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Variations in nitrate isotope composition of wastewater effluents by treatment type in Hong Kong

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ABSTRACT

Stable isotopes ($\delta^{15}N$, $\delta^{18}O$) can serve as tracers for sources of nitrogen in the receiving environment. Hong Kong discharges ~3×10^6 m^3 d^{-1} of treated wastewater into the ocean from 68 facilities implementing preliminary to tertiary treatment. We sampled treated sewage from 18 plants across 5 treatment types and examined receiving seawater from northeast Hong Kong. We analyzed nitrate and nitrite ($NO_3^- + NO_2^-$, hereafter NO_x) ammonium (NH_4^+), phosphate (PO_4^+) concentrations and $\delta^{15}N_{NOx}$, $\delta^{18}O_{NOx}$. Sewage effluents contained high mean nutrient concentrations ($NO_3^- = 260$ μmol L^{-1}, $NH_4^+ = 1400$ μmol L^{-1}, $PO_4^+ = 50$ μmol L^{-1}) with some indication of nitrogen removal in advanced treatment types. Mean $\delta^{15}N_{NOx}$ of sewage effluents from all plants and treatment types (12‰) was higher than natural sources and varied spatially and seasonally. There was no overall effect of sewage treatment type on $\delta^{15}N_{NOx}$. A mass balance model indicated that sewage (>68%) remains a dominant source of nitrate pollution in seawater in Tolo Harbor.

1. Introduction

Sewage is one of the largest contributors of anthropogenic pollution and sewage treatment plants are important for modulating nutrient concentrations in receiving marine and estuarine waters. Elevated nutrients (nitrogen and phosphorous) from wastewater induce eutrophication, a condition that alters the coastal ocean balance by changing food web structure, increasing primary production and the prevalence and severity of disease (Howarth et al., 2000; Baker et al., 2007; Wear and Vega Thurber, 2015). Numerous studies have documented the indirect effects of sewage pollution on the growth and survival of biologically and structurally complex ecosystems such as coral reefs, with consistent negative impacts on calcification, community structure and biodiversity (Walker and Ormond, 1982; Rodriguez, 1981; Baker et al., 2010; Smith et al., 1981; Baker et al., 2013).

Over the last fifty years, several studies have reported a concomitant decline in water quality and macrofauna, coupled with the frequent incidence of red tides and elevated levels of heavy metals, antibiotics and faecal bacteria in Hong Kong's marine environment (Morton, 1988; Cope and Morton, 1988; Scott, 1990; Ng and Morton, 2003; Fabricus and McCorry, 2006; Connell et al., 1998; Yeung, 2000; Yin and Harrison, 2007). A fine example of this is Tolo Harbor in northeast Hong Kong (Fig. 1; Yim et al., 1982; Scott and Cope, 1982). Hard coral species richness at the mouth of the Tolo Channel decreased by 27% from 1986 to 2000 (McCorry and Blackmore, 1998). The progressive decline of water quality and marine life in the harbor owing to residential development has led scientists to refer to it as "Hong Kong's first marine disaster" (Morton, 1988). As a measure to improve water quality, the Hong Kong Government (HKSAR) re-routed all wastewater discharge outfalls from Tolo Harbor to Victoria Harbor in 1996. However, a recent study by Luo et al. (2014) confirmed that severe nutrient pollution persists in Tolo Harbor despite the removal of point-source inputs of wastewater in the region. Therefore, the source of this pollution is unclear and warrants further investigation. Another example is the historical and chronic discharges of sewage effluents into Hong Kong's urbanized Victoria Harbor at the rate of over 2 million m^3 of sewage per day. Close to 75% of this heavily polluted water was discharged without any treatment until 2001 when the Harbor Area Treatment Scheme (HATS) came into effect. Despite these efforts, the effects of eutrophication are ever-present (Xu et al., 2011, 2014; HKSAR DSD, 2014a), signaling that stormwater, untreated wastewater from septic tanks and ferries, improper or damaged sewerage connections, and other non-point sources such as surface run-off are inhibiting mitigation efforts. To date, the sources of nutrients that contribute to persistent eutrophic conditions remain unknown.

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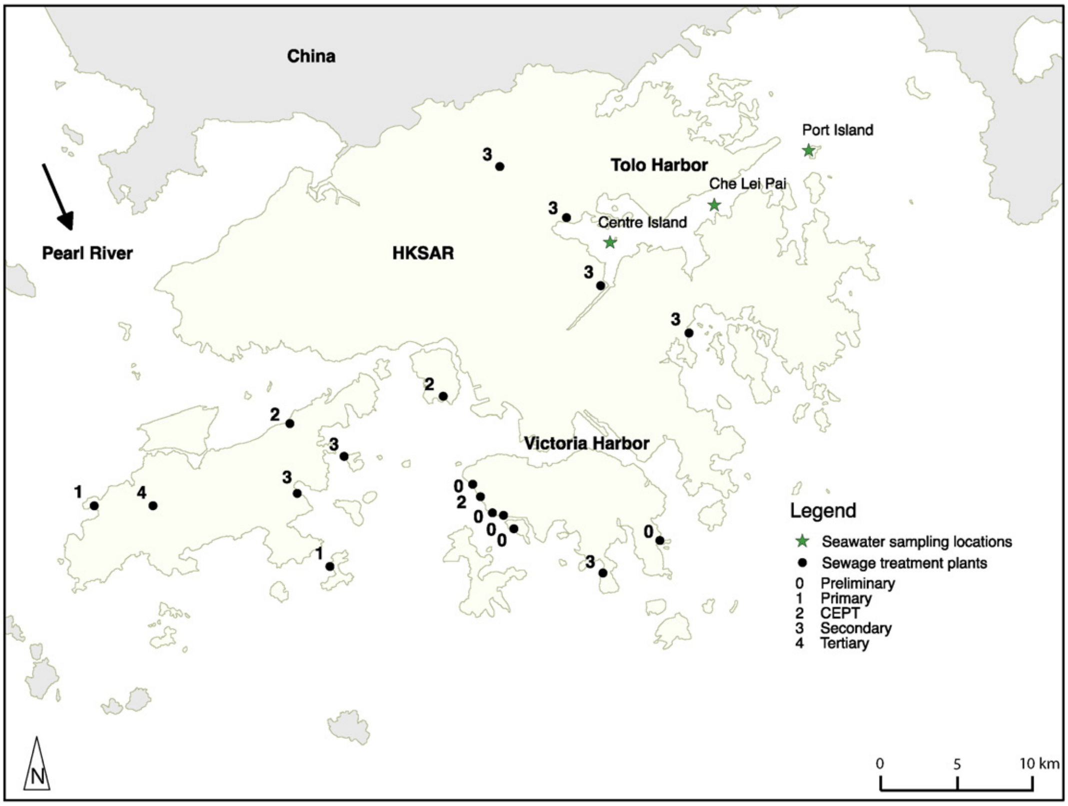

Fig. 1. Study site – HKSAR and sampling locations. 18 sewage treatment plants and 3 seawater sampling locations were selected for this study. Sewage treatment plants were classified into 5 treatment types according to the process employed.

Today, there is a well-defined gradient in water quality from the west to the east of Hong Kong, particularly obvious for total inorganic nitrogen (TIN), ammonium (NH_4^+) and nitrate (NO_3^-) owing to the influence of the Pearl River estuary carrying wastewater, agricultural inputs, and industrial pollutants from the heavily developed Guangdong Province. Urbanized population centers correspond with high TIN loadings. The HKSAR has several management practices involving water quality, including set water quality objectives, beach and open-water quality monitoring programs, long-term phytoplankton monitoring, zoned mariculture areas, three marine parks, one marine reserve, and intensive investment in wastewater infrastructure, including HATS (HK EPD, 2014). However, these management efforts rely on monitoring the concentrations of nutrients in seawater and wastewater, respectively, but cannot differentiate natural sources of nitrogen (*e.g.* fixation and mineralization) from anthropogenic inputs (*e.g.* fertilizers and sewage) originating from the Pearl River Delta region. To our knowledge, there has been no study that has successfully identified the sources of the near-shore water quality problems in Hong Kong.

Stable isotope analysis of nitrogen ($\delta^{15}N$) fills this gap, serving as a tracer for sources and sinks of nitrogen in the environment (Heaton, 1986; Kendall et al., 2010) Although nitrogen is rapidly diluted, diffused and transported by ocean currents, source $\delta^{15}N$ values are preserved in primary producers which can define an isotopic baseline for the marine food web. Moreover, $\delta^{15}N$ measurements are especially useful in pollution monitoring studies because each source of nitrogen has a unique $\delta^{15}N$ composition associated with it. For example, sewage has very different $\delta^{15}N$ signatures relative to natural sources. $\delta^{15}N$ of raw sewage is usually ~6‰ (Kendall et al., 2007), while that of treated sewage is estimated to be between 10 and 20‰ (McClelland and Valiela, 1998). Such enrichment in $\delta^{15}N$ values arises from microbially mediated nitrification and denitrification reactions with fractionation factors (ε) of 10‰ to 40‰ that are dependent on the type of wastewater treatment employed (Mariotti et al., 1984; Risk et al., 2009). Other examples of nitrogen sources that have unique $\delta^{15}N$ values are synthetic fertilizer (~3‰), combustion (~1‰), and precipitation (~−7‰; Table 1; Fry, 2006).

Several studies have successfully used stable isotopes to characterize nitrogen pollution from anthropogenic inputs in sensitive coastal marine habitats around the world (Risk, 2014). For example, Magni et al. (2013) studied $\delta^{15}N$ and $\delta^{13}C$ variations in two dominant bivalve species along the European coast, demonstrating their effectiveness as bio-indicators of sewage pollution. In the tropics, studies of corals and gorgonians have shown that benthic invertebrates take up sewage-derived nitrogen (Baker et al., 2010, 2013). Although the majority of studies focus on biological integrators, only a few have measured the sources of pollution directly, such as the $\delta^{15}N$ of dissolved inorganic nitrogen (DIN) in wastewater effluents. Moreover, there is relatively little information available on the influence of sewage treatment type on $\delta^{15}N$ values of wastewater effluents (Costanzo et al., 2005; Sebilo et al., 2006; Gaston et al., 2004; Table 2). Of the studies that exist, many focus on effluent from a single specific treatment type – preliminary, primary, secondary or tertiary. To our knowledge, there has been no study that provides $\delta^{15}N$ values for wastewater effluent from five different treatment methodologies (CEPT-Chemically Enhanced Primary Treatment, preliminary, primary, secondary, tertiary). Moreover, there has been no study done yet on nitrogen source

Table 1
$\delta^{15}N$ values of different sources of nitrogen (Fry, 2006; Kendall et al., 2007).

Sources	$\delta^{15}N$ (‰)
N fixation	−2 to +2
Fertilizer	−7 to +4
Atmospheric deposition	−15 to +3
Marine nitrate	+4 to +6
Sewage	+6 to +9