Concentration changes and distribution of triclosan in water from Tone Canal.

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Abstract

Recently, pharmaceuticals and personal care products (PPCPs) have been regarded as environment pollutions, and detected various aquatic environments. Triclosan is one of these compounds and has been detected in wastewater plant effluents and aquatic environment. In Japan, however, data about the triclosan concentration in aquatic environment are not enough to evaluate the influence of triclosan on aquatic environment. In this study, the concentrations of triclosan in water collected from Tone Canal, Chiba, Japan, were determined by HPLC/UV-VIS. The triclosan concentrations of the downstream were higher than those of the upstream, and were 11-31 ng/L. This might be due to the inflow of domestic wastewater. Those in the summer were lower than those in the other season. This might be because of the increase of the flow in the rainy season. In the investigation at domestic wastewater inflow point, the triclosan concentrations were 67-134 ng/L, but the tendency of the concentration changes were not appeared obviously. However, the loading amounts of triclosan showed highest value from 10 o'clock to 12 o'clock. This tendency might be characteristic pattern of the domestic wastewater.

Introduction

Up to now, environmental pollution with various chemicals has become a serious problem. Recently, pollution with pharmaceuticals and personal care products (PPCPs) such as medicines and cosmetics has been of great environmental concern, since these compounds have high biological activity^{1,2}. Therefore, the adverse effects of these compounds on aquatic environment have been concerned.

Triclosan, 5-chloro-2-(2,4-dichlorophenoxy) phenol (Fig.1), is a broad-spectrum antibacterial agent widely used in personal care products such as soap, shampoo, and toothpaste, etc. Its photochemical conversion to 2,8-dichlorodibenzo-*p*-dioxin, fish-toxicity, and weak estrogen activity have already been reported^{3,4}. To consider influence of triclosan on aquatic environment, the data about triclosan concentration in river and lake water are very important. However, few investigations about concentrations of triclosan in river and lake water were carried out. Therefore, the purpose of this study was to monitor the concentrations and to evaluate the seasonal changes and distribution of triclosan in river water of Tone Canal, Chiba, Japan.

ÇI OH	M.W.	289.54
	рКа	7.9
	m.p.	54-57.3 °C
	logPow	4.16
Cl ² ~ Cl	water solubility	10 mg/L

Fig.1. Chemical structure and physical-chemical property of triclosan^{5,6}.

Materials and Methods

Sample collection

Water samples were collected from 4 sites on Tone Canal (Fig.2). Tone Canal is located in north-west part of Chiba prefecture, north-east of Tokyo, Japan. This Canal flow from Tone River to Edo River and its distance is about 8 Km. Recently, Tone Canal finished the role as the Canal, the water gate of inflow side is generally closed. Therefore, the water of Tone Canal mainly consists of domestic and agricultural wastewater from surrounding area, and this canal have been concerned about water pollution. Sampling sites were set at the inflow point from Tone River (Site A), the middle point of this canal near the Unga station (Site B), the outflow point to Edo River (Site C), and the point of domestic wastewater inflow (Site D).

Sample collections for investigation into concentration changes and distribution of triclosan concentrations were carried out from April 18, 2006 to December 1, 2006 at Site A, B, and C. For Site D, sample collections for investigation into daily variation of triclosan concentrations in domestic wastewater were carried out seven times a day on November 11 and November 15, 2006. The flows at Site D were also measured when the water samples were collected.

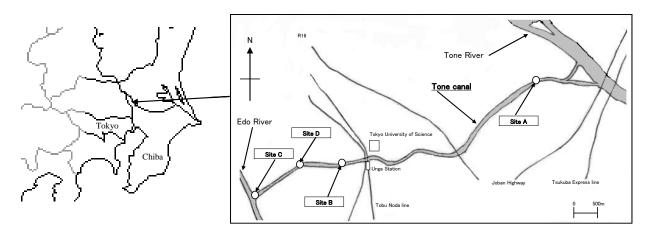


Fig.2. Map of Tone Canal, surrounding area, and sampling sites.

Sample preparation

Sample preparation was based on the approach described by Okumura et al. (1996) with minor modifications⁷. Five hundred milliliters volume of a sample was filtrated with 1.0 μ m glass filter (Whatman GF/B). Five grams of NaOH dissolved into the filtrated sample. After NaOH completely dissolved, it was washed with 50 mL of hexane. The water phase was transferred into a beaker and adjusted pH 2-3 with 6 N HCl. The adjusted water was extracted twice with 50 mL of hexane. The hexane phase was combined, and dehydrated with anhydrous Na₂SO₄. The dehydrated hexane phase was concentrated 3-5 mL by a rotary evaporator, and further evaporated to dryness under nitrogen gentle stream. The sample was dissolved in 0.5 mL of MeOH and analyzed by HPLC/UV-VIS. Recovery in this sample preparation was 95.1 % (C.V.=1.8 %, n=3).

<u>Analysis</u>

HPLC separation was carried out using an LC-9A (Shimadzu). HPLC column Mightysil RP-18 (4.6×150 mm 5 μ m; Kanto Chem. Co., Ltd.) with mobile phase 7:3 MeOH/20 mM ammonium acetate buffer (pH 5.5) was used. The detection wavelength was 240 nm. The flow rate was 1.0 mL/min, column temperature was 40°C, and the injection volume was 20 μ L. The quantification limit was 3 ng/L.

Results and Discussion

The results of investigation into distribution and seasonal changes of triclosan concentrations were shown in Fig.3. The frequency of detection in water (expressed as the number of samples detected vs. the number of samples analyzed) was in the following order; Site A (0/9), Site B (3/9), Site C (9/9). Comparing triclosan concentrations in each of sampling sites, those of Site C were higher than those of Site A and B (Fig.3). At Site C, triclosan was most frequently detected throughout the investigation period, and its concentrations were 11-31 ng/L. The reason of relatively high concentration of triclosan might be due to inflow of domestic wastewater which was containing a lot of triclosan. Actually, high concentrations of triclosan (67~134 ng/L) were detected from domestic wastewater inflow (Site D).

Triclosan was lower concentrations in water samples collected from June to July than in water samples collected on the other period. As shown Fig.4, flows at Site C were increasing from June to July because of the rainy season, and triclosan concentration decreased during this period. Therefore, the reason of the low concentrations from Jun to July might be increase of the flow during the rainy season. In Tone Canal, seasonal changes of triclosan concentrations might depend on flow.

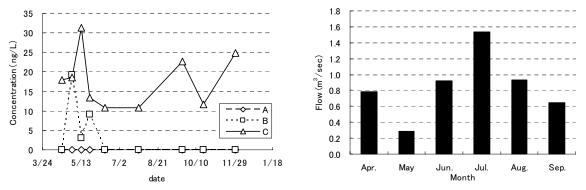


Fig.3. Seasonal changes of triclosan concentration in Tone Canal.



The results of investigation about daily variation of triclosan concentrations were shown in Fig.5. Triclosan was detected in the concentrations of 67-134 ng/L, but the tendency of concentration changes were not appeared obviously. The loading amounts of triclosan which were calculated from their concentrations and measured flows were shown in Fig.6. The tendency increasing of loading amounts from 10 o'clock to 12 o'clock was appeared, it was different than that of clinical wastewater reported by previous study⁴. In clinical wastewater, triclosan concentrations showed highest value at night. On the other hand, in domestic case, triclosan might be used in the morning, tooth blushing, and hand washing, etc., and the difference of tendency between domestic and clinical wastewater might be owing to the difference of usage.

Total loading amounts of triclosan were calculated from 6 o'clock to 20 o'clock, and those were about 1.0 g. Those amounts exceeded daily loading amounts of triclosan at Site C roughly calculated from the value shown in Fig.3 and Fig.4 (data not shown). As shown in Fig.1, triclosan is hydrophobic compound, and hydrophobic chemical compounds generally tend to adsorb to organic matter in the sediments. Therefore, it might be relating adsorption on the sediment, biodegradation⁸, and conversion to other compounds of triclosan^{3,11,12}.

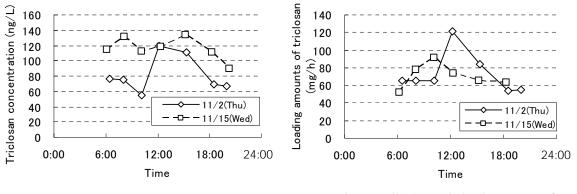


Fig.5. Daily changes of triclosan concentrations at Site D.

Fig.6. Daily changes in loading amounts of triclosan loads at Site D.

The concentrations of triclosan detected in this study were far lower than the acute toxic concentration reported by previous studies^{9,10}. However the risks of chronic toxicity exposed by very-low-concentration of triclosan are still unclear. Furthermore, the formation of methyl-triclosan, chlorinated-triclosan, and dioxins from triclosan have already been reported^{3,11,12}. Methyl-triclosan is more hydrophobic than triclosan, and have detected in fishes¹³. Chlorinated-triclosan are relatively unstable compounds, and easily degraded to 2,4-dichlorophenol and 2,4,6-trichlorophenol which are well-known toxicity and endocrine-disrupter activity¹⁴. And it was reported that 2,8-dichlorodibenzo-*p*-dioxin in aquatic environment might be generated from triclosan ¹⁵. Although the concentrations of triclosan were very low, the presence of above compounds generated from triclosan might be indicated. Therefore, it is necessary to continue monitoring triclosan in various aquatic environments.

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