INVESTIGATION ON DISINFECTANT TRICLOSAN IN ENVIRONMENTAL AND WASTE WATERS

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Introduction

The intensive use of chlorinated disinfectants such as triclosan due to the increasing awareness of public and personal hygiene in the post-SARS era has caused growing concerns over environmental contamination in Hong Kong. The chemical can be found as an antiseptic component in medical products such as hand disinfecting soaps, medical skin creams, dental products and many household cleansers[1]. Also, triclosan is a widely employed antimicrobial that has been found as a contaminant of rivers and lakes[2]. Triclosan is a relatively stable, lipophilic compound. Its environmental occurrence has been reported, and the compound has been detected in coastal water[3]. As a consumer product ingredient, the majority of triclosan may be transported to wastewater sewage treatment plants. Triclosan has been found in sewage sludge, discharge effluent, receiving surface waters and sediments[3]. This compound has also been found at ng/L levels in rivers, lakes and the open sea[4-6].

The toxicity of triclosan on human had been investigated for many years. The adverse effects include mild itching and allergic redness on sensitive skins, so the compound is regarded as a low toxicity chemical[7,8]. Attention has been drawn to its degradation products due to their chemical structural similarity with highly toxic contaminants, such as dioxins. Recent reports indicate that triclosan can undergo photo-degradation converted to dioxins upon the exposure of sunlight. On the other hand, photo transformation was demonstrated to be the main elimination process of triclosan in surface water. Recent studies suggested that triclosan can be undergone cyclization to form 2,8-dichlorodibenzo-p-dioxin (2,8-DCDD) in aqueous solution under UV irradiation[2]. Furthermore, triclosan can easily be chlorinated by sodium hypochlorite solution to produce chlorinated derivatives that can be converted to chlorinated dioxins upon heating and UV irradiation[9]. Thus, it is important to investigate the fate of triclosan in environmental and wastewater waters.

Materials and Methods

Triclosan and $^{13}C_{12}$-labeled internal standard are purchased from Wellington Laboratories (Ontario, Canada). HPLC grade of organic solvents of hexane, ethyl acetate and methanol were obtained from Riedel-de Haen® (Hanover, Germany). Stock solution was prepared by dissolving 1.0 mg of triclosan in 1.0 mL of ethyl acetate. The calibration standard solutions containing the analytes and internal standard are prepared by diluting the stock solution in proportional. Chemicals of anhydrous sodium sulfate and 0.1 % v/v formic acid were used. All standard solutions were kept under 4 ^{o}C in a refrigerator.

Thermo Finnigan Trace GC system interfaced with a Polaris Q ion trap mass spectrometer was used for the quantification of triclosan. DB-5MS (30 m x 0.25 mm x 0.25 μm film thickness) column was used. The GC temperature program was set as follows: initial temperature was 80 ^{o}C and held at 1 min, then increased at 20

°C/min to 280 °C where it was held for 6 min. The transfer line and ion source temperature are 300 °C and 265 °C respectively. The carrier gas was helium at a flow rate of 1 mL/min at constant flow with vacuum compensation. The injected volume was 1 μL in splitless mode. For the ion-trap mass spectrometer, the setting was operated with electron impact ionization (EI) at 70 eV; a solvent delay of 4 min was used. Multiple-reaction-monitoring (MRM) mode was applied for the quantitative analysis.

Water samples were collected from a local river, the Victoria Harbour and a wastewater treatment plant located in Sha Tin, New Territory. 6 samples were collected from each site (n=6). River water was collected in two stations closed to residential and industrial areas. Coastal water samples were collected in the vicinity of a major sewage outfall in Victoria Harbour in March and December 2005.Three stations were chosen in the wastewater treatment plan. The first was the inlet of raw wastewater, the second site was the water after primary treatment, and the third site was the treated effluent emitted to the sea.

Prior to the water sample collection, amber glass bottles were consequently pre-cleaned with detergent water, tap water, distilled water, methanol and distilled water. After the collection, the samples were acidified with concentrated phosphoric acid to pH 2. The bottles were threaded with caps lined with Teflon and placed in an ice-filling cooler. The samples were then immediately delivered to the analytical laboratory and stored at 4 °C in a refrigerator until the sample analysis.

The water samples were undergone vacuum sucking filtration to filter away the grit or small particles. 0.1 % v/v formic acid was added into the sample to increase the recovery. 200 mL water sample was then flowed through a pre-washed C-18 cartridge with a flow rate of approximately 3 mL/min under vacuum. The cartridge was rinsed with 5 mL of 5 % methanol in Milli-Q water to wash the interferences from the column and aspirated for about 15 min to remove water residue. Triclosan was eluted with 3 × 2 mL ethyl acetate at a slow rate of 1 mL/min, and the extracts were dried by adding 0.05 g of anhydrous sodium sulfate, concentrated under a slow stream of gentle stream of nitrogen to dryness in water bath of 40 °C, and reconstituted in 200 μL ethyl acetate contaning 40 ng of internal standard.

Results and Discussion

EI-MS analysis of triclosan showed that the $[M-2Cl]^+$ ion at m/z 218 was the predominant peak. Subsequent MS/MS analysis was conducted by selecting the ion of m/z 218 as precursor ion. The base peak at m/z 155 was then selected as quantitation ion for MRM analysis of triclosan. Calibration curve was obtained by plotting the peak area ratio of the analyte to the internal standard against the concentrations of triclosan. The SPE extraction efficiency with the C-18 cartridge was 85.0 % with RSD 5.5 % (n=6). Method performance was evaluated by analyzing six 200-mL standard water samples spiked with 14 ng, 24 ng and 40 ng triclosan. The relative analytical errors were less than 10% and RSD was less than 13 %. The method detection limit defined when the triclosan signal-to-noise of 3 was 1.2 ng/L when the water sample volume was 200 mL.

The developed method was applied to the analysis of the river, coastal and waste water samples. The analytical results indicated that triclosan presented in environmental water samples ranging from the 25 ng/L to 134 ng/L. Higher levels of triclosan were found in the wastewater samples. Figure 1 demonstrated the determination of triclosan in the coastal water collected from Victoria Harbour. Triclosan was detected at 39 ng/L in the river water closed to residential area, which was higher than that in industrial area (25 ng/L). Possible reason was the

popular use of triclosan in many household commercial products such as antibacterial mouth rinse and hand wash. Higher levels of triclosan at 134 ng/L in the seawater collected in Victoria Harbour in December were detected. The levels of triclosan in the seawater collected from the same area in March, however, were significantly lower with an averaged value of 49 ng/L, probably because of the water dilution during the rainy season in the March.

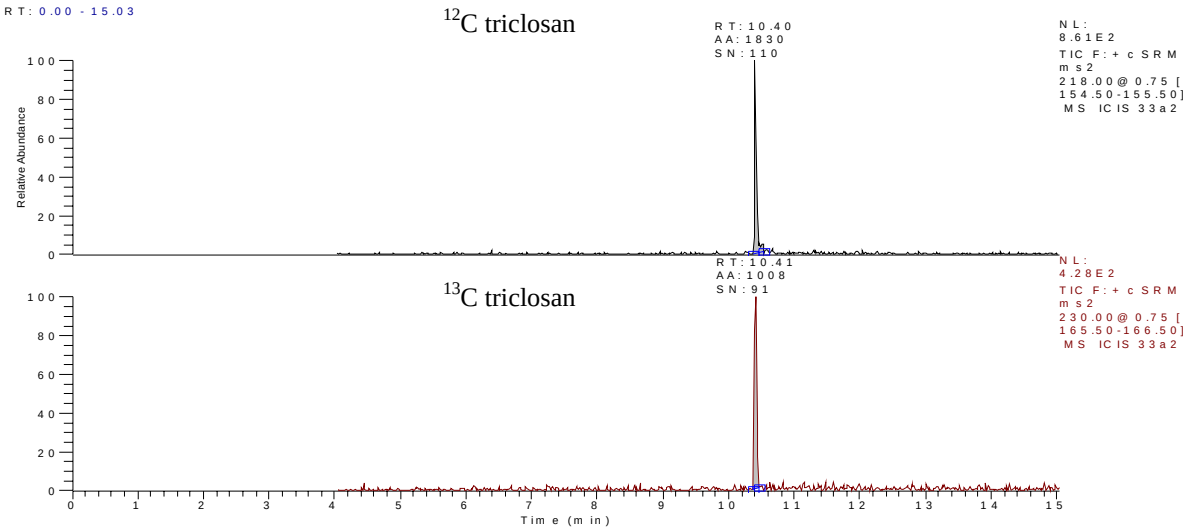

Figure 1. The sample analysis of the coastal water collected from Victoria Harbour in Dec. 2005.

Triclosan was detected at concentrations ranging from 422 ng/L to 491 ng/L in the wastewater influent, from 683 ng/L to 705 ng/L in primary treated water and from 18 ng/L to 25 ng/L in the effluent water. The results suggested that the treatment applied in wastewater treatment plant eliminated triclosan up to 95%. However, it was surprised to observe higher levels of triclosan in the wastewater samples collected after the primary treatment. Further investigations are needed for studying this interesting observation. In the secondary treatment, biodegradable organics and nutrients are removed from the wastewater by biological treatment. Sewage was passed to the aeration tanks for biological treatment. Air is supplied continuously into the aeration tanks for the growth and reproduction of microorganisms, which may decomposes the organic matter in the sewage.

Studies have revealed that triclosan in wastewater and environmental water might be degraded to dioxins when exposed to sunlight. Furthermore, the relatively high concentration of chlorine and peroxide chemicals may lead to and/or speed up the formation of dioxins. Thus, it is of environmental and toxicological importance to investigate whether dioxins, especially those with 2,3,7,8-chlorine substitution, may be formed under environmental conditions of heavy discharge of chlorinated disinfectants into the coastal environment and to study the mechanisms and pathways of their formation.

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