Elsevier Editorial System(tm) for Physics and Chemistry of the Earth
Manuscript Draft

Manuscript Number: JPCE-D-09-00168

Title: Ratio of Nitrogen to Phosphorus in the Pearl River and Effects in the Estuarine Coastal Waters: Nutrient Management Strategy in Hong Kong

Article Type: Special Issue: Managing Water Pollution

Keywords: N:P Ratio, Nutrient limitation, Eutrophication, Sewage treatment strategy, HATS, Hong Kong, Pearl River estuary, water quality

Corresponding Author: A/Prof. Kedong Yin, Ph.D.

Corresponding Author's Institution: Griffith University

First Author: Kedong Yin, Ph.D.

Order of Authors: Kedong Yin, Ph.D.

Abstract: The Pearl River in the southern China is the second largest river in China in freshwater discharge volume, covering 454,000 square km drainage basin. Excess nutrients in aquatic ecosystems can result in algal blooms, or even harmful algal blooms and subsequent DO consumption leads to hypoxia. However, not all nutrients are equal; only one nutrient relative to other nutrients is the most limiting for algal biomass production. As long as the concentration of the most limiting nutrient is low, it will limit excess algal biomass production. The other nutrients in excess will not produce an algal bloom. Therefore, the strategy of nutrient pollution control is to remove the most limiting nutrient from the sewage effluent to minimize the eutrophication impact on the receiving waters. This, in turn, determines the type and level of sewage treatment. In general, either nitrogen (N) or phosphorus (P) is the most limiting nutrient in aquatic ecosystems. In the Pearl River, N is very high and P is relatively low and therefore, N:P ratio is very high. When high N:P ratio nutrients in the Pearl River freshwater flow into coastal waters which usually have low N:P ratios, environmental impacts may be produced. The Pearl River flows into coastal waters in South

China Sea and heavily influences Hong Kong waters located to the east of the Pearl River estuary. The sustainable objective of nutrient control strategy is to improve water quality without significant environmental impacts on ecosystem. When the Hong Kong government planned to upgrade domestic sewage facility to biological treatment, this triggered the scientific question of whether N or P is the most limiting nutrient and the answer to this question became critical in making the management decision on which nutrient, N or P, should be removed and what type of treatment facility should be build. The decision on different removal strategy could make a huge financial difference in treatment facility and operation. In the past, because nitrogen is high in the southern waters, it has been thought that any addition of nitrogen would exceed the environmental capacity and result in algal blooms. Therefore, nitrogen has been typically considered for removal from sewage effluent. However, evidence revealed that the N relative to P in the Pearl River estuary is very high and P is found to be the most limiting nutrient. As a result, P in the southern water of Hong Kong is so low that it actually limits phytoplankton biomass accumulation, even though N is very high. Low P concentration will dictate not only the final phytoplankton biomass, but may also limit the bacterial DO consumption. Thus, under present conditions P appears to play the dominant role in controlling the environmental assimilative capacity for nutrient enrichment, and hence, it could be argued that the removal of phosphorus should receive priority over N removal, if there is a need for the future elevation of treatment levels. However, as this conclusion is reached with respect to the present condition of the Pearl River, it may be prudent to retain flexibility such that treatment levels can be adjusted to accommodate future changes in the estuarine conditions, in particular if changes in the nutrient loads entering the Pearl River should cause the N:P ratio to drop.

Ratio of Nitrogen to Phosphorus in the Pearl River and Effects in the Estuarine Coastal Waters: Nutrient Management Strategy in Hong Kong

Kedong Yin^{1,2}

- ^{1.} *Australian Rivers Institute, Griffith University (Nathan Campus), Brisbane, QLD4111, Australia, Fax: +61 7 3735 4245, Email: k.yin@griffith.edu.au*
- ^{2.} *Key Laboratory of Tropical Marine Environmental Dynamics, South China Sea Institute of Oceanology, Chinese Academy of Science, Guangzhou, China*
kdyin@scsio.ac.cn

Abstract

The Pearl River in the southern China is the second largest river in China in freshwater discharge volume, covering 454,000 square km drainage basin. Excess nutrients in aquatic ecosystems can result in algal blooms, or even harmful algal blooms and subsequent DO consumption leads to hypoxia. However, not all nutrients are equal; only one nutrient relative to other nutrients is the **most** limiting for algal biomass production. As long as the concentration of the **most** limiting nutrient is low, it will limit excess algal biomass production. The other nutrients in excess will not produce an algal bloom. Therefore, the strategy of nutrient pollution control is to remove the **most** limiting nutrient from the sewage effluent to minimize the eutrophication impact on the receiving waters. This, in turn, determines the type and level of sewage treatment. In general, either nitrogen (N) or phosphorus (P) is the most limiting nutrient in aquatic ecosystems. In the Pearl River, N is very high and P is relatively low and therefore, N:P ratio is very high. When high N:P ratio nutrients in the Pearl River freshwater flow into coastal waters which usually have low N:P ratios, environmental impacts may be produced. The Pearl River flows into coastal waters in South China Sea and heavily influences Hong Kong waters located to the east of the Pearl River estuary. The sustainable objective of nutrient control strategy is to improve water quality without significant environmental impacts on ecosystem. When the Hong Kong government planned to upgrade domestic sewage facility to biological treatment, this triggered the scientific question of whether N or P is the most limiting nutrient and the answer to this question became critical in making the management decision on which nutrient, N or P, should be removed and what type of treatment facility should be build. The decision on different removal strategy could make a huge financial difference in treatment facility and operation. In the past, because nitrogen is high in the southern waters, it has been thought that any addition of nitrogen would exceed the environmental capacity and result in algal blooms. Therefore, nitrogen has been typically considered for removal from sewage effluent. However, evidence revealed that the N relative to P in the Pearl River estuary is very high and P is found to be the most limiting nutrient. As a result, P in the southern water of Hong Kong is so low that it actually limits phytoplankton biomass accumulation, even though N is very high. Low P concentration will dictate not only the final phytoplankton biomass, but may also limit the bacterial DO consumption. Thus, under present conditions P appears to play the dominant role in controlling the environmental assimilative capacity for nutrient enrichment, and hence, it could be argued that the removal of phosphorus should receive priority over N removal, if there is a need for the future elevation of treatment levels. However, as this conclusion is reached with respect to the present condition of the Pearl River, it may be prudent to retain flexibility such that treatment levels can be adjusted to accommodate future changes in the estuarine conditions, in particular if changes in the nutrient loads entering the Pearl River should cause the N:P ratio to drop.

Keywords

N:P Ratio, Nutrient limitation, Eutrophication, Sewage treatment strategy, HATS, Hong Kong, Pearl River estuary, harmful algal blooms

1. Introduction

Hong Kong is situated in the south coast of China, facing the northern part of the South China Sea. The Pearl River estuary is to the west of Hong Kong. Thus, the coastal environments are profoundly influenced by three water regimes: estuarine waters in the Pearl River estuary, oceanic waters from the South China Sea and coastal waters from the China Coastal Current from the northeast. These influences are strongly subject to two seasonal monsoons.

Seasonal monsoons and the Pearl River discharge as well as rainfall are important in determining coastal currents, coastal water circulation, mixing and residence time in the Pearl River estuary, and Hong Kong coastal waters and other semi-enclosed bays as well in the region. There are seasonal monsoons: northeastern winds in winter and southwestern winds in summer. The frequency distribution of wind direction is not balanced over a year, with eastern winds prevailing most of the year. The annual average freshwater discharge from the Pearl River into the Pearl River estuary is $10,524 \text{ m}^3 \text{ s}^{-1}$, with 20% occurring during the dry season in October-March and 80% during the wet season in April-September (Yin, 2002).

There is a rainy season during the wet season in the region with the maximal rainfall in June-August. Rainfall not only adds freshwater to the water column and strengthens the stratification, but it also brings in nutrients directly to the photic zone. During the wet season, Hong Kong coastal waters are heavily influenced by the Pearl River discharge except for its eastern side. The coastal waters of Hong Kong is very dynamic and complex due to advection, mixing and the interaction of freshwater from the Pearl River estuary, and runoff, and oceanic waters from oceanic currents.

1.1 Sewage Treatment Strategy Development in Hong Kong

To improve the water quality of the Victoria Harbour, the Environmental Protection Department (EPD) initiated the Harbour Area Treatment Scheme (HATS or the Project) (formerly known as the 'Strategic Sewage Disposal Scheme' (SSDS)) in the late eighties.

The originally-envisaged final configuration of HATS was intended to comprise a network of deep tunnels that would deliver sewage from around the harbour to a primary treatment plant at Stonecutters Island, from where the treated effluent would be discharged through a long tunnelled outfall to deep waters south of Hong Kong. The Project was divided into two stages. The first stage, which has been completed, collects sewage from the most densely populated and industrialized areas and conveys it to a sewage treatment works at Stonecutters Island (SCI) for chemically enhanced primary treatment (CEPT) before discharge into the western harbour via an interim outfall. The collection of the sewage from Hong Kong Island, and the long tunnelled outfall were to follow subsequently. In 2000, an International Review Panel (IRP, 2000) reviewed the Project and proposed for the next stage four alternative treatment and discharge options, all involving the use of CEPT plus Biological Aerated Filters (BAF) as the preferred treatment technology, deep tunnels for the sewage transfer system, and short outfalls for disposal. These options (Options 5a, 5b, 5c, and 5d by the IRP) differ in the degree of centralisation and the proposed sewage treatment works (STW) and outfall locations.

1.2 Types of Treatment and Environmental Assimilative Capacity

The IRP (2000) recommended that before final decisions on further stages were made, consideration should be given to upgrading the treatment level to nitrification, and denitrification, if necessary, and further work be undertaken to establish whether effluent treated to the higher treatment level(s) could be discharged into the harbour area (following the four possible options they identified), without the need for a long oceanic outfall. While denitrification would be to remove the one nutrient, ie, nitrogen from the sewage effluent, the associated, but critical question is: would it be more appropriate to remove the other nutrient, ie phosphorus? The question appears to be an engineering one, but the answer turns upon the scientific understanding of the environmental assimilative capacity (environmental capacity)

for nutrients in the receiving waters, as the water quality criteria is based on the environmental assimilative capacity.

1.3 Environmental Impact and Conceptual Model for Environmental Capacity

Whether sewage effluent results in a significant impact depends not only on the amount of sewage discharged, but also on the assimilative environmental capacity of the receiving waters. The amount of sewage effluent is relatively constant over the short term, but will gradually increase as the population grows. The objective of this study is to examine the environmental processes regulating the assimilative capacity for nutrients and identify the vulnerability of the receiving environment for the present and future eutrophication. The assimilative environmental capacity for nutrients in Hong Kong waters is determined by both physical and biological oceanographic factors and processes. When an input of nutrients exceeds the capacity, an impact such as excessive algal biomass, red tides and/or low oxygen waters can occur.

1.3.1 Nutrients and Algal Blooms

Sewage contains inorganic nutrients such as nitrate, nitrite, ammonium, phosphate, a very small amount of silicate and organic nutrients. Phytoplankton utilize these inorganic nutrients and grow exponentially with cell division rates of 1 to 3 times per day, producing a rapid increase in biomass, i.e. a phytoplankton bloom, when the water column is stable (usually by stratification or no vertical mixing).

Further growth of the bloom is usually terminated by one nutrient, designated the most limiting nutrient. Normally in relatively pristine coastal waters, N limits phytoplankton biomass production whereas in freshwater, P usually is the most limiting nutrient (Hecky and Kilham, 1988; NRC, 2000). P is low in the Pearl River and other Chinese rivers, and therefore in the southern waters of Hong Kong (Yin et al., 2001) and much of the coast of China (Harrison et al., 1990), P potentially limits phytoplankton biomass production in the summer when the Pearl River influence is dominant (Yin et al., 2000 and 2001; Yin, 2002; Yin et al., 2008).

Algal blooms are normally measured in terms of the amount of chlorophyll which usually range between 1-10 µg/L. Concentrations of chl *a* ranging from 10 to 100 µg/L are representative of excessive blooms, which are usually fuelled by excessive anthropogenic nutrients from point sources such as sewage or non-point sources such as agricultural runoff and rainfall. The rapid increase in algal biomass which may take place in a few days during a bloom usually can not be consumed by zooplankton due to the extremely high growth rates of the phytoplankton as compared to the zooplankton. Consequently, the phytoplankton outgrow the zooplankton.

1.3.2 Harmful Effects of Algal Blooms

When phytoplankton run out of a nutrient, they become nutrient-stressed and the cells may clump together forming aggregates that sink to deeper waters where the cells die, and are decomposed by bacteria. This bacterial decomposition uses up O₂ in the deeper water and this process could lead to hypoxic conditions (dissolved O₂ < 2 mg/L). Therefore there is usually a link between excessive nutrients and low O₂ in deep water. This excessive biomass can

cause 'harm' by sinking, decomposing and creating low oxygen conditions and could cause an impact on deep water organisms including commercially important fish species. Such excessive blooms are often referred to as harmful algal blooms (HABs). HABs are often dominated by dinoflagellates, some of which produce toxins that can be transferred up through the food chain and cause a threat to humans. Thus, the term HABs is a very broad term and it may refer to both diatom and dinoflagellate blooms.

1.3.3 Conceptual Models for Algal Biomass Production and Oxygen Consumption

In the natural aquatic environment, production of algal biomass and the consequential dissolved oxygen consumption can be generally described by the following conceptual models.

Algal growth in a batch culture mode

When algae are confined in a bottle with full nutrient-enriched medium under a set of suitable conditions (light, temperature, salinity), they will grow exponentially until one nutrient becomes depleted. The initial concentration of that nutrient determines the algal biomass produced. This type of the culture is termed a batch culture and many algal blooms in nature are similar to this batch culture mode when the water column is very stable, e.g., in freshwater lakes.

Algal growth in a semi-continuous culture mode

If we dilute the culture during the exponential stage of the batch culture growth with new medium (e.g. half new medium+half of the culture), the algal biomass in the bottle will be reduced by the dilution (by half). If the algae double each day, the algal biomass can be kept constant by a half dilution each day. This type of algal growth is termed a semi-continuous culture. If the growth rate (μ) of the algal cells is less than the dilution rate (D), algal biomass will gradually decrease because the cells are being diluted faster than they are growing (i.e. $\mu < D$). If D is too large, it can cause a washout effect (i.e. few cells will be left in the bottle after some time). If $\mu > D$, the algal biomass will gradually accumulate. In nature, D is largely controlled by physical dilution such as wind mixing (i.e., $D > \mu$).

Algal growth often behaves like a batch culture in a freshwater lake, as well as in marine waters when the water column is stable. However, usually coastal marine waters behave more like a semi-continuous culture. This is because many physical factors such as winds, tidal cycles and river discharge or rainfall dilute the water column. Winds and tides may result in a dilution of surface waters due to vertical mixing between euphotic zone and aphotic zone, and this can occur over different temporal scales (hours, days, weeks, or seasons) and different spatial scales (channels, semi-enclosed bays, open coastal waters). When physical processes are dominant, dilutions may be so high that algae in the water column can not accumulate and nutrients will not be depleted. When physical processes are weak, dilutions are low and algae in the water column can grow. However, if there are no nutrients or low concentrations of nutrients, the algal biomass will not be high. For algae to reach its maximum biomass (a bloom) in the presence of abundant nutrients, it may take several days (up to a week). When high and low dilutions of the water column alternate, which is more like a rapid semi-continuous culture in coastal waters, algal blooms may never be able to develop fully to the environmental capacity and this is typically what happens from

late autumn to early spring in the temperate marine waters due to wind mixing, and in estuaries where freshwater outflow is large.

Dissolved oxygen in the bottom water column

Dissolved oxygen (DO) consumption in the water column is mainly caused by bacterial degradation of organic matter. Thus, this DO consumption process in nature is similar to what occurs in a bacterial culture in batch or semi-continuous culture modes. DO consumption is determined by the amount of algal biomass plus other organics that reach the deeper layers as well as the stability of the water column. When the aphotic layer of the water column is stable (like a batch culture), the amount of organic matter will determine the final DO concentrations. When the aphotic layer alternates between batch and semi-continuous cultures, the final DO will depend on rates of DO consumption and rates of dilution.

2. Environmental Variability of Water Quality in Hong Kong

The marine environment including some semi-enclosed waters of Hong Kong are largely influenced by the Pearl River discharge and the southeast Asian monsoons due to Hong Kong's geographical setting. Therefore, there are large spatial gradients and strong seasonality in marine environmental conditions in terms of salinity, temperature, water column stratification, dissolved oxygen, and nutrients as well as algal blooms. When describing the marine environment of Hong Kong and making an assessment of environmental impacts, these spatial gradients and the seasonality must be considered.

2.1 Water Column Structure in Different Water Control Zones in Hong Kong

Spatial and temporal distribution of salinity and temperature reflects the coastal circulation and vertical mixing as well as the stability of the water column. Based on the valuable ten year data set obtained by the EPD's regular monitoring program in seven water control zones (Figure 1), we examined spatial and temporal variability in water quality. Surface salinity decreases to the lowest values during July in all 7 zones, and geographically the values increase from west to east (Figure 2). Surface temperature increases to a maximum in June and remains relatively constant from July to September. Bottom salinity increases to the maximal value in July in all zones except for NM-Northwest waters. An increase in salinity in the bottom water corresponds to a decrease in salinity at the surface in July, indicating upwelling circulation in the semi-enclosed bays (TM, MM and PM) and open waters (SM, VM and WM). During this upwelling, surface waters flow offshore (southwards) due to the southwest monsoon-induced winds which draw the oceanic waters (high salinity and cold temperature) from the continental shelf to nearshore. Superimposed on the upwelling is estuarine circulation, where the river discharge at the surface and rainfall cause entrainment of deep water in the estuary and the nearshore waters. A decrease in temperature of the bottom water in July provides evidence of the estuarine circulation (Figure 2). Haline stratification (the difference in salinity > 1.0 between the surface and bottom) starts in March at NM (in the estuary), one month later (in April) in zones TM, MM, PM, SM and WM, but even later in June at VM. Thermal stratification (the difference in temperature $> 1^{\circ}\text{C}$) starts two months later than haline stratification, i.e. in May at NM and in June at WM, but earlier in March at TM and MM, in the same month (in April) at PM and SM and in June at VM (Figure 2). Haline and thermal stratification indicates the stability of the water column, which influences the potential formation of phytoplankton blooms and low dissolved oxygen waters.

2.2 Average Water Quality in Different Water Control Zones in Hong Kong Waters

Chlorophyll a (Figure 3) Average chlorophyll *a* concentrations are low in PM and MM all year around. There is a peak in chlorophyll *a* concentrations in May at NM, but the peak moves to July at SM, WM and SM. Chl *a* is the highest at TM among all 7 zones. Average chl *a* concentrations are generally < 5 µg/L except for peaks which vary among the zones, but generally <20 µg/L. Bottom chl *a* increases in May at NM and in July at VM, but remains low and relatively constant in other zones.

Dissolved oxygen (DO) (Figure 3) Dissolved oxygen at the surface is > 6 mg/L at TM, PM and MM all year around, but decreases in summer and fall at DM, and NM. Surface DO appears to decrease in spring, increase in summer and decrease again in fall at WM, VM and SM. During March-April, DO at the bottom starts to decrease earlier in the northeast zones at TM, MM and PM than other zones. The lowest DO occurs during June-August in all the zones, but the monthly average DO at the bottom is > 3 mg/L and appears to suggest that hypoxia seems to be a rare event or short-lived at these stations (the sampling frequency of the EPD regular monitoring program may not be sufficient to catch short-lived episodes of hypoxia).

TIN (Figure 4) Surface TIN ($\text{NO}_3 + \text{NO}_2 + \text{NH}_4$) concentrations at NM are below 20 µM in winter. They start to increase in April, reach a maximum of 80 µM in July due to river discharge, and then decrease and return to winter values in October. TIN concentrations at WM follow a similar temporal change as observed at NM, but the maximum concentration in

July is only $<30\ \mu\text{M}$. Surface TIN at SM increases in summer (June-August), and only in July at MM. TIN at PM, MM and TM is below $20\ \mu\text{M}$ during all months.

Phosphate (Figure 4) Surface PO_4 concentrations are usually $< 1\ \mu\text{M}$ at NM, SM, WM, MM and PM. At WM, VM and TM, PO_4 is lowest in summer, but PO_4 does not appear to have any seasonal variations in other zones.

TIN/P Ratios (Figure 5) Molar TIN/ PO_4 ratios are near 16:1 in winter in all zones. During summer months, TIN/ PO_4 ratios increase to >32 at MM and VM, and to $>48:1$ at NM, WM and SM due to river inputs.

3. Physical Oceanographic Processes and Environmental Capacity

Physical processes are important in regulating the environmental assimilative capacity of the receiving waters by switching the water column between batch and semi-continuous culture modes. For example, if receiving waters are frequently diluted by horizontal advection or vertical mixing, algal growth may never be able to lead to an accumulation of algae to cause an algal bloom. In this case, the environmental assimilative capacity can be large enough to accommodate the discharge of inorganic nutrients without leading to an algal bloom. Therefore, the environmental assimilative capacity is largely dependent on geographical settings and seasonality such that it varies spatially and temporally. The primary driving forces in Hong Kong are monsoons, river outflow, tidal cycles and rainfall, which drive coastal circulation and mixing as well as water column stability (stratification). Consequently, light penetration, distribution of salinity and nutrients as well as nutrient ratios will be strongly influenced by these physical processes, which also vary spatially and

temporally. These factors will ultimately influence nutrient utilization, nutrient limitation and algal growth/biomass in the marine-estuarine environments.

Hong Kong waters progress through seasonal changes in water masses, circulation, and stratification. In winter, the China Coastal Current brings coastal waters from the northeast, which becomes dominant in the Hong Kong waters (Chau and Wong, 1960; Williamson, 1970; Watts, 1971a; b; 1973), as observed in satellite images as well (Yin et al., 1999). In summer, the Pearl River estuarine influence is dominant in Hong Kong waters. These processes will set the coastal waters to a batch culture mode or semi-continuous culture mode, ie., they would promote or prevent the formation of phytoplankton blooms and subsequent low oxygen in bottom waters.

3.1 Monsoons

Northeast monsoonal winds are dominant in winter, and this brings surface offshore waters to Hong Kong and causes downwelling of coastal waters along the south China coast. Wherever there are coastal embayments or semi-enclosed bays opening to the south, coastal waters flow shorewards at the surface, resulting in downwelling along the shore.

The assimilative capacity of Hong Kong waters can be influenced by different processes induced by the seasonal monsoon. Processes that may increase the capacity are:

- (1) Winds and surface currents: during winter, northeast winds push the estuarine waters to the west side of the estuary; this reduces the estuarine influence in Hong Kong waters to a minimum (Mao et al., 2004);

- (2) Dilution and mixing: offshore waters flush through open Hong Kong waters during the dry season; this can clear or reduce the accumulative eutrophication effect of the previous year (Yin, 2002);
- (3) Summer upwelling: during summer, the estuarine waters influence many zones of Hong Kong waters at the surface, but the oceanic waters invade at the bottom and thus can serve as a seasonal flushing mechanism because oceanic waters are poor in nutrients, and unfortunately relatively low in oxygen (Yin, 2002; Yin et al., 2004a).

Monsoon induced processes that may decrease the environmental assimilative capacity are:

- (4) Downwelling and residence times - during winter, in semi-enclosed bays, surface offshore waters become dominant, and the residence time of the water in the bays is longer due to downwelling. This can lead to favourable conditions for the aggregation of dinoflagellates for two reasons: vertical migration of dinoflagellates can play a role in concentrating cells in the surface, and local input of nutrients may be trapped in the bays due to the longer residence time.
- (5) Invading oceanic waters: upwelling circulation also results in the invasion of oceanic waters during the wet season, which are low in oxygen and this water forms the bottom water of Hong Kong waters; this could decrease the availability of DO before the hypoxic level is reached.

3.2 *Pearl River discharge*

The Pearl River discharge is low from October to March; it starts to increase in April and reaches a maximum in July (Zhao 1990). The widespread Pearl River plume influences

Hong Kong waters dramatically. The plume causes Hong Kong waters to become more estuarine-like with decreased salinity, increased turbidity, high nitrogen relative to phosphorus, and therefore, has high N/P ratios. The outflow of the estuarine plume into the South China Sea also entrains the deep oceanic waters into the Hong Kong region. The outflow of Hong Kong surface waters into the South China Sea leads to shorter residence times and therefore, increases the environmental capacity by increasing dilution. The nutrient-poor oceanic water that is drawn into Hong Kong's semi-enclosed bays does not favor the nutrient acquisition strategy by vertical migrating dinoflagellates. This also increases the environmental capacity. Rainfall follows the temporal pattern of the Pearl River discharge and strengthens the Pearl River estuarine circulation described above.

4. Most Limiting Nutrient and Nutrient Control Strategy

Phytoplankton require different nutrients for growth. The nutrient with the lowest concentration relative to the other nutrients is used up first and starts to limit phytoplankton growth and biomass production. This nutrient is referred to as the most limiting nutrient. Molar ratios of nutrients are usually used to indicate which nutrient is potentially the most limiting nutrient compared with the average phytoplankton nutrient ratios. Generally, the molar ratio of N:P that is required for phytoplankton growth is 16:1 (Hecky and Kilham, 1988). When ambient ratios of N:P exceed 16:1, phytoplankton may be limited by P and if the ratio is <16:1, N may be limiting to phytoplankton growth.

The most limiting nutrient can define the environmental capacity of the receiving waters for algal blooms when the water column is in a batch culture mode (very stable). For example, if nitrogen is very abundant while phosphorus is in shortage relative to nitrogen (high N/P

ratios), then any increase in phosphorus from sewage effluent can result in excessive algal growth. In this case, the assimilative capacity of the receiving water is small in terms of P discharge and will be rapidly filled and exceeded. On the other hand, given the abundant nitrogen but with relatively low phosphorus in ambient waters, a further increase in nitrogen from the sewage would not result in excessive algal growth since P sets this limit of phytoplankton biomass. In this case, further additions of nitrogen from the sewage effluent will not cause an increase in algal biomass.

Changes in nutrient concentrations are related to the dominance of different water masses during seasonal shifts. The South China Sea is an oligotrophic ocean and thus, coastal waters of Hong Kong in winter and deep waters in summer are nutrient poor. Therefore, any long-term increases in the concentration of nutrients must be due to the estuarine influence and eutrophication. Comparing the NO_3 concentration at SM to that near Waglan Island (near SM19) during 1973 (Morton and Wu, 1975) indicates that NO_3 at SM19 has increased at least 3 times during this 30 yr period. However, the concentration of phosphorus does not appear to have increased since then, and remained below $1 \mu\text{M}$. Even a large scale investigation in the region in 1980 to 1981 (Thompson and Ho, 1981) showed similar concentrations of phosphorus to this study.

Based on average TIN/PO_4 ratios, which largely exceed average phytoplankton chemical composition N:P ratios of 16:1, it is apparent that P is potentially the most limiting nutrient in the zones of Northwestern waters (NM), Western Buffer (WM), Victoria Harbor (VM), Southern Water (SM) and Mirs Bay (MM) during summer (June-August). Note that the term, ‘potentially’ the most limiting nutrient, means that a particular nutrient will become limiting

when/if it is used up. In Victoria Harbor, nutrients rarely become limiting to phytoplankton growth.

The impact areas for HATS are the Northwest Water Control Zone, the Lamma Channel including the Western Buffer Water Control Zone, the Southern Water Control Zone and the Victoria Harbour Water Control Zone. These zones are heavily influenced by the Pearl River discharge. These influences occur mainly in the wet season (April-September), and include a decrease in salinity at the surface, water column stratification, high nitrogen vs low phosphorus and hence high N:P ratios ($>$ Redfield ratio 16:1). In the Northwest WCZ, Lamma Channel and Victoria Harbor, high algal biomass occurs in summer, but nutrients are rarely depleted, indicating that nutrients are not limiting in these waters. Lower layer waters with low dissolved oxygen waters only occur where there is a deep water column. In the Southern waters, there appears to be a region of maximum phytoplankton biomass (Yin et al., 2004b), which moves from west to east during June-July as the Pearl River discharge increases (Yin et al., 2001). This is the region where P was found to limit phytoplankton biomass production (Yin et al. 2001, Yin et al., 2008). In the maximum biomass region, there is often excess N. Further investigation showed that P in the Pearl River estuary is too low to allow phytoplankton to utilize all of the ambient N and hence, low P results in excess N in the southern waters in summer (Yin et al., 2004c). This explains why the EPD 10 year data set shows high N:P ratios in southern waters in summer (Figure 4). The extent of excess N can be further increased across the entire southern waters of Hong Kong when there is a heavy rainfall event (Yin et al., 2000). Given the high concentrations of N, one would expect eutrophication to be worse than it is at present. Indeed, potential P limitation plays a role in preventing high phytoplankton biomass accumulations, and consequently preventing the

formation of seasonal hypoxia which could develop if the high N were to be transformed into high algal biomass, which would sink and be decomposed.

P limitation may play an important role in controlling eutrophication in some areas of the Hong Kong waters. The present N concentrations in the Pearl River are comparable to those of the Mississippi River (60 to 120 μM , Dortch and Whittedge, 1992; Rabalais et al., 1996) and to Chesapeake Bay, where NO_3 in the freshwater region ranged between 70 and 120 μM (Fisher et al., 1988). However, severe large scale eutrophication effects like the “dead water zone” in the Gulf of Mexico due to the high nutrient loading from the Mississippi River (Rabalais et al., 1994; Malakoff, 1998) have not been reported for the Pearl River estuary. In contrast to the Mississippi River and Gulf of Mexico, where the phosphorus concentration is high (3 to 5 μM , Dortch et al., 1992), phosphorus is low in the Pearl River estuary and the coastal plume (Yin et al., 2000; 2001). The phosphorus concentration in the South China Sea is also low ($<0.5 \mu\text{M}$, SCSIO, 1985). Dissolved PO_4 in 1980 in the Pearl River estuary (SCSIO, 1985) was generally $<1 \mu\text{M}$ in summer, which is similar to present concentrations, suggesting that PO_4 enrichment has not occurred in the Pearl River estuary during the last two decades. Therefore, low P could be a factor limiting a further increase in eutrophication in the Pearl River estuarine and coastal ecosystem. The fact that chl *a* values from 1991 to 2000 in the estuarine-influenced waters (NM, WM, VM and SM) were relatively low (usually $<5 \mu\text{g l}^{-1}$) despite very high N concentrations, supports this notion.

5. Conclusions

The most important objective of HATS is to improve water quality and to reduce environmental impacts in the HATS influenced water control zones in Hong Kong waters.

The major impacts of concern in the HATS related waters are red tides or excessive algal blooms and subsequent low dissolved oxygen in bottom waters.

During the dry season, nutrients in the HATS water control zones (Victoria Harbor, Western Buffer, Northwest, Lamma Channel and Southern waters) are not a concern for water quality related impacts for the following reasons: 1) offshore waters dominate the Hong Kong water control zones; 2) all nutrients are low in the offshore waters; and 3) physical processes (horizontal dilution and vertical mixing due to wind) generally control algal bloom processes during this period.

During the wet season, nitrogen is high and phosphorus is relatively low in waters which are estuarine-influenced by the Pearl River. As the river is rich in nitrogen, P becomes potentially the most limiting nutrient and hence it controls the amount of phytoplankton biomass in these estuarine-influenced waters. The estuarine-influenced waters cover the HATS water control zones, particularly in June, July and August. Therefore, our assessment is that under present conditions, removal of nitrogen from sewage effluent will not likely reduce algal blooms and alleviate low dissolved oxygen in bottom waters during the wet season.

Red tides (mainly dinoflagellates such as *Noctiluca*) in Hong Kong occur more frequently in the northeast semi-enclosed waters beyond the HATS region than in the estuarine-influenced waters and more frequently during spring than summer. Since the low ambient nutrients can not produce the high algal biomass observed in the harmful algal blooms, the formation of most such blooms is likely due to factors such as aggregation other than nutrients. Our assessment is that the best and most economical strategy to reduce nutrient-driven algal

blooms in the HATS region initially is to control P, especially during the more critical summer period when the algal biomass is the highest.

Based on the 10 year data set collected by EPD's routine monitoring program, data from Yin et al. (2000; 2001) and data from the HATS-Environmental and Engineering Study (EEFS) field survey, it is clear that where ever there is an estuarine influence, the situation of high nitrogen and relatively low phosphorus, i.e. high N:P ratios normally dominate. This fact is important in determining the sewage treatment strategy. When ambient waters have excess N, adding more N from sewage effluent would not likely increase the chance of impacts in southern and western Hong Kong waters. It is P that determines the environmental capacity in summer and therefore, removal of P should be considered. There are several reasons to consider removing P. 1) High N:P ratios indicate potential P limitation in the estuarine influenced waters. 2) Ambient P concentrations are generally low and can not produce high phytoplankton biomass comparable to that of red tides since many red tides are likely due to aggregation mechanisms. 3) P needs to be controlled in order not to cause Si limitation since P addition may cause Si limitation due to the Si requirement by fast growing diatoms and that can promote dinoflagellate dominance, particularly during times of low Si when there is less estuarine influence (e.g., low river discharge or strong east winds). 4) The total P in CEPT sewage effluent from the Stonecutters Island Sewage Treatment Works (SCISTW) discharged into ambient waters is reduced compared to the pre- SCISTW operation before November 2001. However, a single outfall of sewage effluent may cause some high P concentrations in the Western Buffer Zone, and parts of Northwest WCZ and Lamma Channel when compared with P in these waters from the outflow of Victoria Harbour (if Victoria Harbour is treated like a big outfall). 5) While the fate of excess N in the offshore waters is unknown, controlling P would help slow utilization of excess N and hence, the area

of dispersion of excess N would be larger than if P is not controlled. When excess N is used up over a larger area, the effect of excess N on phytoplankton biomass and subsequent DO consumption will be diluted compared with that if excess N is used up within a smaller area.

However, as this conclusion is reached with respect to the present condition of the Pearl River, it may be prudent to retain flexibility such that treatment levels can be adjusted to accommodate future changes in the estuarine condition, in particular possible changes in the nutrient loads entering the Pearl River that may cause the N:P ratio to drop.

Since there has been very little comprehensive scientific research on eutrophication in Hong Kong waters over the long term, and present modeling technique has its limitations due to the application of average conditions as the model forcing functions, there will be some uncertainty in our assessment. The uncertainties include the prediction of episodic events of hypoxia during low periods of winds and/or high rainfall in summer, red tides/HABs related to wind-induced aggregations, or climatic-induced large scale changes (e.g., El Niño) which may exacerbate local impacts.

Acknowledgements

This study is part of RGC Projects: HKUST6478/05M and NSFC40676074. The results, findings and views have been used in the HATS-Environmental and Engineering Feasibility Study (EEFS: CE42/2001).

References

- Chau, Y.K., Wong, C.S., 1960. Oceanographic investigations in the northern region of the South China Sea off Hong Kong. *Hong Kong University Fisheries Journal* 3: 1-25.
- Dortch, Q., Whittedge, T.E., 1992. Does nitrogen or silicon limit phytoplankton production in the Mississippi River plume and nearby regions? *Continental Shelf Research* 12: 1293-1309.
- Fisher, T.R., Harding Jr., L.W., Stanley, D.W. and Ward, L.G., 1988, Phytoplankton, nutrients and turbidity in the Chesapeake, Delaware and Hudson estuaries. *Estuarine, Coastal and Shelf Science*, 27: 61-93.
- Harrison P.J., Hu, M.H., Yang, Y.P., Lu, X., 1990. Phosphate limitation in estuarine and coastal waters of China. *Journal of Experimental Marine Biology and Ecology* 140: 79-87.
- Hecky, R.E., Kilham, P., 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: a review of recent evidence on the effects of enrichment. *Limnology and Oceanography* 33: 786-822.
- I.R.P. (International Review Panel), 2000. Review of Strategic Sewage Disposal Scheme. Hong Kong Government. <http://www.info.gov.hk/ssds.review>.
- Malakoff, D., 1998. Death by suffocation in the Gulf of Mexico. *Science* 281: 190 – 192.
- Mao, Q., P. Shi, K. Yin, Gan J., Y. Qi., 2004. Tides and tidal currents in the Pearl River estuary. *Continental Shelf Research*.
- Morton, B., Wu, S.S., 1975. The hydrology of the coastal waters of Hong Kong. *Environment Research* 10: 319-347.

- N.R.C. (National Research Council), 2000. Clean coastal waters: understanding and reducing the effects of nutrient pollution. National Academy Press, Washington, DC. USA, 405 p.
- Rabalais, N.W., Wiseman, Jr W.J., Turner, W.J., 1994. Comparison of continuous records of near-bottom dissolved oxygen from the hypoxia zone of Louisiana. *Estuaries* 17: 850-861.
- S.C.S.I.O. (South China Sea Institute of Oceanology), 1985. Report of multidisciplinary investigation of the South China Sea II. Academic Press, Beijing, 432 p.
- Thompson, G.B, Ho. J. 1981. Some effects of sewage discharge upon phytoplankton in Hong Kong. *Marine Pollution Bulletin* 12: 168-173.
- Watts, J.C.D., 1971a. The hydrology of the continental shelf area south of Hong Kong. 1. Oceanographic observation for the year 1969. *Hong Kong Fisheries Bulletin* 2: 51-57.
- Watts, J.C.D., 1971b. A general review of the oceanography of the northern sector of the South China Sea. *Hong Kong Fisheries Bulletin* 2, 41-50.
- Watts, J.C.D., 1973. Further observation on the hydrology of the Hong Kong territorial waters. *Hong Kong Fisheries Bulletin* 3: 9-35.
- Williamson, G.R., 1970. The hydrography and weather of the Hong Kong fishing grounds. *Hong Kong Fisheries Bulletin* 1: 43-49.
- Yin, K., Harrison, P.J., Chen, J., Huang, W., Qian, P.Y., 1999. Red tides during spring 1998 in Hong Kong: is El Niño responsible? *Marine Ecology Progress Series* 187: 289-294.
- Yin, K., Qian, P.-Y., Chen, J.C., Hsieh, D.P.H., Harrison, P.J., 2000. Dynamics of nutrients and phytoplankton biomass in the Pearl River estuary and adjacent waters of Hong Kong during summer: preliminary evidence for phosphorus and silicon limitation. *Marine Ecology Progress Series* 194: 295-305.

- Yin, K., Qian, P.Y., Wu, M.C.S., Chen, J.C., Huang, L.M., Song, X.Y., Jian, W.J., 2001. Shift from P to N limitation of phytoplankton biomass across the Pearl River estuarine Plume during summer. *Marine Ecology Progress Series* 221: 17-28.
- Yin, K., 2002. Monsoonal influence on seasonal variations in nutrients and phytoplankton biomass in coastal waters of Hong Kong in the vicinity of the Pearl River estuary. *Marine Ecology Progress Series* 245: 111-122.
- Yin, K., 2003. Influence of monsoons and oceanographic processes on red tides in Hong Kong waters. *Marine Ecology Progress Series* 262: 27-41.
- Yin, K., Lin, Z., Ke, Z., 2004a. Temporal and spatial distribution of low oxygen waters in the Pearl River discharge and adjacent coastal waters. *Continental Shelf Research*: 1935-1948.
- Yin, K., Qian, P.-Y., Chen, J.F., Huang, L., Zhang, J., Wu, M.C.S., 2004b. Effect of wind events on phytoplankton blooms in the Pearl River estuary during Summer. *Continental Shelf Research*: 1909-1923.
- Yin, K., Song, X., Sun, J., Wu, M., 2004c. Potential P limitation leads to excess N in the Pearl River estuarine coastal plume. *Continental Shelf Research* 24(16): 1895-1907.
- Yin, K., and P.J. Harrison. 2008. Nitrogen Enrichment in Subtropical Pearl River Estuarine Coastal Waters. *Continental Shelf Research* 28(12): 1435-1442.
- Zhao, H., 1990. Evolution of the Pearl River estuary. Ocean Press, Beijing, China, 358 p (in Chinese).

Note: NM-Northwest, WM-Western Buffer, VM-Victoria Harbour, SM-Southern, PM-Port Shelter, MM-Mirs Bay,
and TM-Tolo Harbour

Figure 1 Map Showing Hong Kong's Water Control Zones and EPD's Regular Water Quality Monitoring Stations

Note: Data collected for each month (e.g. April) at a station (e.g. TM6) were averaged from 1991 to 2000 to obtain the April average for TM6. Then the monthly averages from all the stations (TM1 to TM8) in Tolo Harbour were averaged to obtain a monthly (April) average for the Tolo Harbour water control zone

Figure 2 Monthly Averages of Salinity and Temperature in 7 Water Control Zones

Figure 3 Monthly Averages of Chl a and Dissolved Oxygen (DO) in the 7 Water Control Zones (as in Figure 1) During 10 years (1991-2000)

Figure 4 Monthly Averages of Dissolved Inorganic Nitrogen (TIN=NO₃ +NO₂ +NH₄) and Phosphate (SRP) in the 7 Water Control Zones (as in Figure 1) During 10 years (1991-2000)

Figure 5 Monthly Averages of Molar N:P Ratios (TIN/PO₄) in the 7 Water Control zones (as in Figure 1) during 10 years (1991-2000)