

Monitoring of Triclosan in the Surface Water of the Tone Canal, Japan

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Abstract Triclosan, which is used widely as an antibacterial agent, was ubiquitously found in the water samples collected from the Tone Canal, Chiba, Japan. The concentrations of triclosan ranged from 11 to 31 ng/L. Higher concentrations of triclosan were observed in water samples collected from downstream, as compared to in the water samples collected upstream. The daily monitoring of a selected point from where the domestic wastewater inflow occurs showed that the triclosan levels in the water samples ranged from 55 to 134 ng/L; the levels of the loading amounts peaked from 10:00 to 12:00.

Keywords Triclosan · Concentration changes · Distribution · HPLC/UV–VIS

Environmental pollution by hazardous chemicals such as pharmaceuticals and personal care products (PPCPs), including medicines and cosmetics, has been of great concern since these compounds have high biological activity. As a result of an incomplete elimination of PPCPs in wastewater treatment plants, their residues are found both in wastewaters and in surface waters. A number of surveys have reported chemicals such as PPCPs in wastewaters and surface waters (Ternes 1998; Nakada et al. 2006). However, till date, there has been little information with regard to the monitoring of PPCPs in domestic wastewaters and surface waters in Japan.

One of the PPCPs is the compound triclosan [5-chloro-2-(2,4-dichlorophenoxy)phenol, (Fig. 1)]. Triclosan is a

broad-spectrum antibacterial agent. It is introduced into water systems through its use in medicated soaps, shampoos, toothpastes, and deodorants. Its photochemical conversion to 2,8-dichlorodibenzo-*p*-dioxin, fish-toxicity, weak estrogen activity, and the formation of various chlorinated and brominated derivatives have already been reported (Onodera et al. 1987; Latch et al. 2003; Arizono and Takao 2006; Inaba et al. 2006).

To determine the influence of triclosan on aquatic environments, data regarding triclosan concentration in river and lake waters are very important. However, few such investigations have been carried out in Japan. Therefore, the purpose of this study was to monitor the concentrations and evaluate the seasonal changes and distribution of triclosan in the river water of the Tone Canal, Chiba, Japan because at present, the water in this river is heavily polluted by agricultural and domestic wastewaters.

Materials and Methods

Triclosan [5-chloro-2-(2,4-dichlorophenoxy)phenol] is commercially available (purity, >99.3%); a standard solution of this compound was prepared by dissolving it in methanol (MeOH) and subsequently diluting it. Water samples were collected from four sites at the Tone Canal. The Tone Canal is located in the northwest part of Chiba Prefecture, northeast Tokyo, Japan (Fig. 2). This canal links the Tone River and the Edo River, and its length is approximately 8 km. Recently, the Tone Canal closed down, and the water gate of the inflow side is now generally closed. This resulted in pollution of the water of the Tone Canal mainly with domestic and agricultural wastewaters from the surrounding area.

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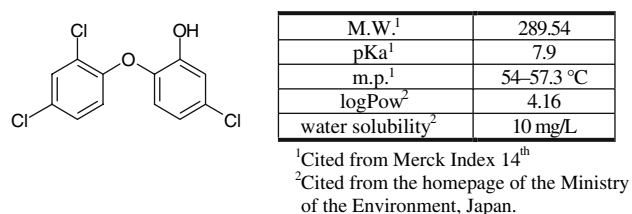


Fig. 1 Chemical structure and physico-chemical properties of triclosan

Sampling sites were set at the inflow point from the Tone River (Site A), middle point of the canal near Unga station (Site B), and outflow point of the Edo River (Site C). Additional water samples were also collected from the point (Site D) of inflow of domestic wastewater into the canal.

The triclosan surveys were carried out during the period from April 18 to December 1, 2006 at Sites A, B, and C in order to obtain the information concerning the distribution and seasonal variation in the levels of this compound in the water. At Site D, triclosan surveys were carried out seven times a day on November 11th and 15th, 2006 in order to obtain information concerning the daily variations in the levels of this compound in the water. In addition, the water discharges were measured at Site D.

Analytical samples were prepared according to the method reported by Okumura and Nishikawa (1996) with minor modifications. Five hundred milliliters volume of a sample was filtrated with 1.0- μ m glass filter (Whatman GF/B), and dissolved 5 g of NaOH into the filtrated sample. After dissolving NaOH completely, it was washed with 50 mL of hexane. The water phase was transferred into a beaker and adjusted pH 2–3 with 6 mol/L HCl. The pH-adjusted water was extracted twice using with 50 mL of hexane. The hexane phase was combined, and dehydrated with anhydrous Na₂SO₄. The dehydrated hexane phase was concentrated up to 3–5 mL by a rotary evaporator, and further evaporated to dryness under a gentle stream nitrogen gas. The sample was dissolved in 0.5 mL of MeOH

and analyzed by high-performance liquid chromatography (HPLC)/ultraviolet–visible spectrophotometry (UV–VIS).

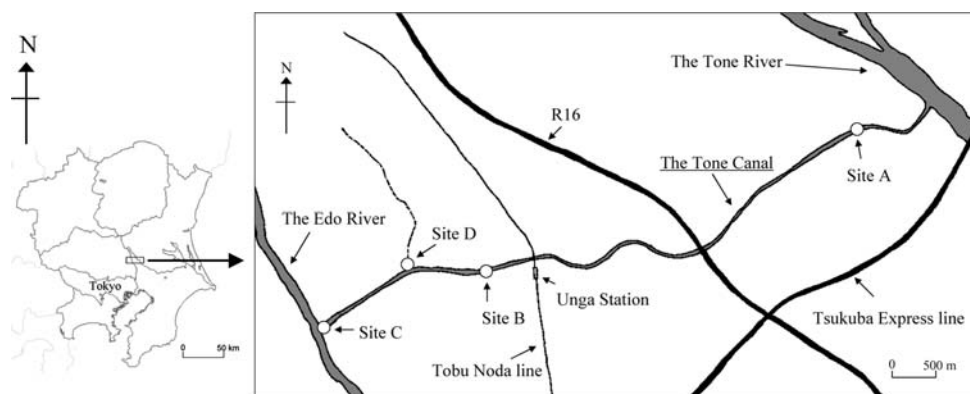
HPLC separation was carried out using the LC-9A model (Shimadzu). HPLC column Mightysil RP-18 (4.6 \times 150 mm, 5 μ m; Kanto Chem. Co., Ltd.) with a mobile phase comprising a 7:3 mixture of MeOH and 20 mM ammonium acetate buffer (pH 5.5) was used. The detector was an SPD-Avp (Shimadzu) at a wavelength of 240 nm. The flow rate was maintained at 1.0 mL/min; column temperature, 40°C; and injection volume, 20 μ L. The recovery in this sample preparation was 95.1% (CV = 1.8%, n = 3), and the quantification limit was 3 ng/L.

Results and Discussion

Figure 3 shows the distribution and seasonal variation of triclosan in waters sampled at Sites A, B, and C of the Tone Canal from April to December 2006. The frequency of its detection in water samples (expressed as the number of samples in which triclosan was detected vs. the number of samples analyzed) was in the following order; Site A (0/9), Site B (3/9), and Site C (9/9). Higher levels of triclosan (11–31 ng/L) were observed in the water samples collected at Site C as compared to in those collected at Sites A and B. Since higher levels of triclosan (55–134 ng/L) were detected in the water samples at Site D where the domestic wastewater were discharged into the Tone Canal, the presence of more triclosan in the water samples collected at Site C might be due to this inflow of domestic wastewater.

The levels of triclosan were lower in the water samples collected in June and July as compared with those observed in the water samples collected during other months. The low levels of triclosan in the water samples can be explained by heavy rains (rainy season) during the sampling period. A similar decrease in several pesticide concentrations due to dilution effects has also been reported in a previous paper (Kawakami et al. 2005). Therefore,

Fig. 2 Map of the Kanto Plain (left) and the Tone Canal, surrounding area, and sampling sites (right)



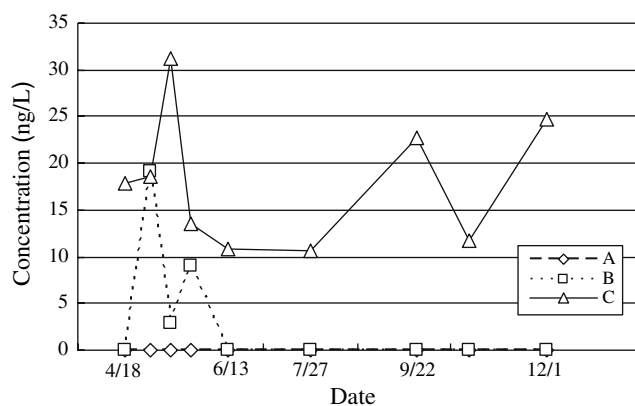


Fig. 3 Seasonal variation of triclosan concentration in the water samples collected from the Tone Canal

seasonal variation in the triclosan levels in the water samples from the Tone Canal might depend on the water levels of the river.

Figure 4 shows the daily variation of triclosan concentration in the water samples collected at Site D in November 2006. Triclosan was detected, ranging from 55 to 134 ng/L; however, large variations in its concentration were not observed among the wastewater samples. Figure 5 shows the relationships between the sampling times and the loading amounts of triclosan that were calculated from its concentration and the amount of water discharged at Site D. The peak in the loading amounts was observed from 10:00 to 12:00; however, this phenomenon was different from that in the case of clinical wastewater (Arizono and Takao 2006). In the clinical wastewater, the highest level of triclosan was observed at nighttime.

The total loading amount of triclosan was calculated from 6:00 to 20:00, and the value was approximately 1.0 g. These amounts exceeded the daily loading amounts of triclosan at Site C, roughly calculated from the values shown in Fig. 3, and the data regarding the water flow at Site C obtained from the Edogawa River office. The

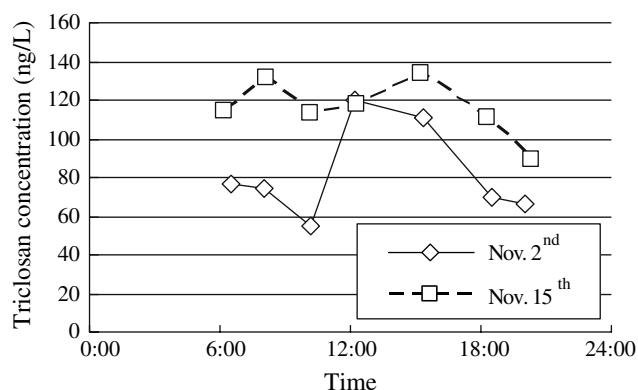


Fig. 4 Daily variations in triclosan levels at Site D

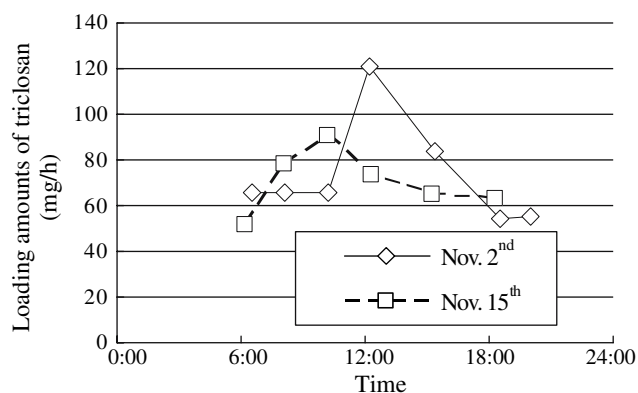


Fig. 5 Daily variations in loading amounts of triclosan loads at Site D

difference of the loading amounts between Site C and D might be due to adsorption on the sediment (Morrall et al. 2004). Biodegradation, bioconversion, and photochemical conversion to other compounds of triclosan might also be related (Latch et al. 2003; Morrall et al. 2004).

The concentrations of triclosan detected in this survey were far lower than the acute toxic levels reported in previous studies (Bhargava and Leonard 1996; Orvos et al. 2002). However, triclosan is a hydrophobic compound and has a high potential for bioaccumulation. The value of the bioconcentration factor was 4157 in zebra fish when the triclosan concentration of the test solution was 3 $\mu\text{g/L}$ (Orvos et al. 2002). The risks of chronic toxicity due to exposure to very low concentrations of triclosan remain unclear. Furthermore, the formation of methyl triclosan, chlorinated triclosan, and dioxins from triclosan has already been reported (Miyazaki et al. 1984; Onodera et al. 1987; Latch et al. 2003). Methyl triclosan is more hydrophobic than triclosan and has been detected in fishes (Miyazaki et al. 1984). Chlorinated triclosans are relatively unstable compounds and easily degraded, to 2,4-dichlorophenol and 2,4,6-trichlorophenol, which are well known for their toxicity and endocrine-disrupting activity (Canosa et al. 2005). It has been reported that in aquatic environments, 2,8-dichlorodibenzo-*p*-dioxin might be generated from triclosan (Kobayashi et al. 2003). Therefore, it still appears necessary to monitor triclosan and its various derivatives in various aquatic environments.

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