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Trophic state, natural organic matter content, and disinfection by-product formation potential of six drinking water reservoirs in the Pearl River Delta, China

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Summary This study examined spatial and seasonal variation of nutrients, algal biomass, and natural organic matter (NOM) in six subtropical drinking water reservoirs in the Pearl River Delta region, China, during the period from 2004 to 2006. We also tested the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) as disinfection by-products (DBPs) via chlorination of the water samples from these reservoirs. This study showed that these reservoirs were mesotrophic with the average chlorophyll a (Chl a) levels ranging from 2.31 to 7.79 $\mu g\ l^{-1}$. The average dissolved organic carbon (DOC) in the six reservoirs was 2.70 $mg\ l^{-1}$, and the degree of aromaticity of NOM indicated by UV_{254} (absorbance at 254 nm) was 0.048 cm^{-1}. Total phosphorous (TP) was significantly correlated with chlorophyll a, as well as DOC and UV_{254}. It suggested that the major component of NOM, with a specific UV_{254} value (SUV_{254}) of 1.78 $l\ mg^{-1}\ m^{-1}$, was algal-derived organic matter. Existing models from other studies could be used to predict THM yield from NOM level in the present study, but the relationship between HAAs and NOM suggested that aromatic portion of the NOM in the investigated reservoirs had a greater potential to produce HAAs.

Introduction

Natural organic matter (NOM) in lakes, reservoirs and streams is derived from various natural organic materials as a result of complex biotic and abiotic processes (Wetzel,

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2001). Aquatic NOM can be derived from soils and plants in the terrestrial watershed (allochthonous NOM) or from the algal and bacterial growth in the water (autochthonous NOM) (Tate and Meyer, 1983; Baron et al., 1991; Aiken and Cotsaris, 1995). Frequently, NOM is a heterogeneous mixture of various organic materials, including humic substances (humic and fulvic acids) and non-humic matter (mainly proteins, amino acids, carbohydrates, etc.) (Nikolaou and Lekkas, 2001; Wetzel, 2001). Most NOM is in dissolved form, which is commonly indicated by the levels of DOC (dissolved organic carbon) and UV_{254} (the degree of aromaticity indicated by UV absorbance at 254 nm) (Nikolaou and Lekkas, 2001). Specific UV_{254} (SUV_{254}, $l\ mg^{-1}\ m^{-1}$), defined as UV_{254} times 100 divided by DOC, was a good parameter to indicate specific DOC aromaticity (Reckhow et al., 1990; Liang and Singer, 2003).

Since 1974, when the occurrence of chloroform in chlorinated drinking water was reported (Rook, 1974), NOM has become the focus of drinking water industries worldwide because it is regarded as the precursor of disinfection byproducts (DBPs) such as chloroform. As the primary water quality concern is microbiological quality due to its direct link to enteric diseases (WHO, 2006), chlorination has to be applied during the drinking water treatment as a major chemical disinfection measure throughout the world, including Hong Kong and mainland China. Due to various human health risks from DBPs, regulations and guidelines have also been set up based on the levels of DBPs in drinking water (USEPA, 1998, 2006; WHO, 2006). Generally, balancing microbial and chemical risks (from chlorination) is crucial in ensuring safe drinking water.

The chemical basis for DBPs formation from the chlorination of NOM remains unclear. Earlier studies suggested that DBPs are mainly formed by chlorination of activated aromatic rings, which are mostly contained in humic substances (Reckhow et al., 1990; Nikolaou and Lekkas, 2001). On the other hand, the aliphatic fraction of NOM, which mostly consists of algal-derived material, may also contribute substantially to the yields of DBPs, but algal cells as well as the algal extracellular organic matter showed a less or similar DBP yield per unit concentration of organic carbon as compared with humic substances (Graham et al., 1998; Plummer and Edzwald, 2001). In this regard, the major concern lies in the fact that algal-derived organic matter is less easily removed by coagulation and filtration and they can penetrate filters and lead to DBP formation upon pre- and post-chlorination (Widrig et al., 1996; Henderson et al., 2005). Therefore, establishing the relationships among trophic status, NOM properties, and DBP formation is essential for managing the drinking water sources.

However, there is a major data gap regarding the characteristics of NOM in source water and its associations with DBPs in Hong Kong and the adjacent area. Previous studies showed that the trophic state of the downstream area of the Dongjiang River, which provides 70–80% of Hong Kong's drinking water supply, is eutrophic (Han et al., 2003), and THM levels in tap water are rather high (>100 $\mu g\ l^{-1}$) within the districts of Yuen Long, Tsuen Wan, North, and Tai Po in Hong Kong (Yu and Cheng, 1999). This study investigated spatial and seasonal changes of nutrients, algal biomass, DOC, and UV_{254} in local drinking water reservoirs. Concentrations of DBPs including trihalomethanes (THMs) and haloacetic acids (HAAs) were also measured after chlorination of the water samples. These data allowed us to (1) investigate factors controlling the distribution pattern of nutrients and NOM in the reservoirs; (2) examine sources and compositions of NOM in the reservoirs; and (3) study the relationships between NOM, in terms of quality and quantity, and DBP formation after chlorination. This is the first study simultaneously comparing trophic status, NOM properties, and DBP formation in this region, and the results should provide important information on Hong Kong and the Pearl River Delta region, China for drinking water source management.

Materials and methods

Field sampling

The sampling sites included six reservoirs: Xingfengjiang Reservoir (XFJR) at the upstream of the Dongjiang River, in Heyuan city, China, with little human activity. Shenzhen Reservoir (SZR), at the downstream of the Dongjiang River, in Shenzhen city, China, with a great deal of local human activity; Tai Lam Chung Reservoir (TLCR), Plover Cove Reservoir (PCR), and High Island Reservoir (HIR) in Hong Kong, which receive and store water from the Dongjiang River (SZR); and Shek Pik Reservoir (SPR) in Hong Kong, which only collects rainwater (Fig. 1).

Ten liters of water were collected at each site from approximately 0.1–0.5 m below the water surface with an open-mouthed bottle. There were 2–4 sampling points at each reservoir, and all samples were transported to the laboratory in coolers on ice within the same day and stored at 4 °C before further analysis. The detailed sampling information is shown in Table 1.

Analysis of water quality

The following parameters were characterized using the Standard Methods (APHA, 1998): pH (using a pH meter, Orion, model 420A), total nitrogen (TN, $\mu g\ l^{-1}$) (by the $K_2S_2O_8$ digestion method), total phosphorous (TP, $\mu g\ l^{-1}$) (by the molybdate-blue method), dissolved organic carbon (DOC, $mg\ l^{-1}$) (using a TOC analyzer, Shimadzu TOC 5000), and UV absorbance at 254 nm (UV_{254}, cm^{-1}) (using a UV–visible spectrophotometer, Shimadzu UV-1601). Unfiltered whole water samples were used for the determination of TN and TP, and the filtered water samples (using a glass fiber filter GC-50, pore size = 1.2 μm) were used for DOC, UV_{254} and SUV_{254} measurements.

Water samples for Chl a ($\mu g\ l^{-1}$) measurement were stored in 1 l brown bottles and preserved by adding 3-5 ml of 1% saturated magnesium carbonate. The water samples were filtered through glass fiber filters (CG-50). Twelve milliliters of 95% ethanol was then added to the filtrate for Chl a extraction; the filtrate was allowed to stand for 24 h in a refrigerator at 4 °C and then centrifuged at 3000 rpm for 12 min. Chl a concentration was examined by using a UV–visible spectrophotometer (Shimadzu UV-1601) according to the following equation (Wintermans and De Mots, 1965):

$$\mathrm{Chl\ a} = [13.7(A_{665}\text{–}A_{750}) - 5.76(A_{649}\text{–}A_{750})] \times E/F \times l,$$