Sediment Oxygen Demand and Nutrient Release in An Eutrophic Estuarine Embayment in Hong Kong[*]

H. Chua[1], P.H.F. Yu[2] and M.W.L. Cheung[3]

[1]Department of Civil and Structural Engineering
[2]Department of Applied Biology and Chemical Technology Hong Kong
Polytechnic University, Hung Hom, Hong Kong, China
[3]Department of Contruction Support, Airport Authority, Wan Chai, Hong Kong, China

Abstract: *Tolo Harbour has received massive discharges of municipal sewage, agricultural wastes and cottage industrial effluents, via three river systems, in the past two decades before the mid Eighties. The Harbour is almost land locked and poorly flushed. The soft sediment acted as a sink for nutrients and organic pollutants. After a decade of efforts in establishing and enforcing water pollution control legislations and upgrading wastewater treatment facilities, the sediments have turned into sources of nutrients and exert a measurable oxygen demand upon the overlying waters. In vitro measurements showed that the sediments oxygen demand (SOD) was between 17.6 and 54.3 $mgo_2 \cdot m^{-2} \cdot h^{-1}$. The maximum rates of release of ortho-phosphate phosphorus and ammonia nitrogen were 15.0 and 206.0 $mg \cdot m^{-2} \cdot h^{-1}$, respectively.*

Keywords: *eutrophication, land-locked estuaring embayment, Hong Kong, sediment nutrient release, sediment oxygen demand.*

1. Introduction

Dissolved oxygen (DO) and nutrient concentrations are important indicators of water quality. The rates of DO depletion have often been investigated to determine the balance between oxygen supply and utilization within the water system. When utilization significantly exceeds supply, DO depletion may result in the death of aquatic or marine lifeforms and upset of ecosystems. The principle oxygen sinks in aquatic systems are microbial and macrophyte respiration in the water column and uptake by bottom sediments (McDonnell and Hall, 1969). Excessive nitrogeneous and phosphoric nutrients contribute significantly to eutrophication of streams, lakes and other water bodies (Boynton *et al.*, 1980).

Marine sediment deposits have been widely recognized as having a potentially severe impact on water qualities. These deposits exert a measurable oxygen demand upon overlying waters, and act as a source of nutrients that contribute to eutrophications (Hanes and

Irvine, 1968; Pomeroy *et al.*, 1965). Sediment oxygen demand (SOD) has received relatively little attention compared to chemical oxygen demand in the water column. However, SOD can represent a significant percentage of total oxygen uptake in certain aquatic systems. Hanes and Irvine (1968) and Seiki *et al.* (1989) reported that SOD in certain water bodies may account for as much as 50 % of the total oxygen demand. The importance of lake sediments in controlling nutrient concentration in overlying waters has long been a subject of concern. Carpenter and Capone (1983) and Pomeroy *et al.* (1965) demonstrated that sediment release could maintain nutrient concentrations in overlying waters at levels high enough to support significant algal growth for a long period of time. Harter (1968) found that eutrophic lake sediments had a large capacity to temporarily absorb phosphorus and later release it, which might prevent or delay expected improvement in the lake following nutrient diversion.

Tolo Harbour in the north-eastern territories of Hong Kong is a nearly land-locked estuary embayment (Figure 1). In the past two decades before the mid Eighties, rapid developments of the adjacent satellite cities, immense commercio-industrial activities and lack of legislative control resulted in large quantities of untreated municipal sewage, agricultural wastes and cottage industrial effluents being discharged into rivers and watercourses that flow into the Tolo Harbour (Chua *et al.*, 1995a; 1995b; Environmental Protection Department, 1996). Due to the poor oceanic tidal flushing (Morton and Wu, 1975; Trott, 1973; Chau and Abesser, 1958), exogenous organic materials and nutrients were decomposed and recycled within the embayment. These resulted in significant decrease in dissolved oxygen levels, upset of the ecosystems, frequent occurrences of red tides and loss of inland and coastal amenity values (Environmental Protection Department, 1996).
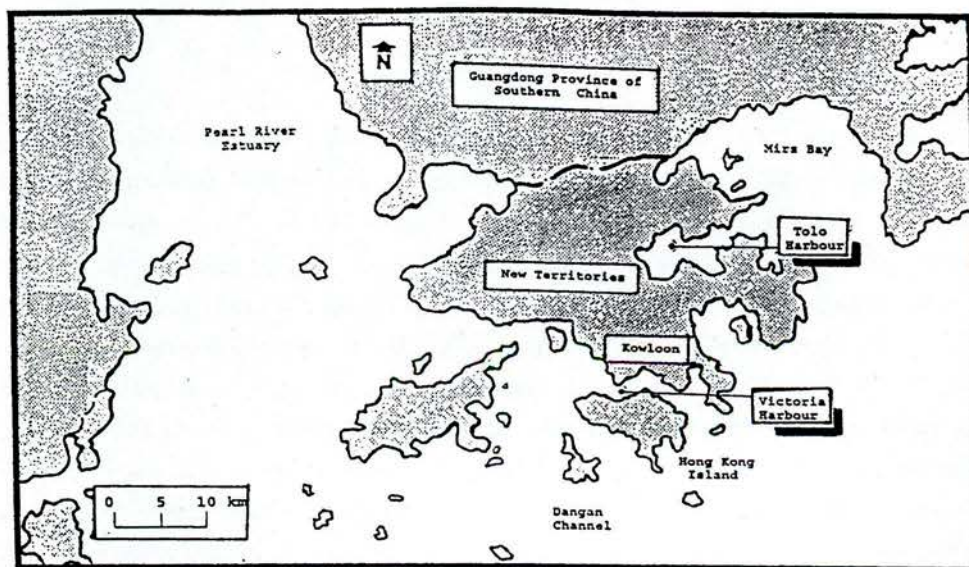

Fig.1 Geographic Location of the Tolo Harbour

After a decade of efforts in establishing and enforcing water pollution control legislations and upgrading wastewater treatment facilities since the mid Eighties, improvements in the water quality of Tolo Harbour have been less significant than expected (Environmental Protection Department, 1996). This was attributed to the fact that the soft sediment, which acted as a sink for nutrients and organic pollutants, had turned into a source of nutrients and exert a measurable oxygen demand upon the overlying waters (Chua *et al*., 1995b). Invstigations into the SOD and rates of nutrient release have become of immense interest.

2. The Tolo Harbour

The main waterbody of Tolo Harbour is about 16 by 3 km and the Tolo Channel, the opening that leads into the South China Sea, has a maximum width of only 1.3 km (Morton and Wu, 1975) (Figure 2). Tolo Harbour is relatively shallow with an average depth of 12 m, while the narrow Tolo Channel is deeper at about 20 m. The oceanic tidal flushing rate in the almost land-locked embayment is very weak, resulting in a hydraulic residence time in the harbour of as long as 35 days (Trott, 1973; Chau and Abesser, 1958). Tolo Harbour has a subtropical monsoonal climate. It is affected by warm and moist tropical oceanic wind. The annual average air temperature is 22.8 degree centigrade. Monthly highest air temperature is over 28.6 degree centigrade, and monthly lowest air temperature is about 15 degree centigrade. Therefore, there is no distinct cold winter. On the western end of the Harbour, three river systems with about 150 km of water courses and 65 km2 of catchment area, flow through two satellite cities of 1-million population and drains into the *inner Tolo* Harbour. Numerous pig and poutry farms and industrial estates are located amidst these river systems.
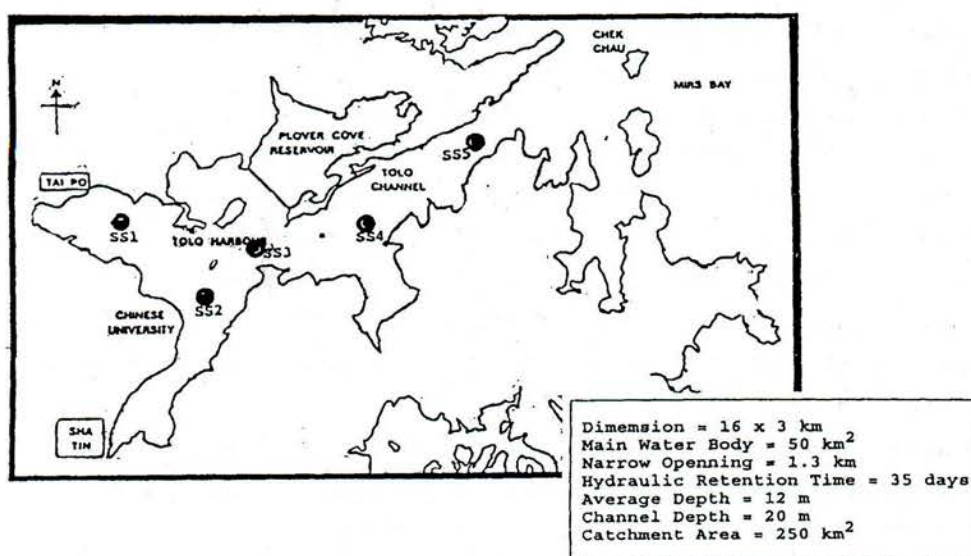

Fig.2 Tolo Harbour and the Sampling Stations

In the past decades, livestock wastes contributed more than two-thirds of total pu-
trescrble matters and nutrients entering the river systems, and eventually, enhanced eutro-
phication in the Tolo Harbour. Furthermore, in the later half of the Eighties, treated efflu-
ents from the sewage treatment works in the satellite cities contributed heavy loads of nu-
trients to the Tolo Harbour. Monitoring data in the early Ninties for total nitrogen and
phosphorus in the Harbour were 0.23-1.06 mg·L^{-1} and 0.03-0.20 mg·L^{-1}, respectively (Envi-
ronmental Protection Department, 1994). By 1988, the frequency of occurrence of red tides
had reached its peak of 40 occurrences in that year (Environmental Protection Department,
1996). Massive blooms of dinoflagellate algae, Noctiluca scintillans, which contain red,
orange and yellow pigments resulted in occurrence of red tides, which caused intense de-
oxygenation of the water and physical clogging of fish gills. When the algae drifted ashore,
they created glutinous putrid slimes that fouled beaches and killed fish (Hodgkiss and Chan,
1983). In 1989, a toxic red tide was first discovered. Toxins accumulated in shellfish,
which resulted in poisoning when consumed. Paralytic Shellfish Poisoning (PSP) toxin
levels as high as 13 500 mu·kg^{-1} were recorded.

3. Methods

Sediment samples were taken from the Tolo Harbour and Tolo Channel once a week
between June and September, 1996, by using a Phlege Core Sediment Sampler (Kahl Sci-
entific Instrument Corporation, U.S.A., Model 217WA200). Three undisturbed sediment
cores were extracted at each of the five sampling stations (SS1-SS5) (Fig.2). The depths at
different sampling stations varied : 5-8 m at SS1 and SS2, 10-14 m at SS3 and SS4, and 22
m at SS5. The samples were placed in a 4 ℃ ice chest during the delivery to the labora-
tory. The core samples were tested for SOD and rate of release of nutrients as soon as they
were delivered to the laboratory in order to avoid the formation of thin oxidized layers.
Water samples were also collected at 2 m below the surface at the five sampling stations,
using an Acylic Horizontal Water Sampler (Wildlife Supply Company, U.S.A.).

In the in vitro SOD measurements, water samples were pretreated by filtering with 0.42-
um glass microfibre filter papers (Whatman Company, England, Model: GF/C) and aerating
for than 8 hours in a dark room. Each of the core sediment sample was transferred to sever-
al BOD bottles, which were then filled to the rim with the pretreated corresponding water
sample. Precaution was taken to ensure absence of air settling. The DO in the water was
measured with a Dissolved Oxygen Meter (Yellow Spring Instrument Company, U.S.A.,
Model 58) at 30-minute intervals, for 3-5 hours.

In the in vitro measurements of rate of release of nutrients, two core sediment samples at
each sampling station were placed into a settling column with 50 cm in height and 9.6 cm
in inner diameter. A measurement of 1.8 L of the pretreated corresponging water sample
was slowly added to each column. The overlying water was then mechanically stirred at 4
rpm. This set-ups were placed in a dark, air-conditioned room with the ambient temperature

maintained at 20 ℃. The initial nutrient concentrations of the overlying water in the settling column were determined. The overlying water was then periodically analyzed for nutrient concentrations for 4-5 days. In the nutrient analyses, the water samples were filtered with 0.42-μm glass microfibre filter papers (Whatman Company, England, Model: GF/C). Phosphorus concentration was determined using the ascobic acid reduction technique, catalyzed by antimony for ortho-phosphate phosphorus and total phosphorus. Nitrate and nitrite nitrogen was determined by using cadmium reduction method with a spectrophotometer (Milon Roy Company, U.S.A., Spectronic 601). Ammonia nitrogen and total kjeldahl nitrogen (TKN) were determined by ammonia selective electrode method with Ion Analyzer (Orion Research Incorporation, U.S.A., Model EA940) and automatic TKN analyzer (Tecator Company, Sweden, System 61007 and Kjeltec Auto 1030 Analyzer), respectively. The measurement procedures for these analyses were in accordance with Standard Methods (Greenberg *et al*., 1992).

4. Results and discussion

4.1 Sediment oxygen demand

The DO depletion profiles in the water overlying the sediment samples collected from sampling stations SS1-SS5 are graphically presented in Figure 3. The rates of oxygen consumption were calculated from the slopes in each time interval along the DO versus time profiles. With the known volume of the overlying water sample and the area of sediment-water interface, SOD was expressed as the oxygen consumption per unit interfacial area per time ($mgO_2 \cdot m^{-2} \cdot h^{-1}$). The ranges of SODs of sediment samples from each sampling stations are summarized in Table 1.

Tab.1 Sediment oxygen demands from different sampling stations

Sampling Stations	SS1	SS2	SS3	SS4	SS5
SOD($mgO_2 \cdot m^{-2} \cdot h^{-1}$)	20.9-44.6	26.0-40.9	31.8-47.8	17.6-54.3	25.4-43.3

These SOD values were obtained while DO concentrations in the overlying water remained above 4 $mg \cdot L^{-1}$. These values were comparable with that reported in the literature for typical eutrophic water bodies (Seiki, 1989). Generally, the range of SOD values at each sampling station were similar. Water pollution at SS1 and SS2 that were adjacent to the inner Harbour where sewage and wastes were discharged in the past, was expected to be more serious than that at the remote SS5 station. However, sediments extracted at SS1 and SS2 were observed to be more sandy while sediments at other stations were of fine silt-clay compositions, the latter of which could adsorb and accumulate pollutants more easily. Therefore, the difference between SODs from SS1 and SS5 was not obvious. The range of SOD values at SS4 stretched to a little higher than other stations, reaching 54.3$mgO_2 \cdot m^{-2} \cdot h^{-1}$,

because the water around SS4 station was once a breeding area for fish and the sediments were therefore fertilized. During this investigation, it was also observed that salinity of the overlying water had hardly any effect on SOD. Seawater and mixed water (one third of seawater and two thirds of freshwater) were used as overlying water with the similar sediment samples to determine the SOD and no apparent distinction was observed.
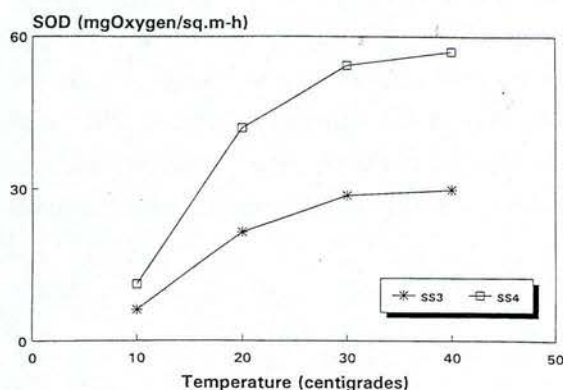

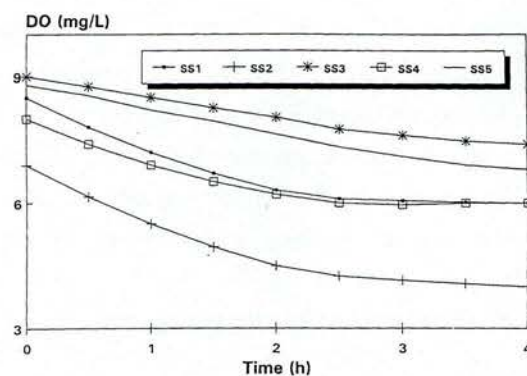**Fig. 3 Oxygen uptake of sediment samples**

Fig. 4 Effect of emperature on SOD

Sediment oxygen demand comprises two elements, namely biological respiration of living organisms in the sediment and chemical oxidation of reduced substances in the sediment, such as divalent iron and manganese, and sulfide. The mechanism by which sediment oxygen demand is exerted is an integration of numerous complex physical, chemical and biological processes. However, the expected difference between SOD value of sediments at the upper layer and that at the 1-m depth lower layer was not observed in this study. The reason could be that the SOD at the upper 1-m layer mostly depended on the biological respiration. Oxidation of reduced substances only occured in much deeper layers. On the other hand, when two of the sediment samples, namely SS3 and SS4, were measured for SOD under different temperatures, a distinct trend was observed (Figure 4). As temperature rised, SOD increased. The increment in SOD value was more significant at lower temperatures than that at higher temperatures, with the same temperature increment. These were attributed to increased rate of biological respiration at higher temperatures. These results were consistent with McDonnell and Hall (1969), which reported that biological processes increased two-fold for each 10°C rise in temperature within the optimum

Tab. 2 Rate of release of nutrients from sediments

Nutrients	Rate of Release $(mg \cdot m^{-2} \cdot d^{-1})$
Ortho-phosphate phosphorus	1.0 - 15.0
Total dissolved phosphorus	3.7 - 19.6
Nitrate-nitrite nitrogen	24.7 - 31.3
Ammonia nitrogen	13.9 - 206.0
Total kjeldahl nitrogen	20.3 - 215.0

temperature, which was around 35 °C for mojority of the mesophiles. Beyond the optimum temperature, the increment of SOD was smaller for a similar increase in temperature.

4.2 Sediment nutrient release

The nutrient release measurements showed that a significant amount of various forms of nutrients were released from the sediments to the overlying waters (Tab. 2). During the 4-5 days period of measurement, the system remained aerobic and DO concentrations maintained over 4 mg·L^{-1}.

Eutrophic water sediments contained significant quantities of phosphorus, existing in both organic and inorganic forms. The organic forms included nucleic acids, nucleotides, phospholipids and a variety of polyphosphate esters. The inorganic forms included calcium phosphate, aluminium phosphate, iron phosphate complexes, phosphates absorbed on clays, and ortho-phosphates dissolved in the interstitial water of the sediment. The absorption capacity of sediments under aerobic conditions was attributed to a thin aerobic layer several millimeters thick on top of the sediments. When conditions became anaerobic, the ferric complexes were reduced, the sorption capacity was substantially lowered, resulting in a free exchange of dissolved substances between the sediments and the overlying water. Therefore, the sediments gradually released phosphorus into the overlying water. The phosphorus released was mainly in the form of ortho-phophates at a highest rate of 15.0 mg · m^{-2} · h^{-1}, accounting for 76.5 % of total dissolved phosphorus released.

The process of release of nitrogen from sediments was complex, involving the inter-conversion of various nitrogen species. Tab. 2 shows that ammonia nitrogen, at a rate of 206.0 mgO$_2$ · m^{-2} · d^{-1}, was the main nitrogen species released from the sediment. This agreed with results reported by Boynton *et al.* (1980). The ammonia nitrogen was mainly due to decomposition of the accumulation of a high concentration of organic nitrogen from the organic loads of agricultural wastes. Concentrations of organic nitrogen in the interstitial water within the sediment were often more than two orders higher than that in the overlying water (Carpenter and Capone, 1983). Nitrate-nitrite nitrogen was absorbed into or released from the sediment, depending on the concentration gradient across the sediment-water interface. In whichever direction, the movement of nitrate-nitrite nitrogen remained at relatively low rates.

5. Conclusion

In vitro studies of the Tolo Harbour sediments showed that the SOD ranged from 17.6 to 54.3 mgO$_2$·m^{-2}·h^{-1}. There were no apparent difference at the five sampling stations, although the overlying water quality at these stations had much variance. Release of nutrients from the sediment was significant, especially in ortho-phosphates and ammonia nitrogen. The maximum release rates were 15.0 and 206.0 mg·m^{-2}·d^{-1}, respectively. Therefore, when the external nutrient sources were cut off from the Tolo Harbour, nutrients released from

contaminated sediments supported the growth of planktons and algae. These resulted in delayed improvement of the water quality.

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