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# Characterization of precursors to trihalomethanes formation in Bangkok source water

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#### Abstract

Resin adsorption techniques using three types of resin (DAX-8, AG-MP-50, and WA-10) were employed to characterize the raw water (RW) from the major 3 million m<sup>3</sup>/day (793 million gal/day) drinking water treatment plant in Bangkok, Thailand. The dissolved organic carbon (DOC) mass distribution sequences of the six organic fractions in raw water, from high to low, were hydrophilic neutral (HPIN), hydrophobic acid (HPOA), hydrophobic acid (HPOA), hydrophobic neutral (HPON), hydrophilic base (HPIB), and hydrophobic base (HPOB). HPIN and HPOA were the two main precursors for trihalomethanes formation (THMFP) in this water source following chlorination. The chlorination of HPON and HPIN fractions only led to the formation of mostly chloroform, while other organic fractions formed both chloroform and bromodichloromethane. The linear dependency between each organic fraction concentration and THMFP indicated that the reactions of each organic fraction with chlorine were first-order.

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### 1. Introduction

Often, surface water is reported to contain organic matter derived both from natural degradation of some organic substances within the ecological systems and from human activities. Organic contaminants in surface water are different from location to location due to the differences in the ecosystem and the activities of human beings in each specific location. This organic matter cannot easily be captured using normal water treatment techniques such as coagulation, and therefore it can enter the municipal water treatment system and then distributed through the water supply network. Moreover, during the disinfection process with chlorine, which is a common treatment technique in municipal water supply facilities, the organic matter could potentially be converted to potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs). THMs are identified as potential adverse health agents for which U.S. Environmental Protection Agency (USEPA) proposed the drinking water standard under the disinfectants/disinfection by-products (D/DBP) rule (with a maximun contaminant level of 0.04 mg/L). THMs are usually measured in terms of the sum of four methane

*Abbreviations:* RW, raw water; NOM, natural organic matter; DBPs, disinfection by-products; THMs, trihalomethanes; HAAs, haloacetic acids; HAN, haloacetronitrile; THMFP, trihalomethane formation potential; DOC, dissolved organic carbon; TOC, total organic carbon; TOXFP, total organo-halide formation potential; HPIA, hydrophilic acid; HPIB, hydrophilic base; HPIN, hydrophilic neutral; HPOA, hydrophobic acid; HPOB, hydrophobic base; HPON, hydrophobic neutral

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derivatives, i.e. chloroform, bromodichloromethane, dibromochloromethane, and bromoform concentrations. The general reaction of organic matter with chlorine can be expressed as follows [1]:

organic matter + free chlorine

$$\rightarrow \text{THMs} + \text{HAAs} + \text{HANs} + \text{cyanogen-halides}$$
$$+ \text{other DBPs} \tag{1}$$

To better understand the formation kinetics of THMs, one can characterize the organic matter. The differentiation between each organic species might not be practical and therefore several past researches focused on grouping the organic matters into several common groups according to the physical/chemical properties of organic species, e.g. size, polarity, molecular weight, etc. Resin adsorption has lately been successfully employed as a successful fractionation technique for organic matter. Generally, DAX-8 resin was used to fractionate dissolved organic matter (DOM) into hydrophobic and hydrophilic fractions [2–5]. With a proper arrangement of a few adsorption resins, Leenheer [6] could separate DOMs into six organic fractions, i.e. hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), and hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). This technique was then employed for the characterization of other water sources [7–9]. The fractionation allowed a thorough investigation of the formation of THMs from the organic matters in water sources. For instance, hydrophobic fraction was often found to have higher THMs reactivity than the hydrophilic [3]. Korshin et al. [7] tested total organo-halide formation potential (TOXFP) of water samples. The hydrophobic acid fraction exhibited the highest level of TOXFP, and TOXFP decreased in the order from HPOA > HPIA > HPIN. Marhaba and Van [8] reported that hydrophobic base fraction was the most reactive in the formation of THMs followed by the hydrophilic acid fraction. Chang et al. [5] demonstrated that 76% of dissolved organic carbon (DOC) was the hydrophilic and hydrophobic acid fractions and it was the hydrophobic acid fraction that exhibited the greatest ability in the formation of THMs.

Lately, Marhaba et al. [10] modified the technique proposed by Leenheer [6] by replacing one of the resins to reduce the contamination from the back elution of the organics. This allowed a more reliable result of the fractionation particularly for the water source that contained low levels of total organic carbon (TOC), less than 5 mg/L.

The main purpose of this paper was to investigate the mass distribution of dissolved organic fraction and their relationship with THMFP using the adsorption technique proposed by Marhaba et al. [10]. The water samples were taken from the Bangkhen Water Treatment Plant (Bangkok, Thailand), which takes raw water (RW) from the Chao Phraya River, the main river in Thailand. This plant is the largest water supply facility (from the total of three water supply facilities) in Bangkok, and produces about 3 million m<sup>3</sup>/day (793) million gal/day). The characterization of this water source will be useful in the future management of this water treatment facility which services the millions of people living in Bangkok.

#### 2. Methodology

Experimental work herein follows the steps specified in Fig. 1 and is detailed as follows. Note that: Milli-Q water (ELGA, Ultra Analytical) was used for all dilutions, samples and chemicals preparation, and final glassware cleansing in this work.

#### 2.1. Sample collection and preservation

The collection of raw water sample was only performed once, with 400 L of sample being collected on 5 August 2003. This water sample was used for all experiments in this work.

Samples were prepared by filtering through a 0.45  $\mu$ m membrane and stored in a cold room with a temperature controlled at 4 °C before and after fractionation.

## 2.2. Fractionation

The resin adsorption procedure as proposed by Marhaba et al. [10] was used to classify DOC into six fractions; HPOA, HPOB, HPON, and HPIA, HPIB, and HPIN by using three types of resin (DAX-8, nonionic resin (Supelco), AG-MP-50, cationic resin (Bio-Rad), and WA-10, weak anionic resin (Supelco)). Only one sample was obtained for each organic fraction, and each sample was then diluted to four concentration levels for the THMFP tests. The fractionation follows the steps below (see also Fig. 2):

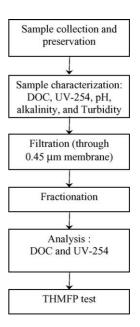


Fig. 1. Experimental procedure.

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