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Distribution of Various Nitrogenous Compounds and Respiratory Oxygen Consumption Rate in Masan Bay, Korea During Summer 1986

DONG-BEOM YANG
Korea Ocean Research and Development Institute
Ansan, P.O. Box 29, Seoul, 425-600, Korea

1986년 하계 마산만의 각종 질소화합물분포와 산소소비율에 대한 연구

양 동 범
한국해양연구소

Studies on the distribution of nitrogenous compounds, and respiratory oxygen consumption rate were carried out in Masan Bay, Korea where large amount of industrial and domestic wastewaters are discharged. In August 1986 the surface layer was significantly influenced by freshwater input. Below the seasonal pycnocline, an oxygen-deficient condition developed in a large area of Masan Bay. Concentrations of DIN, DON and PN were 735.6, 1261.8 and 48.5 μmol/*l* at the head, and 79.1, 73.0 and 39.5 μmol/*l* at the mouth of the inner Masan Bay, respectively. Phytoplankton carbon production was 2,695 mgC/m^2/day at the mouth of inner Masan Bay. Dissolved oxygen contents were lower than 1 ml/*l* from 3 m depth in inner Masan Bay and from 10 m depth in the outer Masan Bay. The high concentration of ammonium and phosphate in the lower layer suggests the active degradation of organic materials in the bottom waters and leaching from sediments. The ETS activity was 212.1 μ*l* O_2/*l*/h in the surface waters of the innermost part of Masan Bay and respiratory oxygen consumption is likely to proceed at a rate of 442 ml O_2/m^2/day in the bottom waters of this bay. Nitrate removal rate was estimated to be 0.25 μmol/*l*/day via denitrification in the bottom waters of the Masan Waterway. It is estimated from the ETS activity that, at the mouth of inner Masan Bay, 9.3-10.5% of carbon fixed in the upper layer was decomposed below the thermocline.

산업폐수와 도시하수의 유입이 심한 마산만에서 하계에 각종 질소화합물의 분포와 산소소비율에 대한 연구를 수행하였다. 1986년 하계에 마산만은 육수유입의 영향을 강하게 받았으며 수온약층 아래에는 빈산소층이 형성되었다. 용존성무기질소 (DIN), 용존성유기질소 (DON), 입자성질소 (PN) 는 내만 육수유입을 직접 받는 곳에서 각각 735.6, 1261.8 and 48.5 μmol/*l*의 분포를 보였으며 마산내만입구에서는 각각 79.1, 73.0 and 39.5 μmol/*l*를 나타냈다. 마산내만입구의 일차생산력은 2,695 mgC/m^2/day 였다. 용존산소량은 내만입구에서는 3 m 아래에서부터, 마산수로에서는 10 m 아래에서부터 1 ml/*l* 이하를 보였다. 저층수중의 높은 암모니아와 인산염의 농도는 유기물의 활발한 분해나 저층퇴적물로부터의 용출에 의한 것이라 생각된다. ETS 활동도는 마산내민 가장안쪽에서 212.1 μ*l* O_2/*l*/h였고 마산내만입구의 저층수에서는 산소소비가 442 m*l* O_2/m^2/day 의 비율로 진행되었다. 마산수로저층수에서의 탈질화 속도는 0.25 μmol/*l*/day 였으며 마산내만입구에서는 표층에서 일차생산에 의해 생성된 유기물의 9.3-10.5%가 저층수에서 분해되는 것으로 보인다.

INTRODUCTION

Concentration of nitrogen, an important element composing protein, is generally low in seawater and limits the growth of primary producers. In the coastal areas, however, the excess supply of nitrogenous nutrients due to the input of domestic and industrial wastes frequently result in the phenomenon called eutrophication and red tides.

Masan Bay is a long and narrow inlet located on the southeastern coast of the Korean peninsula (Fig. 1). Recently, the bay became a focus of public concern because of deterioration of its environment. From Changweon and Masan industrial areas large amounts of domestic and industrial wastewaters are discharged into inner Masan Bay. Frequent red tide outbreaks have been reported in this bay and many studies have been done to elucidate the relation between nutrient input and massive phytoplankton blooms(Cho, 1979 ; Park, 1982 ; Yang and Lee, 1983 ; Yoo and Lee, 1980). However the composition of various forms of nitrogen in this narrow inlet has not yet been systematically studied.

In a marine ecosystem respiration is a basic activity in any living organism. It is a variable that must be understood quantitatively, before accurate ecosystem models or budgets of the carbon or energy flow can be constructed. Oxygen is consumed in the sea largely by the respiratory metabolisms and not by inorganic chemical reactions (Hobbie et al, 1972). Oxygen consumption is regarded as a ubiquitous process, occurring at all depths and in all regions where oxygen is present. Thus it is interesting to measure the respiratory oxygen consumption rate where massive damages of fishery ground occur due to an anoxic condition.

The present work aims to describe the distribution pattern of various forms of nitrogen and to determine the oxygen consumption rate in order to provide further knowledge on the process of eutrophication and evolution of anoxia in the study area.

MATERIALS AND METHODS

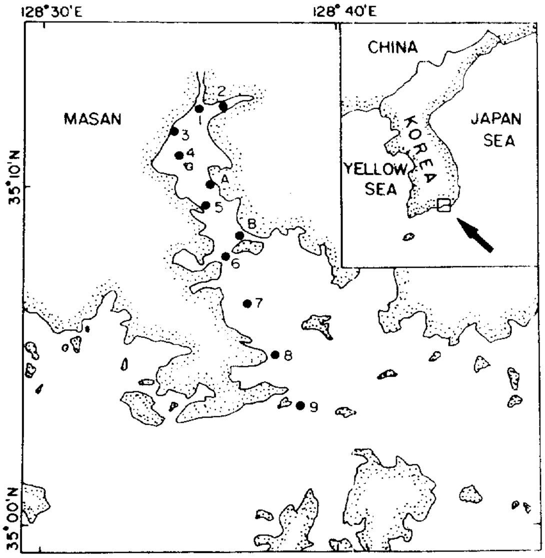

Fig. 1. Sampling stations of Masan Bay.

Sampling was done between August 11-13, 1986. Three stations (St. 1,2 and 3) were located in inner Masan Bay and St. 4 was chosen at the mouth of inner Masan Bay. Five other stations (St. 5 through 9) were located in the Masan Waterway.

Temperature and salinity were measured using TS Bridge (Type M. C. 5 National Institute of Oceanography) and dissolved oxygen was determined with a DO meter (Yellow Springs Instrument). Nutrient concentrations, except ammonium, were analyzed on Technicon Autoanalyzer AAII following the method of Zimmermann et al.(1977). Ammonium content was measured in situ using the method of Koroleff(1969).

Analysis of pariculate carbon and particulate nitrogen followed the method of Kerambrun and Szekielda(1969). Dissolved organic carbon and nitrogen were measured from the solids which remained after freeze drying the seawater by the method of Gordon and Sutcliffe(1973). All these analyses were done on Perkin Elmer 240 B Elemental analyzer.

Primary productivity was measured by the method of simulation *in situ*. 10 μCi of C-14 labelled $NaHCO_3$ was innoculated in the 300 m*l* seawater sample contained in BOD bottle(Parsons et al., 1984).

For the measurement of Electron Transport System (ETS) activity 200-500 m*l* seawater was filtered onto GF/F filterpaper. After grinding the filterpaper, the ETS activity was assayed by incubating the filtered material with substrate at 15.5-16.5℃ (Kenner and Ahmed, 1975). The ETS activity in the superficial sediment was measured after centrifuging by the method of Christensen (1983). Activities were converted to *in situ* activity following the equation of Arrhenius.

$$ETS_i = ETS_o \exp\frac{15.8}{R}\left(\frac{1}{T_o} - \frac{1}{T_i}\right)$$

ETS_i : ETS at in situ temperature (μ*l* O_2/*l*/h)
ETSo : ETS at incubation temperature (μ*l* O_2 /*l*/h)
R : 1.987 Kcal/deg/mole
T_o : Incubation temperature (℃)
T_i : In situ temperature (℃)

RESULTS AND DISCUSSION

Hydrology

Results of physical and chemical parameters are summarized in Table 1. In August 1986, surface waters of inner Masan Bay showed a low salinity because of freshwater inflow from the Masan-Changweon area. Spatio-temporal variation is reported to be great due to the variation of freshwater input in the summer season (KORDI, 1981, 1982). Surface salinity of St. 1 was only 1.8‰ while it increased to 23.0‰ at 1 m depth and to 27.9‰ at 2m depth, which indicates a confined freshwater inflow to a thin surface layer. Dissolved oxygen in the surface layer was 8 m*l*/*l* and it decreased to 0.7 m*l*/*l* at 1 m depth. At St. 2 where the influence of freshwater from the Changweon industrial area is dominant, surface salinity was 5.3‰ and increased to 26.9‰ at 2 m depth and to 29.7‰ at 4 m depth. At this station surface dissolved oxygen content was 2.2 m*l*/*l* and no dissolved oxygen could be detected with our method

Table 1. Distribution of nitrogenous compounds and other related parameters in Masan Bay during summer 1986.

St.	Depth	T	S	DO	NH_4	NO_3	NO_2	DIN	DON	PN	PC	PO_4	Si
	(m)	(℃ C)	(%)	(m*l*/*l*			(μmol/*l*			(μmol/*l*)		(μmol/*l*)	
1	0	24.9	1.8	8.0	349.3	368.9	17.41	735.6	1261.8	48.5	193.8	10.33	
	3	21.0	28.0	0.7	86.3	48.8	4.34	139.4		29.2	87.9	6.86	153.5
2	0	25.2	5.3	2.2	85.5	309.1	8.79	403.4		52.0	182.6	4.73	37.4
	3	23.0	28.0	nd	35.5	1.4	0.92	37.8		5.1	38.4	4.13	21.3
	12	18.4	31.2	nd	54.8					14.6	80.2		
3	0	25.8	12.2	2.9	124.2	7.7	4.81	136.7	148.2	39.7	214.8	2.00	9.4
	6	21.3	30.2	1.6	47.4	4.1	0.45	52.0		17.7	46.3	5.60	8.0
4	0	26.0	22.74	5.08	31.69	36.1	11.35	79.1	73.0	39.5	229.2	3.20	15.8
	10	21.0	31.48	1.13	49.14	4.2	0.78	54.1	16.8	11.5	61.7	5.40	5.5
5	0	24.0	27.63	4.37	29.79	22.7	4.90	57.4	90.0	36.5	133.3	2.66	17.7
	11	17.0	32.47	nd	64.75	1.7	0.67	67.1	60.2	19.9	102.6	7.33	13.4
6	0	25.0	26.92	3.74	48.94	34.0	3.45	86.4	16.8	22.5	132.8	4.20	7.9
	25	17.0	32.64	nd	55.82	nd	0.80	56.6	50.2			5.66	26.6
7	0	24.0	30.46	4.73	7.57		1.12	8.7	46.1	33.2	139.8	1.46	23.4
	14	21.0	32.02	3.53	65.98	0.2	0.43	66.4	75.6	26.8	130.1	7.46	25.0
8	0	23.0	31.10	4.38	2.32	3.4	0.92	6.6	75.2	31.7	141.4	1.53	6.4
	12	21.0	32.29	3.52	13.22	6.1	1.08	20.4				2.80	7.3
9	0	24.0	31.14	5.01	1.09	1.0	0.30	2.4	59.8	63.5	198.4	1.33	9.4
	11	18.0	33.26	3.81	1.57	3.4	0.60	5.6	43.1	50.1	276.9	2.06	7.2

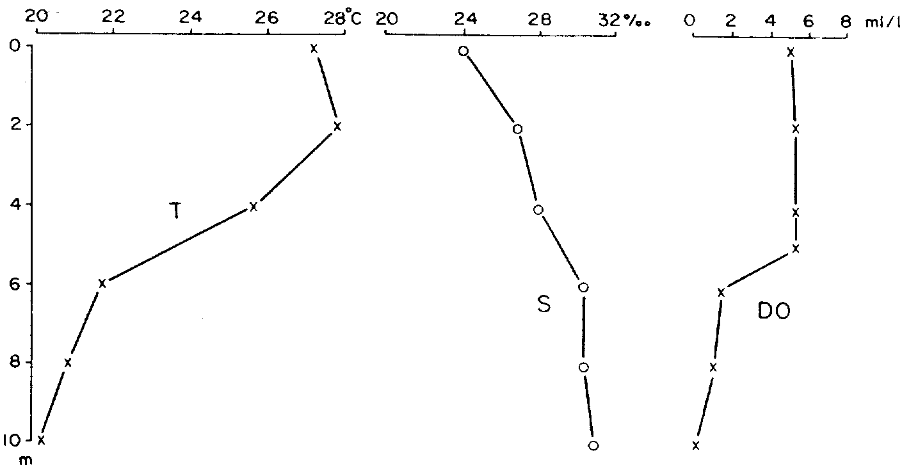

Fig. 2. Vertical distribution of temperature, salinity and dissolved oxygen at St. 4.

below 3 m depth. At St. 4 located at the mouth of inner Masan Bay DO content showed more than 5 m*l*/*l* from surface to 5 m depth. However it decreased from 5.3 to 1.4 m*l*/*l* at 5-6 m depth.

As shown in the temperature and salinity profile (Fig. 2), a strong pycnocline formed in summer inhibits oxygen supply from the surface to bottom layer and extensive degradation of organic materials in the bottom layer is likely to occur. In the Masan Waterway surface temperature ranged from 23.0 to 25.0℃ and bottom temperature from 17.0-21.0℃. Surface salinity was 27.63, 26.92‰ respectively at St. 5 and it exceeded 30‰ thereafter. An anoxic condition was observed in the bottom waters at St. 5 and 6.

Oxygen content in the bottom waters at St. 4 measured by KORDI (1981) in July, August and September, 1981 was N.D. (not-detectable), 0.6, and 1.1 m*l* O_2/*l* respectively, showing an oxygen-deficient condition during the stratified summer season.

Nitrogenous compounds

The highest ammonium content was found at St. 1 where the influence of Masan Industrial Complex is dominant with 349.3 μmol/*l* in the surface waters. At. St. 2 where wastewaters from Changweon area is dominant, its ammonium contents showed 86.3 μmol/*l*. The high ammonium content (309.1 μmol/*l*) at St. 3 seems to be due to the domestic and industrial inflow of wastewater. At the mouth of inner Masan Bay(St. 4), ammonium content is an order of magnitude lower than inshore stations. More than 30 μmol/*l* of ammonium could be measured in the surface waters of St. 4 through St.6. Less than 10 μmol/*l* of ammonium was detected at offshore stations (St. 7 through 9). In the Masan Waterway ammonium content in the bottom waters ranged from 49.1 to 66.0 μmol/*l*, which were greater than the surface contents.

Surface nitrate content at St. 1 and 2 was 368.9 μmol/*l* and 309.1 μmol/*l* respectively. Nitrate contents at 3m depth were 48.8, 1.4 μmol/*l* at St. 1 and 2 respectively, suggesting that the high concentration of nitrate was confined to the surface. At the mouth of inner Masan Bay nitrate content was an order of magnitude smaller than the inshore stations as was the case of ammonium distributions. Nitrate contents in the surface waters decreased with increasing distance from the shore. At St. 8 and 9 surface nitrate contents were only 3.4 and 1.0 μmol/*l*. In the bottom waters of St 5 and 6 nitrate contents were only 1.7 μmol/*l* and N.D. (not detectable), respectively, showing that denitrification proceeds due to the anoxic condition. Surface nitrite contents in inner Masan Bay were 4.81-17.41 μmol/*l* showing the high influence

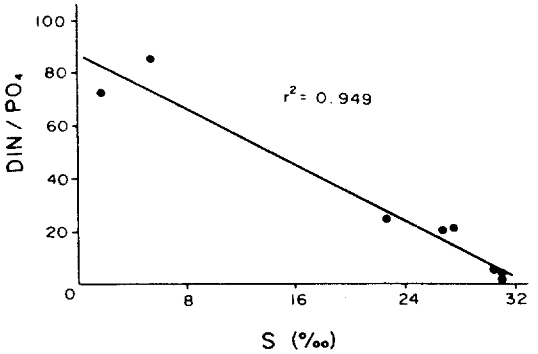

Fig. 3. Relationship between N/P ratio and salinity in the surface waters.

of wastewater discharge. In general high dissolved inorganic nitrogen contents in Masan Bay is believed to be the influence of industrial and domestic wastewaters (Yang et al, 1983).

In inner Masan Bay, composition of dissolved inorganic nitrogen differed from one station to another because of different wastewater sources. Ammonium content was relatively high compared to nitrate at St.3 while nitrate content was high and ammonium content very low at St. 2 where the influence of wastewaters from Changweon Industrial Complex is dominant.

In Masan Bay the amount of phosphorus in the discharged waters are reported to be not so important as that of nitrogen (KORDI, 1981, 1982). As shown in Fig. 3, N/P ratio in the surface waters decreased with increasing salinity which suggests the relative abundance of nitrogen compared to phosphate in the discharged wastewaters.

In Masan Bay ammonium and phosphate contents increased with increasing depth suggesting the active degradation of organic materials in the bottom waters and leaching from sediments to the anoxic bottom waters. High silicate contents were found in the surface waters of St. 2 and 7 (37.4, 23.4 μmol/*l*). Honjo (1974) has pointed out that in Hakata Bay, Japan, phosphate and ammonium are sufficiently supplied into seawater from bottom mud when the concentration of oxygen or pH is low in the bottom layer water.

Dissolved organic nitrogen (DON) content in the surface waters of St. 1 was 1261.8 μmol/*l* which is about 30 times higher than particulate organic nitrogen value. DON contents in the surface waters of St. 4 and 5 were 73.0 and 90.0 μmol/*l* respectively and decreased further at offshore stations. But those DON values are higher than the ones in Toyo River Estuary in Japan (Sasaki and Matsukawa, 1982).

Particulate organic nitrogen and carbon contents at St. 1 were 49.2 and 193.8 μmol/*l* respectively. Pariculate nitrogen introduced via freshwater inflow was not apparent since no concentration difference could be found between inshore and offshore area. Chlorophyll content was not measured in this study. But considering that more than 60 μg/*l* of chlorophyll was frequently measured in this area (KORDI, 1981, 1982) it can be suggested that a large portion of particulate organic materials originated from phytoplankton.

Composition of various forms of nitrogen in the surface waters is shown in Fig. 4. At St.1, the innermost part of Masan Bay, the dominant form of nitrogen was dissolved organic nitrogen (61.7%), while particulate organic nitrogen occupied only 2.4% of total nitrogen. Nitrate (18.0%) and ammonium (17.1%) were also important forms of nitrogen in this bay. At St. 3 dissolved organic nitrogen (45.7%) and ammonium (38.3%) were the dominant forms of nitrogen. At St. 5 (Masan Waterway) the proportion of dissolved organic nitrogen was less than 50% of total nitrogen and that of particulate organic nitrogen 19.8%

ETS activity

Respiratory oxygen consumption rate can be measured by various methods(Eppley and Sloan, 1965 ; Hobbie et al., 1972). In this study was used electron transport system (ETS) activity which is the rate-limiting step in the respiratory oxygen consumption process. ETS activities measured during this study are presented in Table 1. ETS activities were converted to respiratory oxygen consumption rate using the factor of 0.15 for the surface waters where phytoplankton is dominant and 0.43 in the bottom waters where bacterial action is dominant (Packard, 1985). Since respiratory oxygen consum-

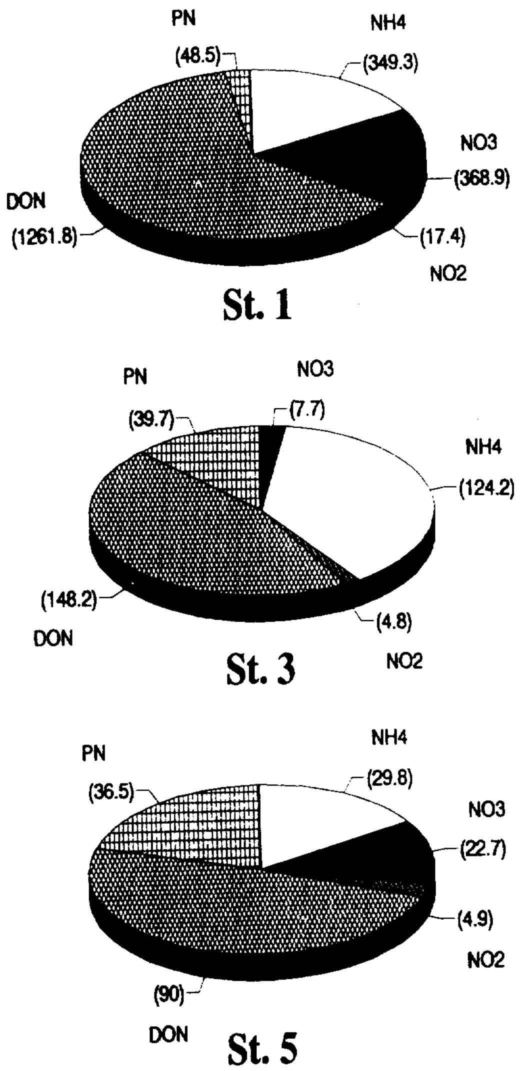

Fig. 4. Composition of nitrogenous compounds in Masan Bay (μmol/*l*).

Table 2. ETS activity and respiratory oxygen consumption rate in Chinhae Bay.

St.	Depth (m)	ETS activity (μl $O_2/l/h$)	R (μl $O_2/l/h$)
1	0	212.1	31.82
	0	11.3	1.70
2	3	10.1	1.52
3	0	7.2	1.08
	6	9.5	4.09
4	0	7.1	1.07
	10	7.2	3.10
5	0	9.8	1.47
	11	2.5	1.08
6	0	5.4	0.81
	25	2.8	1.20
7	0	4.6	0.69
	14	9.1	3.91
8	0	4.4	0.66
	12	13.4	5.76
9	0	4.6	0.69
	11	2.8	1.20

ption rate is related to decomposition of carbon, carbon loss was calculated, assuming R.Q. (Respiratory Quotient) of 1. In the surface waters the ETS activity was 212.1 μl $O_2/l/h$ at St. 1. The ETS activity decreased with increasing distance from the shore. In the bottom waters the ETS activity varied from 2.5-13.4 μl $O_2/l/h$.

Packard (1979) measured the ETS activity of 8.5 μl $O_2/l/h$ in the northwest African upwelling area. The ETS activities in the California Bight, into which wastewaters were being discharged were in the range of 1-5 μl $O_2/l/h$ (Packard, 1985). He succesfully used ETS activity to delineate the polluted water plume with in coastal area.

Oxygen consumption in the waters below the pycnocline can be proceeded by various ways: e.g. bacterial decomposition in the water column, respiration in the phytoplankton, zooplankton and fish and benthic metabolism.

Respiratory oxygen consumption below the pycnocline of St. 4 was calculated to be 442 m*l* O_2/m^2/day from the ETS activity. Yang(1986) estimated the rate of respiratory oxygen consumption by sediment at this station to be 138-197 m*l* O_2/m^2/day. This value is close to the benthic oxygen consumption rate of about 200 m*l* O_2/m^2/day measured in North Baltic (Nedwell *et al.*, 1983).

Bottom layer contained 16,400 m*l* O_2/m^2 of dissolved oxygen at this time of the year. If oxygen supply rate from the surface to bottom layer could be easily calculated, the occurrence of anoxia might be predicted in the bottom waters of Masan Bay. However, many dynamic factors and interactions between them are involved in this oxygen budget, many of which still need to be studied.

At St. 5, where an anoxic condition occurred and nitrate content in the bottom waters was only

1.7 μmol/*l*, denitrification rate could be calculated from the ETS activity. Nitrate removal rate calculated from the ETS activity (2.5 μ*l* O_2/*l*/h) was 0.25 μmol/*l*/day. But this calculation does not include denitrification rate in the sediment and supply of nitrate from surface waters. Furthermore contribution of sulfate reducing activity to the ETS activity in this bottom water was not considered in the above calculation. More sophisticated measurements would be necesssary to predict the occurrence of sulfate reduction which begins after all nitrates are depleted.

Primary productivity at St. 4 (mouth of inner Masan Bay) was 2,695 mg C/m^2/day. At St. 4, carbon loss calculated from the respiratory oxygen consumption rate in the bottom waters and sediments (468-527 m*l* O_2/m^2/day) was 250-282 mg C/m^2/day. So it is suggested that 9.3-10.5% of carbon fixed in the upper layer was decomposed below the thermocline. According to a trap experiment, carried out in Masan Bay, the sinking rate of particulate organic materials into the bottom layer and bottom sediment is relatively low in spite of high amount of wastewater discharge and high productivity, because of intense tidal mixing which would allow these materials to rapidly disperse into the open seawater (Yang, 1990 ; Yang and Hong, 1988). This might be the main reason why only a small amount of organic materials produced in the upper layer of St. 4 is decomposed in the bottom layer.

CONCLUSION

The influence of wastewater discharge with high contents of various forms of nitrogen were noticeable in Masan Bay in summer 1986. Concentrations of DIN, DON and PN were 735.6, 1261.8 and 48.5 μmol/*l* at the head, and 79.1, 73.0 and 39.5 μmol/*l* at the mouth of inner Masan Bay, respectively. Dissolved organic nitrogen appeared to be the most dominant form of nitrogen in Masan Bay.

Below the seasonal pycnocline, an oxygen-deficient condition largely developed in Masan Bay. Respiratory oxygen consumption is likely to proceed at a rate of 442 m*l* O_2/m^2/day in the bottom waters of this bay. Nitrate removal rate calculated from the ETS activity (2.5 μ*l* O_2/*l*/h) was 0.25 μmol/*l*/day. But above calculations do not take into consideration neither horizontal water movement nor biochemical processes in the sediment. More sophisticated measurements would be necessary to predict the occurrence of anoxic condition and sulfate reduction which occurs after the depletion of all nitrates. The cycling of various forms of nitrogen in relation to the massive phytoplankton bloom is still uncertain in Masan Bay. There fore more detailed study on the nutrient distribution, primary productivity and decomposition rate of organic carbon should be carried out.

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