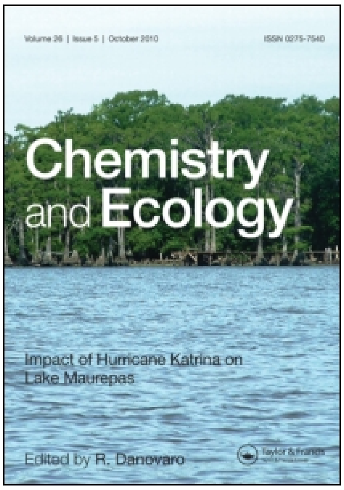

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Dong Beom Yang[a]
[a] Korea Ocean Research and Development Institute, Seoul, Korea

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ON THE POLLUTION CAUSED BY ORGANIC MATERIALS IN CHINHAE BAY, KOREA

DONG BEOM YANG

Korea Ocean Research and Development Institute, Ansan, P.O. Box 29, Seoul, 425–600, Korea

(21 August 1991)

In August 1989, oxygen deficient conditions of bottom waters occurred in the Chinhae Bay together with a steep pycnocline. Dissolved oxygen contents were lower than 1 ml/l from 3 m depth in the inner Masan Bay and from 10 m depth in the outer Masan Bay. In Kohyonsong Bay, surface salinity was about 29‰ and an oxygen deficient condition occurred in the bottom waters. Near Somodo Island, surface waters containing more than 30 μg/l of chlorophyll *α* and over 50 μmol/l of nitrate could be distinguished. In Masan Bay ammonia and phosphate concentrations increased with increasing depth suggesting the active degradation of organic materials in the bottom waters and leaching from sediments.

In Kohyonsong Bay, nitrate contents ranged from 1.9 to 5.4 μmol/l in the surface waters and subsurface maximum of chlorophyll *α* could be observed. ETS activity was 286.1 μl O_2/l-h in the surface waters of Masan Bay and respiratory oxygen consumption is likely to proceed at a rate of 1320 ml O_2/m^2-d in the bottom waters of this bay. Primary productivity was 15.60 gC/m^2-d in the inner Masan Bay and 0.75 gC/m^2-d in Kohyonsong Bay.

In Masan Bay, amino acids content in the sinking materials collected by the sediment trap deployed at the bottom layer was 264 mgC/m^2-d. This amount is equivalent to 6.8% of the amino acids produced in the water column by primary production. In Kohyonsong Bay 95 mg/Cm^2-d of amino acids was collected corresponding to 50.8% of amino acids produced in the water column. In Kohyonsong Bay large faecal pellets produced in shellfish farms were easily settled in the sediment because of the weak current regime.

INTRODUCTION

Chinhae Bay includes large coastal areas of the southeastern coast of the Korean peninsula. Among Korean coastal areas, this bay recently became a public concern because of the deterioration of its environment. From Changweon and Masan industrial area, large amounts of domestic and industrial wastewaters are discharged into the inner Masan Bay, a part of Chinhae Bay.

Frequent red tide outbreaks have been reported in Chinhae Bay and many studies have been done to elucidate the relation between pollutant input and massive phytoplankton blooms (Cho, 1979; Park, 1982; Yang *et al.*, 1983; Yoo and Lee, 1980). While red-tide blooms are occurring almost year round in Masan Bay receiving wastewater discharges, this undesirable phytoplankton bloom occurs less frequently in the western part of Chinhae Bay. Some red tide organisms found in other countries have been related to paralytic shellfish poisoning affecting human beings as well as shellfish, although such cases have not been observed in Korea.

Reported damages are mainly from anoxic bottom waters occurring in summer both in inner Masan Bay and western part of Chinhae Bay (Yang and Hong, 1988). Oxygen deficient conditions occur in Chinhae Bay when a steep seasonal pycnocline separates the bottom waters from well oxygenated surface waters. Among small bays of western Chinhae Bay the worst condition occurs in Kohyonsong Bay.

In the western part of Chinhae Bay large shellfish farms have been established since 1970. In the shellfish farms, eutrophication is accelerated due to the accumulation of the large quantity of organic sediments in the sea floor, largely faecal materials from the shellfish. Activities of shellfish culture are generally centered in the inlets and small bays receiving little wave influence. Densely installed culture facilities further obstruct the circulation. Thus faecal pellets produced by cultured bivalves and other fouling organisms are falling directly to the bottom sediments because of a weak current regime.

The purpose of this study is to compare the process of organic material production and decomposition in two different systems: one is Masan Bay with massive discharge of industrial wastes, and another is Kohyonsong Bay with relatively low primary production and intense activities of bivalve culture.

MATERIALS AND METHODS

The location of sampling stations in shown in Figure 1. Seven stations for water quality measurements were located in the narrow channel of Masan Bay. In this Bay, primary productivity, ETS (Electron Transport System) activity measurements and collection of sinking materials were made at Station 8. Five other stations were occupied for general water quality parameters in Kohyonsong Bay and a detailed biochemical study was done at Station 14. Sampling was done in August, 1989 and sampling time was usually between 9 a.m. and 4 p.m.

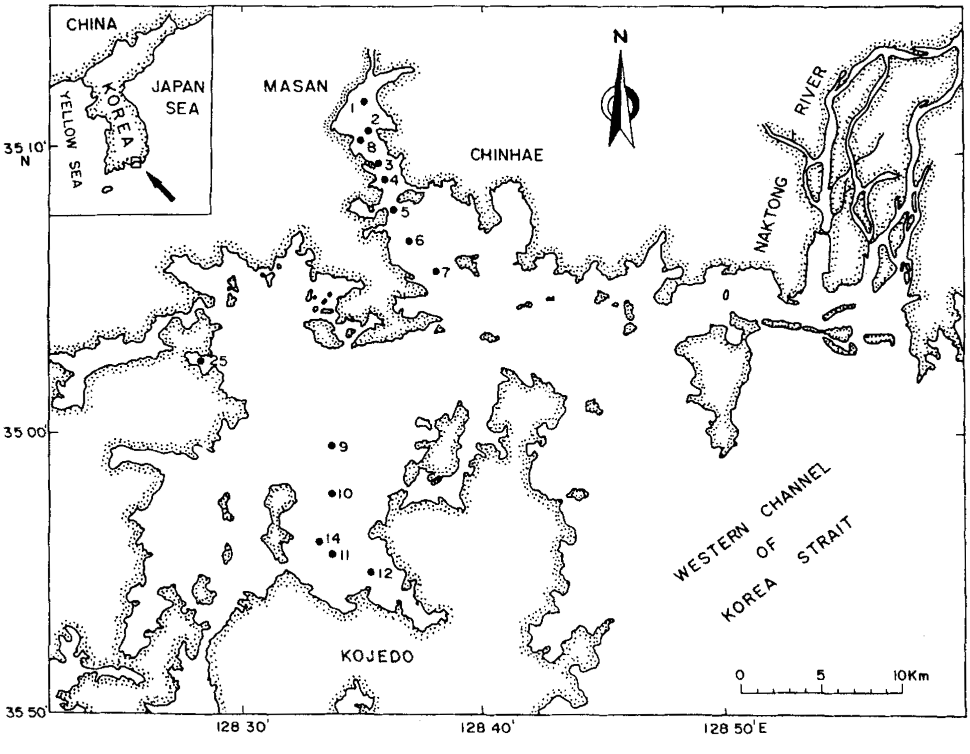

Figure 1 Sampling stations of Chinhae Bay (Masan Bay, Stations 1 through 8; Kohyonsong Bay, Stations 9 through 14).

Temperature and salinity were measured using TS bridge. Dissoved oxygen was measured using dissolved oxygen meter (Yellow Springs Instrument). Analysis of nitrates and phosphates were carried out on the Technicon Autoanalyzer AAII following the method of Zimmermann *et al.* (1977). The determination of ammonium followed the indophenol blue method (Koroleff, 1969) and the extinction at 630 nm was measured in a Perkin Elmer 552 spectrophotometer installed on board. Chlorophyll α was determined on acetone extracts using the method described in Parsons *et al.* (1984).

For the measurements of primary productivity, 220 ml of sea water samples were incubated on deck for 2 to 3 hours with 10 μCi of ^{14}C labelled $NaHCO_3$. Bottles were kept in a polyethylene cylinder covered with a nickel screen which provides the incident light corresponding to each sampling depth. ^{14}C uptake rates were measured on LKB 1215 Liquid Scintillation Counter using Instagel (Packard Co.) as a scintillation cocktail.

For the measurements of ETS (Electron Transport System) activity, 200–500 ml sea water samples were filtered through GF/F filter paper. The filter was ground in a teflon-glass homogenizer at 0–4°C. ETS activity assays were incubated at 15.5–16.5°C (Kenner and Ahmed, 1975). The ETS activity at *in situ* temperature was calculated by the following Arrhenius equation:

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

ETS_i : ETS at *in situ* temperature
ETS_o : ETS at incubation temperature
R : 1.987 Kcal/deg-mole
T_o : Incubation temperature
T_i : *In situ* temperature

Amino acids were separated and quantified by high-pressure liquid chromatography (HPLC) of their fluorescent derivatives and comparison with known amounts of authentic standards. Precolumn derivatization – OPA method of Lee and Cronin (1982) were used and the column for HPLC was Altex Ultrasphere – ODS (4.6mm ID * 15cm, 5μ).

Sediment traps with ID of 140mm (acryl cylinder) were deployed at about 2 m above the bottom for 7 hours (9 a.m. to 4 p.m.) to collect the sinking materials. Traps were bottom tethered and no preservatives were used. Interference from swimmers were found to be insignficant.

RESULTS AND DISCUSSION

General Water Quality Parameters

In the inner Masan Bay, salinity in the surface waters is usually low because of discharge from adjacent rivers (KORDI, 1981, 1982). During summer, a strong pycnocline is formed due to the rise of surface temperature and decreased salinity.

Surface salinty showed less than 27‰ and it increases with increasing depth reaching 31‰ below 10 m depth (Figure 2). Dissolved oxygen contents were lower than 1 ml/l from 3 m depth in the inner Masan Bay and from 10 m depth in the outer

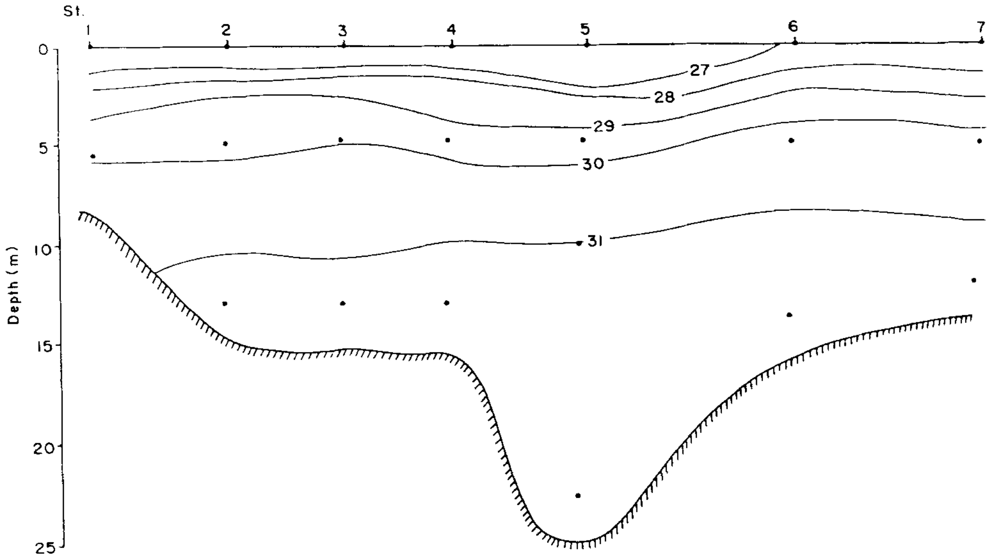

Figure 2 Vertical distribution of salinity in Masan Bay (‰)

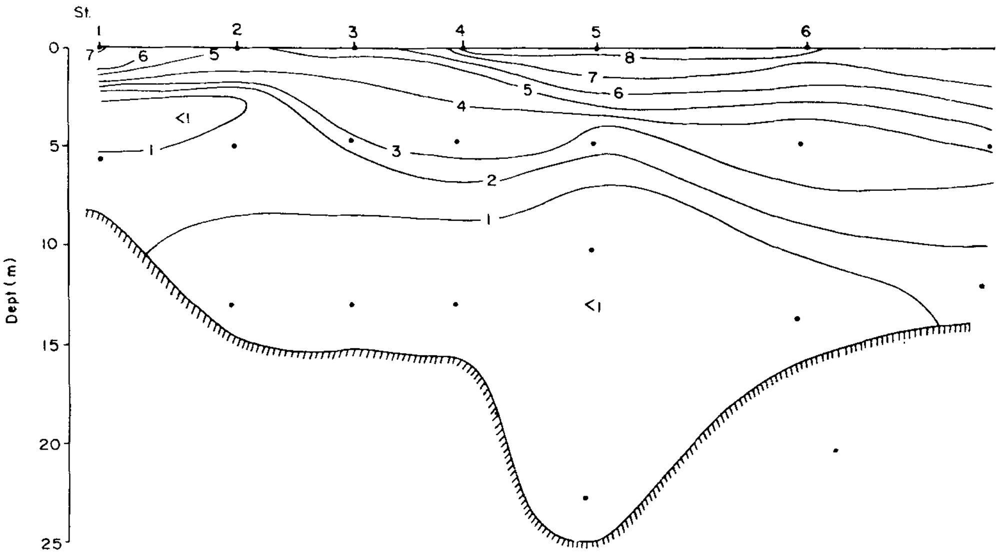

Figure 3 Vertical distribution of dissolved oxygen in Masan Bay (ml/1)

Masan Bay (Figure 3). Oxygen deficient conditions occur in the bottom waters of this bay from spring to mid-autumn (KORDI, 1981, 1982). It has been suggested that the active degradation of organic materials deposited during the phytoplankton bloom in summer occurs in the bottom layer where oxygen supply from the upper mixed layer was considerably reduced by the seasonal pycnocline.

At Station 8, water temperature was 25.9°C in the surface waters and decreases from the pycnocline. Below 7m layer temperature ranged 21–22°C (Figure 4). At this station, DO content in the surface waters exceeded 10 ml/l resulting in supersaturation of 214% whereas less than 1 ml/l could be detected below the sharp oxycline situated at 3 m depth. Abnormally high oxygen saturation rate might be the result of the high photosynthetic activity.

At mid-channel (Station 4 and 5) surface waters containing more than 30 μg/l of chlorophyll α could be distinguished (Figure 5). This type of isolated patch is commonly encountered in Masan Bay. Surface nitrate contents in this patch (Station 4 and 5) exceeded 50 μmol/l which were twice that of the nearest station (Station 1) from the mouth of the river (Figure 6). There is no important source of nitrate at mid-channel and the reason for this high nitrate content in the patch is not clear. Hydrodynamical conditions in this bay are not well understood (KORDI, 1989). On the vertical profile, 10 μmol/l isoline was located at about 5 m depth suggesting that the influence of land runoff is limited to the near-surface waters.

Though nitrate concentration occurring in this bay seems too high to be limiting phytoplankton growth, a good correlationship has been observed between nitrate and chlorophyll α contents (Yang *et al*, 1983) suggesting that the high nitrate waters originated from land discharge might provide favourable conditions for phytoplankton growth. Surface ammonia concentration was the highest at Station. 2 (22.8 μmol/l) and relatively low values were found beyond this station. In the

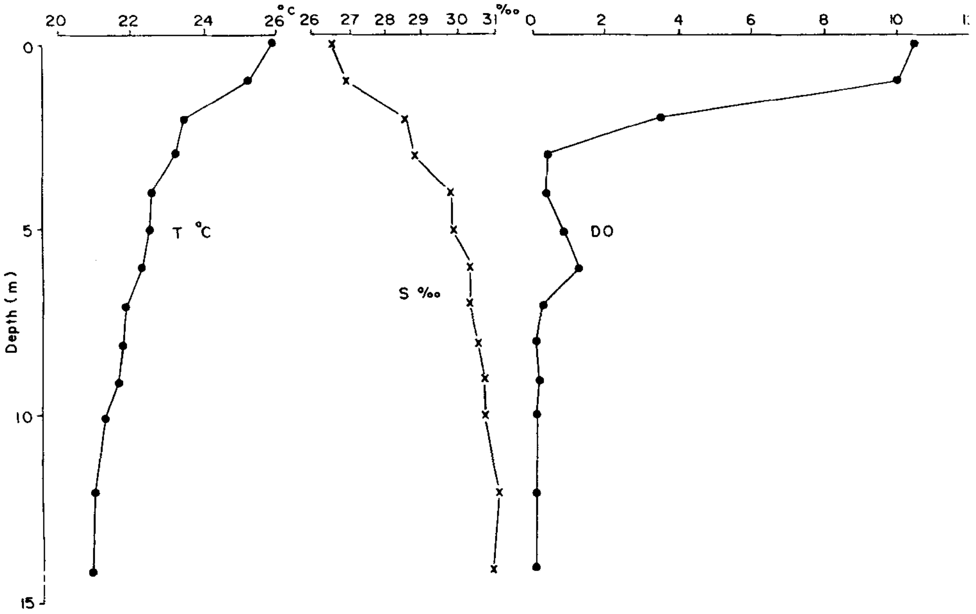

Figure 4 Vertical distribution of temperature, salinity and dissolved oxygen at Station 8.

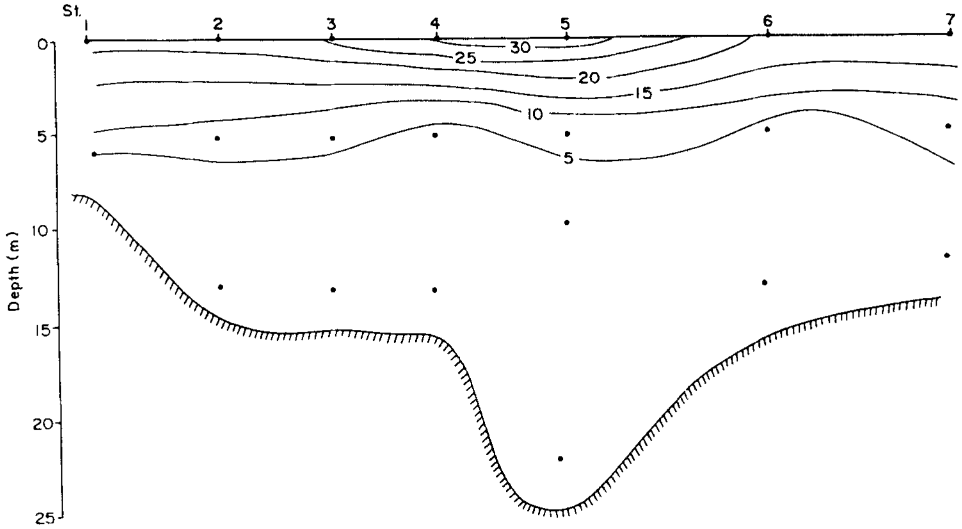

Figure 5 Vertical distribution of chlorophyll a in Masan Bay (μg/l)

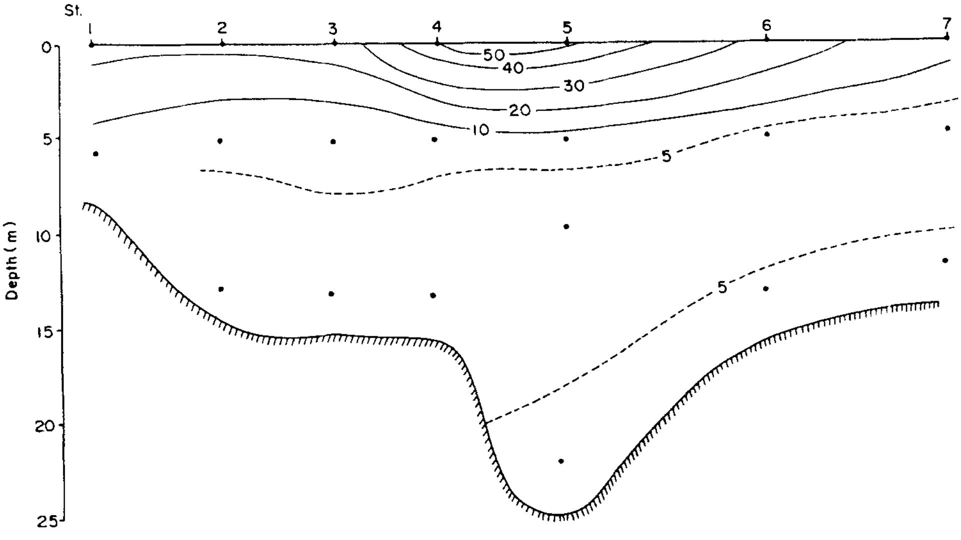

Figure 6 Vertical distribution of nitrate in Masan Bay (μmol/l)

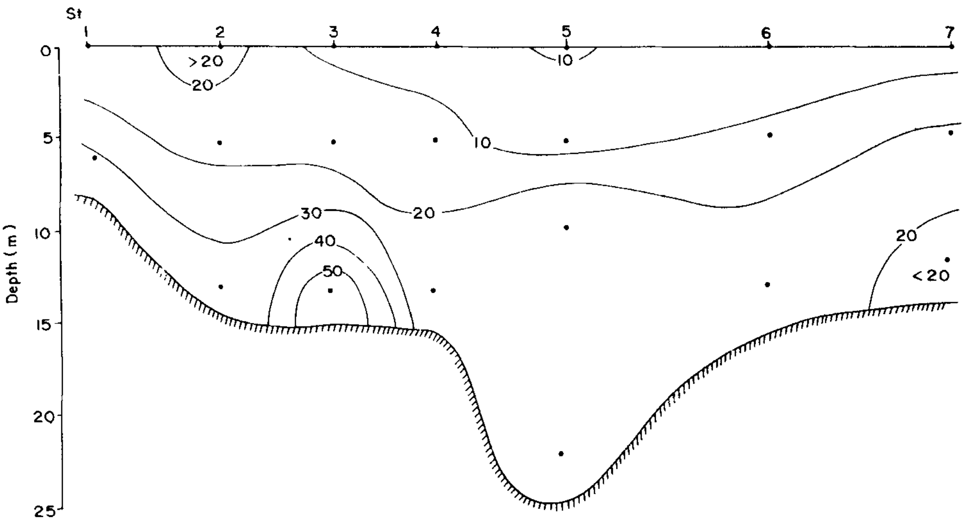

Figure 7 Vertical distribution of ammonium in Masan Bay (μmol/1)

oxygen-deficient bottom waters near the mouth, ammonia contents ranged from 30.4 to 51.7 μmol/l.

The distribution pattern of phosphate is quite different from that of nitrate. At Station 4 and 5 where high nitrate and chlorphyll contents were observed, phosphate contents in the surface waters were only 0.5 μmol/l suggesting phytoplankton consumption of this anion in this patch. In the oxygen-deficient bottom waters, phosphate contents ranged from 5.3–5.9 μmol/l. This might be a result from the leaching of phosphate from the bottom sediments due to reducing conditions. Honjo (1974) has pointed out that in Hakata Bay, Japan, phosphates and ammonia are sufficiently supplied to sea water from bottom mud when the concentration of oxygen and pH are low in the bottom layer water.

In Kohyonsong Bay, surface temperature ranged from 24.9–25.6°C and surface salinity was about 29‰. Detailed results are published elsewhere (KORDI, 1990). At Station 12, although vertical thermal and haline gradients were not so steep as in Masan Bay, dissolved oxygen was less than 1 ml/l from 16 m depth (Figure 8). In this bay where influence of land runoff is negligible, nitrate contents ranged from 1.9 to 5.4 μmol/l, increasing in the lower layer. Ammonia contents varied from 2.3 to 6.5 μmol/l in the surface waters. Chlorophyll *a* concentrations were 0.01–0.34 μg/l in the surface waters. Subsurface maximum of chlorophyll *a* could be observed but its content exceeded 3μg/1 only at Station 11 and 12.

ETS Activity

Respiratory oxygen consumption rate can be measured by various methods. In this study we used electron transport system (ETS) activity which is the rate-limiting step in the respiratory oxygen consumption process. ETS activities measured at Stations 8 and 14 are presented in Table 1. ETS activities were converted to respiratory oxygen consumption rate using a factor of 0.15 for the surface waters where

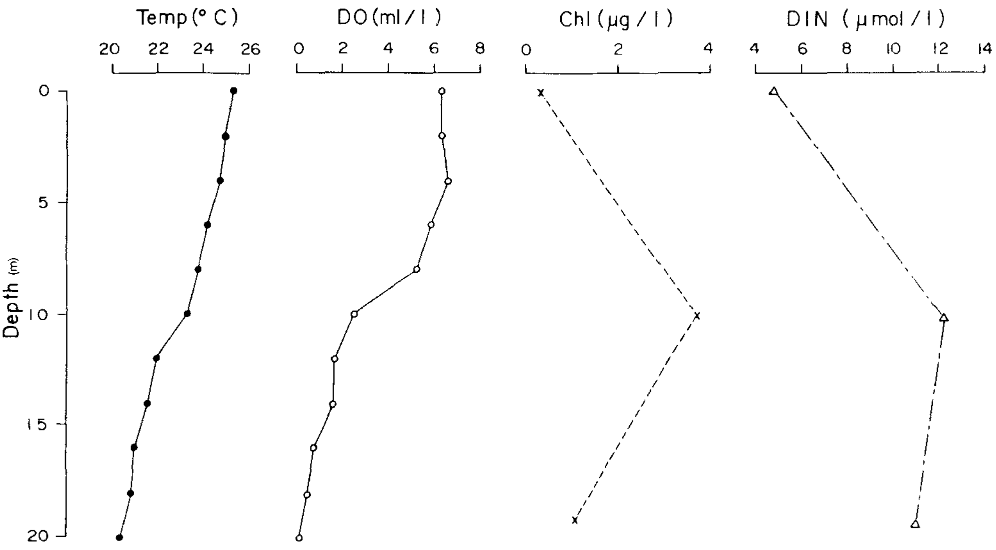

Figure 8 Vertical distribution of salinity, dissolved oxygen, chlorophyll and DIN (Dissolved Inorganic Nitrogen) at Station 12.

Table 1 ETS activity and respiratory oxygen consumption rate in Chinhae Bay.

Station	*Depth* (*m*)	*ETS activity* (μl O_2/l-h)	*R* (μl O_2/l-h)
	0	286.1	42.9
8	5	10.6	4.6
	12	12.4	5.3
	0	6.4	1.0
14	10	3.4	1.5
	20	3.5	1.5

phytoplankton is dominant and 0.43 in the bottom waters where bacterial action is dominant (Packard, 1985). In the surface waters, ETS activity was 286.1 μl O_2/l-h in Masan Bay while it was only 6.4 μl O_2/l-h in Kohyonsong Bay.

Oxygen consumption in the waters below the thermocline can occur by various ways : e.g. bacterial decomposition in the water column, respiration in the phytoplankton, zooplankton and fishes, and by benthic metabolism. If we assume that in the bottom waters of Masan Bay, oxygen is solely supplied by the diffusive vertical flux from surface waters, a one dimensional oxygen budget model can be attempted as follows.

Vertical diffusive flux of dissolved oxygen through the pycnocline can be expressed:

$$\frac{\alpha O_2}{\alpha t} = \frac{\alpha}{\alpha Z}\left[K_z \frac{\alpha O_2}{\alpha Z}\right]$$

For this calculation, a vertical distribution curve of oxygen was fitted to a polynomial curve by the least squares method. Kz is difficult to determine, but 0.05–1.10 cm^2/sec was reported by King and Devol (1979). Assuming Kz value to be 0.1 cm^2/sec and pycnocline to be at 4m depth, oxygen supply through the pycnocline can be estimated as 206 ml O_2/m^2-d.

Respiratory oxygen consumption below the pycnocline of Station. 8 was calculated to be 1320 ml O_2/m^2-d from ETS activity. Bottom layer oxygen at this time of the year has 3810 ml O_2/m^2 of dissolved oxygen. Benthic oxygen consumption was not measured during this study, but in 1986, it amounted to 138–197 ml O_2/m^2-d at this station comparable to a benthic oxygen consumption of about 200 ml O_2/m^2-d measured in the North Baltic (Nedwell *et al.*, 1983). Taking these values into account, it can be assumed that within 3 days dissolved oxygen would be depleted in the bottom waters of Masan Bay. However, factors not considered in this calculation such as a horizontal component of water circulation, might alter this rate of process.

This kind of calculation was not attempted for the bottom waters of Kohyonsong Bay. But relatively slow oxygen consuming processes are expected in the bottom waters of this bay from the low ETS activities. Although the benthic oxygen consumption rate has never been measured in Kohyonsong Bay, a high rate of this process might be suggested from the high sediment carbon content and oxygen deficient condition in the overlying waters observed by Yang and Hong (1988).

Primary Productivity and Amino Acids in Sinking Materials

Water column primary productivity measured during this study was 15.60 gC/m^2-d at Station 8 (inner Masan Bay) and 0.75 gC/m^2-d at Stations 14 (Kohyonsong Bay). Assimilation values in the surface waters of Stations 8 and 14 were 53mgC/mgChl-α/h and 48 mgC/mgChl-α/h respectively, higher than other reported values (Parsons *et al.* 1977).

To date, most studies of the flux of particulate organic matter have considered bulk properties such as total carbon, nitrogen and plant pigments. Individual organic compounds have received much less attention. In shallow areas of high productivity, a larger proportion of surface primary production can reach the sea floor. Sediment trap experiments in Scottish sea lochs have shown that 30–40 percent of annual water column production may be transported to bottom sediments (Steele and Baird, 1972).

Amino acids, the building blocks of protein molecules, make up the largest known reservoir of organic nitrogen in most organisms. Amino acids are useful indicators of decomposition in the marine environment because much is known about their natural occurrence and geochemical behavior (Lee and Bada, 1977 ; Dawson and Gocke, 1978).

In this study amino acids were analyzed on collected materials in sediment traps deployed at Station 8 (Masan Bay) and Station 14 (Kohyonsong Bay). As seen from the primary productivity, these two areas are essentially different in terms of phytoplankton activity – very high at Station 8 while very low at Station 14. Assuming 25% of carbon is in amino acids, production of amino acids by primary producers in the water column of Station 8 approximated 3.9 gC/m^2-d. Amino acid flux in the sinking materials collected by the sediment trap deployed at the bottom layer of Station 8 was 264 mgC/m^2-d. This amount is equivalent to 6.8% of the amino acids produced in the water column by primary production (Figure 9).

It is interesting to note quite a big loss of organic carbon in the water column.

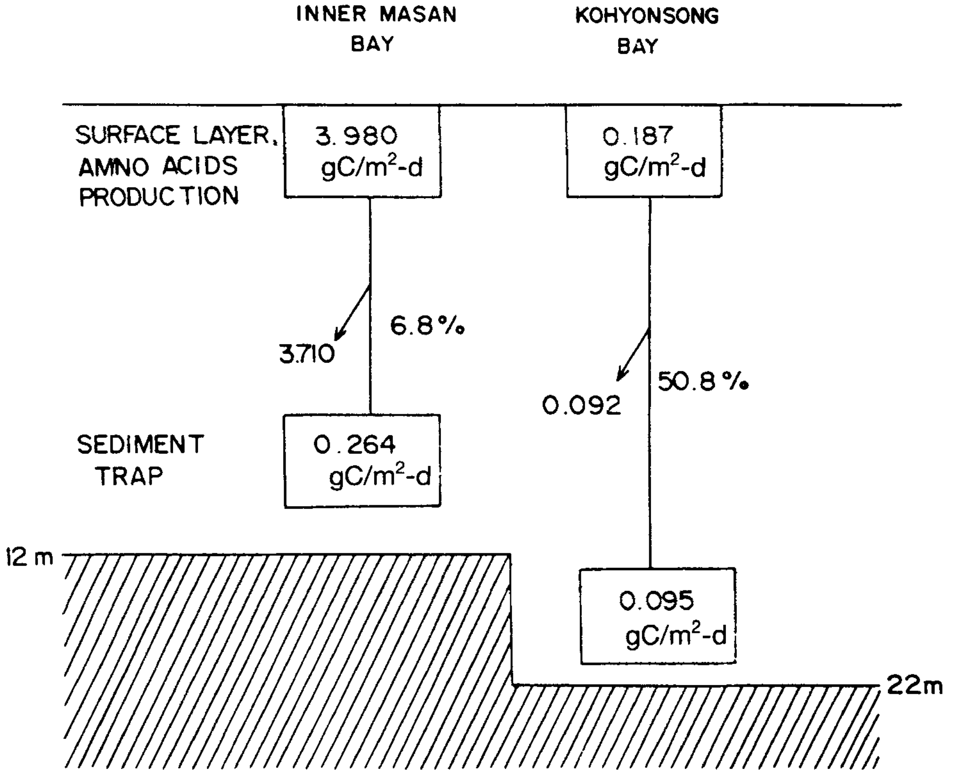

Figure 9 Amino acid production and sedimentation at Stations 8 and 14.

Although a large portion of particulate materials is transported to the outer bay by strong tidal currents (KORDI, 1981), it is likely that much of this extra carbon is in the dissolved pool produced during phytoplankton or zooplankton feeding processes. As dissolved organic matter, the free amino acids are subject to rapid removal from sea water (Hobbie *et al*, 1968; Lee and Bada, 1977; Lee and Cronin, 1982).

At Station 14, amino acid production in the surface layer was estimated to be 187 mgC/m^2-d assuming 25% of carbon is in amino acids. In Kohyonsong Bay, 95 mg C/ m^2-d of amino acids was collected in the sediment trap which corresponds to 50.8% of amino acids produced in the water column.

According to Yang and Hong (1988), geographical distribution of organic materials in the surface sediments in the Chinhae Bay system showed two distinct zones rich in organic materials during an extensive survey in 1983 : one is Masan Bay near an urban and industrial area, and the other is Kohyonsong Bay where shellfish farms are extensive.

In Masan Bay, in spite of the high amount of wastewater discharge and high productivity, the sinking rate of particulate organic materials to the bottom sediment would be relatively low because of intense tidal mixing allowing these materials to be rapidly dispersed into the open sea water. Major grazers of phytoplankton in this area appeared to be small zooplankton which produce faecal materials small enough to show low sinking rates (KORDI, 1982). Thus lack of shellfish farms, and intense tidal mixing would disfavour the accumulation of organic materials to the surface sediments.

There is no important source of terrigenous organic materials in Kohyonsong Bay and the important grazers of phytoplankton in this bay seem to be the cultured shellfish. Even though the phytoplankton production is not high, faecal pellets produced by shellfish can be easily sedimented because of their large size. Moreover, the mean tidal current velocity is reported to be 5–10 cm/sec at ebb in Kohonsong Bay which would further facilitate the settling of faecal pellets (KORDI, 1981).

Sawada and Taniguchi (1969) estimated the settling area of faecal pellets of pearl oysters in Ago Bay, Japan. Taking 1 cm/sec as the sinking velocity of faecal pellets and 3–5 cm/sec as the current velocity, they estimated that faecal pellets would be deposited within 30–50 m of their origin in the bay of which depth was about 10m. A similar assumption may apply in Kohyonsong Bay where a current velocity of 5–10 cm/sec and depth of about 20 m would lead the faecal pellets to be deposited within 100–200 m of their origin. In other words, the accumulation of faecal pellets to be deposited is in proximity of shellfish farms.

The importance of benthic metabolism in the cycling of organic matter and the oxygen consuming processes has been discussed by many authors (Rowe *et al.*, 1975; Christensen and Packard, 1977). Yang and Hong (1988) found a good correlationship between organic carbon content in the surface sediment and DO content in the overlying waters in Kohonsong Bay. Although oxygen consumption by the sediment cannot account for most of the oxygen consumption in the bottom waters, this would be a good indicator for development of oxygen deficient conditions in well stratified coastal waters.

Conclusions

Although this study was designed for only two selected dynamic properties in the marine environment, two different ways by which production and transport of organic material affect the coastal environment of Chinhae Bay could be distinguished.

Several points of significance emerge in comparing the deposition of organic materials to the sediments and degradation of organic materials in two bays. In Masan Bay, settling of organic materials to the surface sediment seemed to be not intense because of tidal mixing and the relatively small size of particulate materials. However, the pycnocline is steep and bottom water oxygen consumption rate is high enough to produce oxygen deficient conditions. In Kohyonsong Bay, large faecal pellets produced in shellfish farms could be easily deposited to the sediment because of poor water exchange.

It was unfortunate that benthic oxygen consumption rate in Kohyonsong Bay was not measured. Comparison of the two different systems in terms of organic material deposit and decomposition within their bottom waters and benthic oxygen consumption rates would lead to a better understanding of pollution caused by organic materials in Chinhae Bay.

Organic matter produced by living organisms in the surface waters of the ocean is subject to rapid biological decomposition in various ways. So more consideration should be given to the big loss of organic material produced in the water column of Masan Bay. Study of the individual amino acid composition of dissolved and sinking materials, together with the bacterial decomposition rate would further document processes in the cycling of organic materials in the highly productive coastal waters under great pertubation by human activities.

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