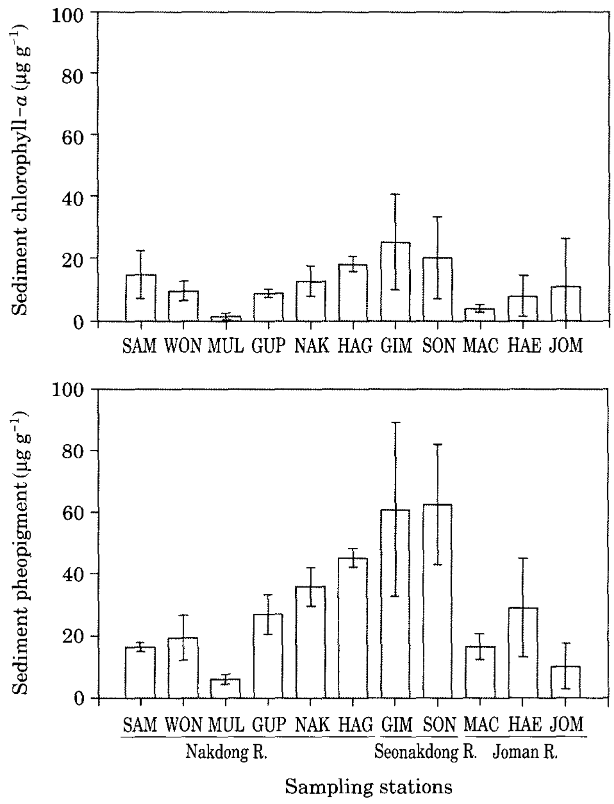

Fig. 1. Algal pigment (active chlorophyll-*a* and inactive pheopigment) concentration of sediment over the eleven stations at the Nakdong River.

Carbon vs AFDW (ash-free dry weight) of freshwater algae ranged 50-56% (minimum 35% and maximum 70%), nitrogen vs AFDW 4-9% and phosphorus 0.03-0.8% (Reynolds 1984). As algal chlorophyll-*a* concentrations encountered for 0.9-3.9% (average 2%) of AFDW,

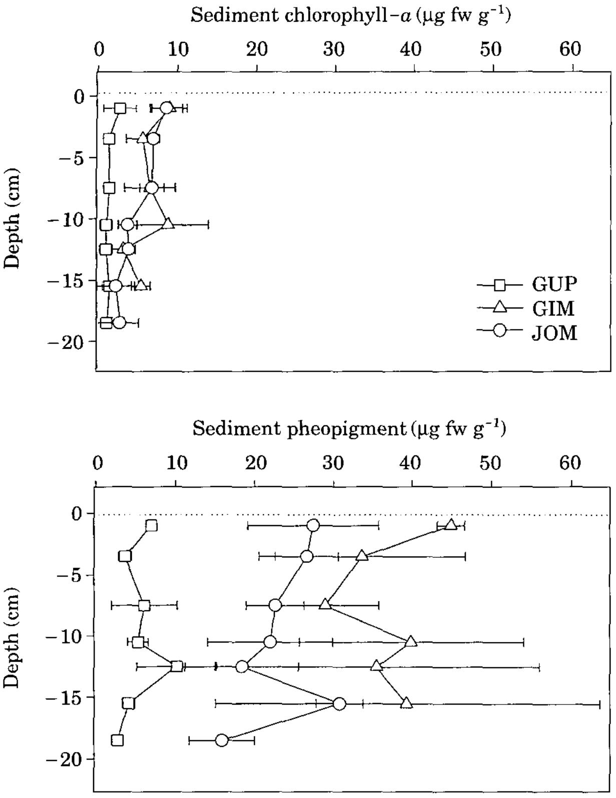

Fig. 2. Algal pigment (active chlorophyll-*a* and inactive pheopigments) profiles of sediment at three stations. Pore waters of sediment were removed through centrifugation before algal pigment determination.

it is possible to estimate organic matters and carbon content originated from the algae. In addition, carbon vs chlorophyll-*a* ratio is about 60 mg C mg^{-1} chl-*a* (25-100 mg C mg^{-1} chl-*a* range) (DiToro 2001). As pigment sum of sediment chlorophyll-*a* and pheopigment in the downstream of the Nakdong River ranged from 8-86 µg fw g^{-1} (mean 42 µg g^{-1}), AFDW, carbon, nitrogen and phosphorus contents estimated from algae were 0.4-4.3 mg fw g^{-1} (mean 2.1 mg g^{-1}), 0.2-2.2 mg C fw g^{-1} (mean 1.1 mg g^{-1}), 26-280 µg fw g^{-1} (mean 137 µg g^{-1}) and 2-18 µg P fw g^{-1}, respectively. Organic carbon and TKN (total Kjeldahl nitrogen) concentrations of sediment were reported as 10.0 mg C dw g^{-1} and 1.0 mg N dw g^{-1} (Jung and Cho 2003). As it is transformed to determine sediment pigments with dry soil, chlorophyll-*a* and pheopigment were 2-110 µg dw g^{-1} and 10-265 µg dw g^{-1}, respectively. While these pigment concentrations are expressed as organic-C and nitrogen, the algal contribution to the carbon and nitrogen pool of the sediment amounted to be approximately 60% and 40%, respectively. When the rapid degradation of the chloropigment is considered in the sediments, phytoplankton would be a major source for organic materials of the sediment (Cowan and Boynton 1996). Chlorophyll-*a* and pheopigments, and organic carbon of sediment showed high correlations (Fig. 3). When chlorophyll-*a* and pheopigment of sediment were expressed as contents per surface are (m^2), their contents were 11-646 mg m^{-2} (mean 172 mg m^{-2}) and 48-1,564 mg m^{-2} (mean 454 mg m^{-2}).

Chlorophyll and pheopigment, and organic-C concentration have high correlation, however, negative correlation between chloropigment and bulk density of sediment (Fig. 3). The amount of the chloropigment accumulation in the sediment is a function of both the eutrophication status of water body and the soil texture or particle composition.

Chlorophyll-*a* and its derivatives are rich in the sediment surface at even oligotrophic freshwaters. Sediment pigments would be originated from phytoplankton and benthic algae such as epipelic (mixed on mud particles) and epipsammic (attached on sand particles) algae in the sediment (Cyr 1998). As living benthic algae wouldn't survive on the bottom sediment by irradiance shortage in the Nakdong River, sediment pigments would be most derived from the settling of planktonic algae. Phytoplankton have bloomed throughout a year in the downstream of the Nakdong River and outbreak of blue-green algae (*Microcystis aeruginosa* and its relatives) in summer and persistent bloom of diatoms (*Stephanodiscus hantzschii* and its relatives) in cold season (Cho and Shin 1998). Chlorophyll-*a* concentration at Nakdong River and Seonakdong/Joman River amounted to be 11-297 mg m^{-2} and 34-647 mg m^{-2} ranges and these values are comparable to those reported in the other freshwaters and sea waters (Table 2). Sediment pigments in this local area were higher than other study area. Sediment pigments were below 240 mg m^{-2} in the mesotrophic or marine coastal zone (Cowan and Boynton 1996; Cyr 1998) and pigment concentrations of this local area were very much compared to those found in the overlying waters.

Algae accumulated on the sediment would be nutri-

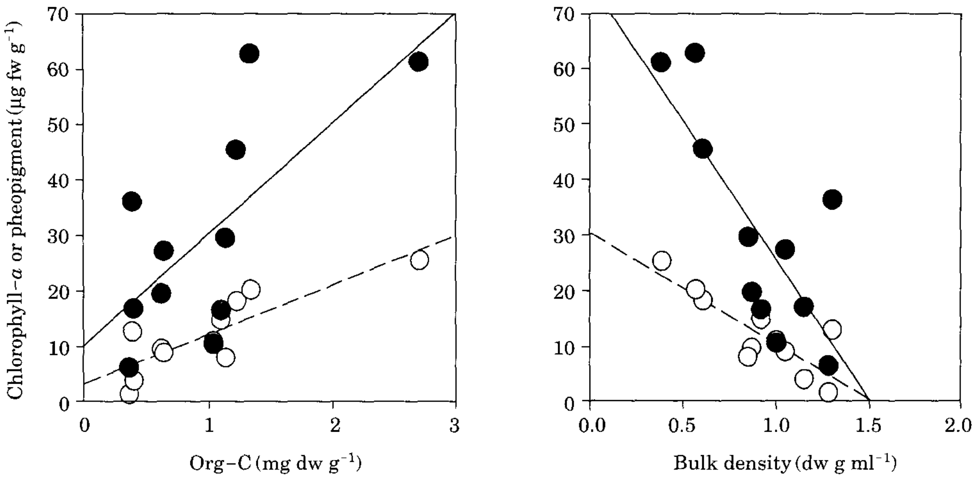

Fig. 3. Relationships between chloropigment (chlorophyll-*a* ○ and pheopigment ●) and organic carbon concentration and bulk density of sediment collected in 11 stations in the Nakdong River.

Table 2. Chloropigment data of sediment at various regions in the world

Study area	Chl-*a** (mg m^{-2})	Pheopigment (mg m^{-2})	Trophic state	References
Three lakes, Canada	32-240	50-120	Mesotrophic	Cyr (1998)
Shear Waters	25-170	–	–	Hickman and Round (1970)
Lake Mikolajskie	11-201	–	–	Wasmund and Kowalczewski (1982)
Lough Neagh	20-450	–	–	Jewson and Briggs (1993)
Masan Bay, Korea	81**	885**	Eutrophic	Chung *et al.* (1999)
Øresund, Baltic Sea	8-82	–	–	Hansen and Josefson (2001)
Carpentaria Gulf, Australia	–	–	–	Burford *et al.* (1994)
Nakdong River	11-650	48-1,564	Hypertrophic	This study

*Chlorophyll-*a* concentration of surface centimeter depth, **These data had different unit (μg chl-*a* dw g^{-1})

tional materials for micro- and macro- fauna and decomposed very rapidly. Spring blooming algae settled on sediment were respired or decomposed within 14 days and decay rate of chlorophyll-*a* was 0.03 day^{-1} (Sun *et al.* 1993). As pigment decay rates have little difference in oxic and anoxic conditions, and porphyrin compound and its derivatives are chemically stable within sediment to preserve for long times, sediment pigment can give informations for past phytoplanktons of the local area (Sun *et al.* 1993). Large amount of sediment pigments and their rapid mobilization could be potential sources of zoobenthos food and also important to sustain the nutrient cyclings of benthic ecosystems.

At the same times with sediment pigment study, chlorophyll-*a* concentrations of water body were monitored at three stations from 1998 to 2000. Seasonal variations of chlorophyll-*a* concentration were clear as phytoplankton increased in winter in GUP station (Nakdong River) and bloomed in summer in GIM (Seonakdong River) and JOM station (Joman River) (Fig. 4). Mean chlorophyll-*a* concentration of surface water at GUP, SON and JOM were 32 μg l^{-1}, 64 μg l^{-1} and 90 μg l^{-1} for three years, respectively. The serial orders of productive status (eutrophication) were Joman River> Seonakdong River>Nakdong River and these trends coincided with chloropigment results of the sediment. Though chlorophyll-*a* difference between surface and bottom waters was little in GUP station, the annual mean differences at GIM and JOM station were 17 μg l^{-1} and 26 μg l^{-1} (Fig. 4). In summer, the weak stratifications occurred even in the shallow waters to have large difference between surface and bottom waters. As chlorophyll-*a* concentrations were expressed on the water column area basis, the contents ranged from 11 mg m^{-2}

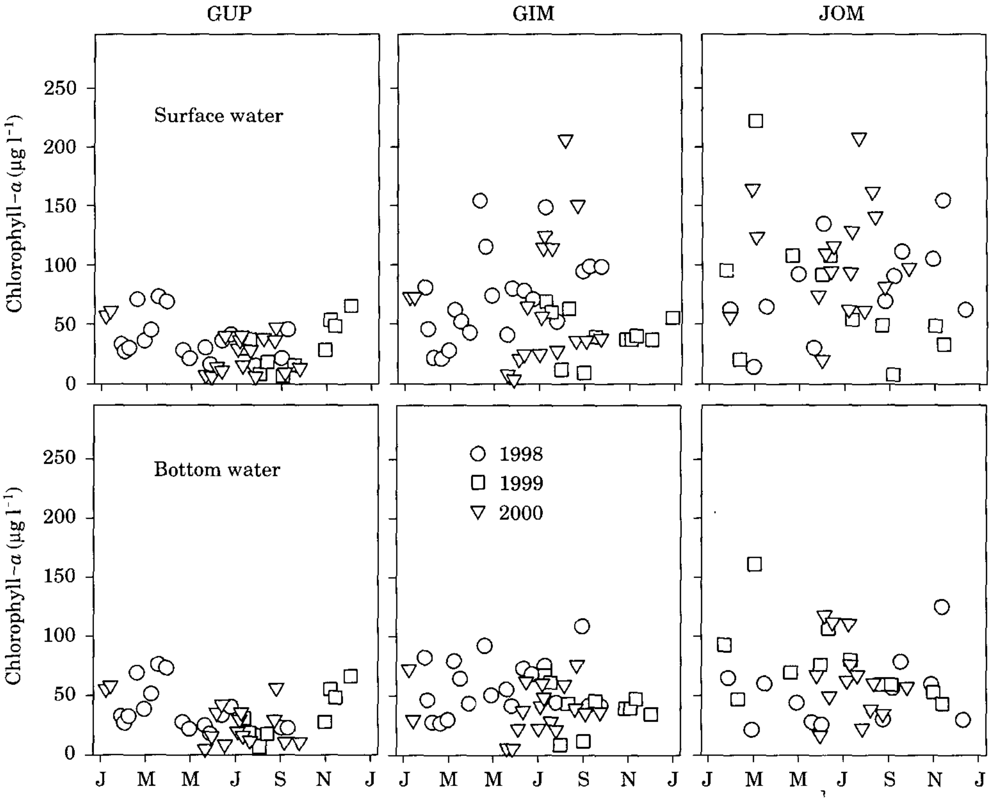

Fig. 4. Chlorophyll-a concentration of phytoplankton of surface and bottom water at three stations in the downstreams of the Nakdong River from 1998 to 2000.

to 650 mg m^{-2} in the Nakdong River and mean contents at three stations were 172 mg m^{-2}, 454 mg m^{-2} and 180 mg m^{-2}, respectively. Total chloropigment (chlorophyll-a plus pheopigment) standing crops of sediment, which is the residuals after the initial degradation, were 2.2-3.6 fold higher than chlorophyll-a contents of overlying water. Such large amounts of chloropigments suggest a potentially important source of high quality food for benthic invertebrates. As the standing crops of chloropigments are considered the residual pigments during the degradation process, the nutritional contribution of sediment have to been taken the high evaluation. Even in the oligotrophic waters, benthic algae would act as major contributors to the sediment pigments (Cyr 1998). Eutrophicatation status, phytoplankton biomass or primary production can be estimated or evaluated with sediment pigment and its accumulation (Gorham *et al.* 1974; Flannery *et al.* 1982).

Sedimentation rate at the upper area of the estuarine watergates in the Nakdong River was reported as 0.34 cm yr^{-1} by Pb^{210} profile method (Kim *et al.* 2000). If we apply this settling rate to the Seonakdong River, in which watergates were constructed in the past 1930s year, 20 cm sediment depth accounts for approximately 50 year's accumulation.

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