

Triclosan Residues in Estuarine Sediments from Valliyar Estuary, Kanyakumari District, Tamil Nadu, India

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Abstract: Triclosan is an antimicrobial agent added to a wide array of consumer goods and personal care products. Through its use, it is introduced into municipal sewer systems where it is partially removed during wastewater treatment. In this study residues of triclosan (TCS) was measured in surface sediments collected from the Valliyar estuary, Kanyakumari district, Tamil Nadu, India. Sediment samples were collected from a total of fifteen sampling sites, at different locations of Valliyar estuary near Arabian Sea. Triclosan was widely distributed in the estuarine environment. Concentration of triclosan ranged from 132 to 3073 ng g⁻¹ d.w. with a mean concentration of 1102.2 ng g⁻¹ d.w. The data obtained provides information on the levels of sources of triclosan in the estuarine environment. When compared with other areas, the triclosan level in the study area are some high. These results underscore the need to improved environmental protection measures in order to reduce the exposure of the population and aquatic biota to this antimicrobial agent.

Key words: Triclosan, sediment, antimicrobial, GC/MS.

Introduction

Accumulating evidences from literature over the past several decades have documented that antimicrobial agents are now commonly included in everyday use products in order to fight against infections (Cha, 2009; Kantiani, 2008). However, non-discriminatory usage poses a serious threat to public health and the environment worldwide. Furthermore, the use of antimicrobial agents in household and personal care products has multiplied the marketplace over the last decades (Cha, 2009; Kantiani, 2008). More than 70% of household and personal care products contain several synthetic chemicals as well as antimicrobial agents, the most common one being triclosan (2,4,4'-trichloro-2'-

hydroxydiphenylether or TCS) (Figure 1). Widely used as a broad-spectrum antimicrobial agent in diverse products such as hand disinfecting soaps, kitchen detergents, body washes, toothpastes and medical disinfectants (Cha, 2009; Kantiani, 2008; Sai, 2008; Adolfson, 2002). Due to its antimicrobial activity ~350 tonnes of triclosan are sold every year as the active

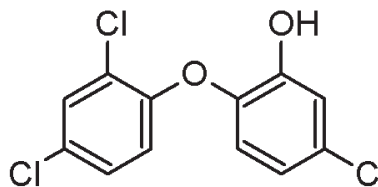


Figure 1: Chemical structure of triclosan (TCS).

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ingredient of pharmaceutical and personal care products, added at levels typically between 0.1% and 0.3% by weight. Incomplete removal of triclosan in wastewater treatment plants or direct discharge of waste water without treatment has resulted in the increased production and release of the triclosan to the environment (Zhao, 2010). The growth in demand of products with antimicrobial properties has resulted in the increase of production and release of the triclosan to the environment. Released TCS has the potential to cause a number of environmental and human health problems including bioaccumulation by aquatic organism, algal growth inhibiting effects, act as an endocrine disrupting compound, the formation of toxic degradation products and the development of microbial resistance (Cha, 2009; Kantiani, 2008; Sai, 2008; Adolfson, 2002; Sabaliunas, 2003; Miller, 2008; Singer, 2002). Furthermore, TCS has been labelled as RED pesticide on the re-registration eligibility decision by USEPA. Therefore, the trace-level determination of TCS following release to the environment has been a challenging task for analytical chemists (USEPA, 2008).

Several studies have documented the occurrence and fate of triclosan in the waste water treatment plant (WWTP) influent, effluent, surface water, aquatic environment and soil sediments (Cha, 2009; Coogan, 2007; Lopez, 1980; Paxeus, 1996; Kolpin, 2002; Hale, 1996). However, most studies documented in literature review the triclosan levels in sediment from marine and river environment. In India, very little field monitoring

data is available for the presence of environmental TCS in soil sediments (Ramachandra Rao, 2003). The Valliyar estuary in Kanyakumari district, an important riverine ecosystem and confluence with Indian Ocean, the Arabian Sea and the Bay of Bengal is characterized by intense industrial and agricultural activities and represents a potential major source of pollutants in Indian coastal waters. Recently, we have documented the distribution of organochlorine pesticide residues in surface sediments from selected areas in Kanyakumari district (Jeyakumar, 2009). However, there is no report on the analysis of TCS in estuarine environment of Valliyar estuary, Kanyakumari district. This prompted us to quantify the residues of triclosan from the Valliyar estuary by GC-MS technique.

Materials and Methods

Chemicals

Triclosan as internal standard for GC-MS analysis were obtained from Accu Standard Inc. USA. All organic solvents were of pesticide residue-free grade. All other reagents used were of analytical grade.

Sites of Sample Collection and Preservation

The sediment samples have been collected from both sides of the estuary and seashore of Valliyar estuary formed by the river Valliyar near Kadiapattinam village, Kanyakumari district (Figure 2). The district lies between 77°36' of the Eastern longitudes and 8°03' and 8°35' on

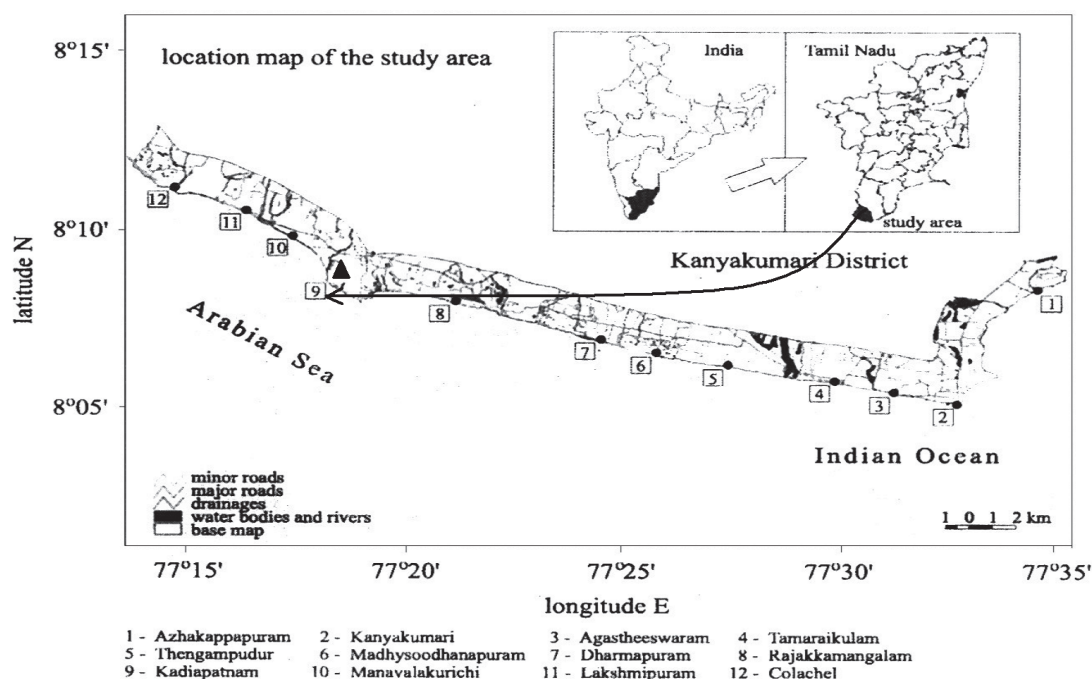


Figure 2: Sediment sampling sites (9) of Valliyar estuarine area.

the Northern latitudes. Totally 15 sampling sites have been selected within the area of 1.5 km from the sea towards different directions (marking as 9 in location map). Each sample was taken at a depth of 100 mm from top soil and was collected in a self locking polyethylene bag and sealed. The samples were labelled as TJ-1 to TJ-15 as per the sequence of their collection. Labels clearly indicated the location from which the samples were collected and legibly tagged. Sediment samples collected in the estuarine environment were commonly air-dried for about 24 hours at room temperature (25–30°C). The samples were then grounded and sieved through a mesh with a grain size of 2 mm, which is used for Soxhlet extraction. The details of the sampling sites are shown in Table 1.

Soxhlet Extraction of Sediment Samples

Approximately 300 ml of toluene was placed in a 500 ml round bottom flask containing one or two clean boiling chips attached with extractor. 2 g of the dried soil samples with anhydrous sodium sulphate were placed in an extraction thimble. The sample was extracted at 82°C for 24 hours. After the completion of extraction the sample was allowed to cool and concentrated by using a Kuderna–Danish concentrator attached with a 10 ml concentrator tube to a 500 ml of evaporation flask. The extract obtained after evaporation have been used for the analysis of triclosan content by GC-MS.

Gas Chromatography-Mass Spectrometry (GC-MS) System

Konik system 4000 series gas chromatograph coupled with Konik-Q12 model mass spectrometer cross linked 5% phenyl methyl siloxane capillary column (DB-60 m × 0.25 mm dia × 0.25 mm film thickness). GC operating conditions were as follows. Initial temperature 125°C (1 min hold) increased at 5°C/min to 210°C then increased at 1.5°C/min to 300°C (4 min hold). Injector temperature 270°C, carrier gas helium (99.999%) flow rate 1 ml/min, ion source temperature 270°C, operated

in the splitless mode; purge off time 1 min; injection volume 1 ml nominal. MS operating conditions were general mode of operating conditions, wherein equipped with computer HP. G1030A chem. station data system. The standard solution of triclosan was spiked with sample extract such that the concentration of triclosan in sample was 1 ppm. The injection volume was of 1 ml. Before analysis relevant standards were run to check column performance, peak height, resolution and limits of detection.

Identification of triclosan was accomplished using relative retention time techniques while quantification was done by comparison of peak areas of samples to those of standards at known concentrations.

Results and Discussion

The concentration of triclosan in an estuarine ecosystem like the Valliyar river estuary is controlled by (i) the amount of triclosan released by the treatment plants, (ii) the total dilution of sewage effluent by both seawater and freshwater inputs and (iii) its adsorption of particulate matter with subsequent deposition into the sediments.

A number of extraction and analytical methods have been reported for the quantification of TCS from various solid samples (Table 1). Here we followed the Soxhlet extraction method and GC-MS analytical technique.

The distribution of triclosan in the estuarine sediments from 15 sampling sites, revealed a wide range of fluctuation. The analytical results for all the samples are presented in Table 2. Typical chromatograms as well as mass spectrum of a standard triclosan and the samples are presented in Figure 3. The concentration of triclosan in sediments samples varied from 132 ng g⁻¹ (TJ-2) to 3073 ng g⁻¹ (TJ-15).

Triclosan is not acutely toxic to mammals but in vitro studies indicate that at low concentrations triclosan may disturb metabolic system and hormone homeostatis (Jacobs, 2005). In humans, triclosan is absorbed through

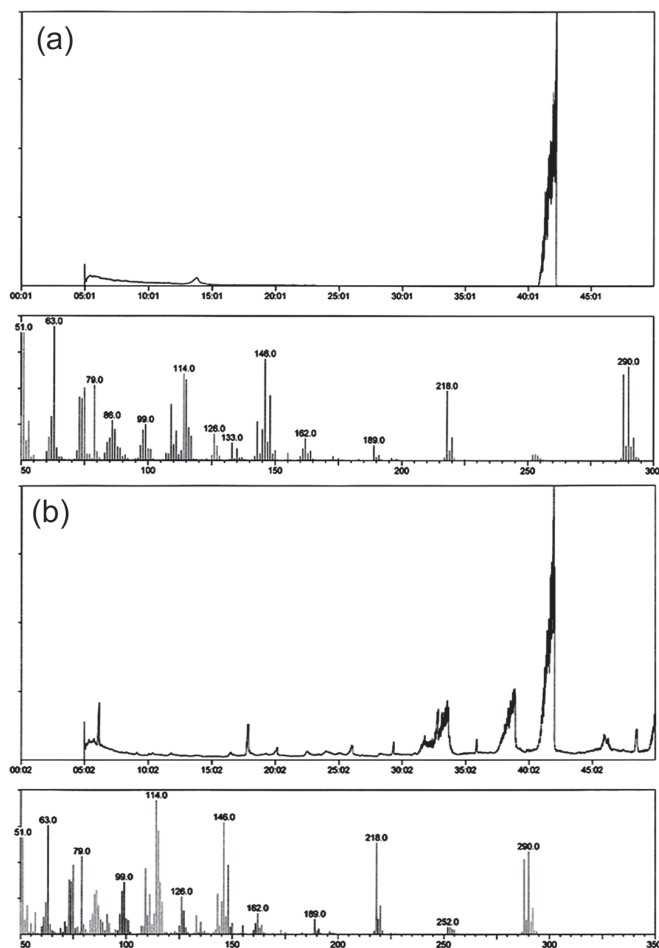
Table 1: Triclosan in various wastewater treatment plant and environmental samples along with detection methods

<i>Sample</i>	<i>Triclosan (ng g⁻¹)</i>	<i>Extraction method</i>	<i>Analytical method</i>	<i>Reference</i>
Digested sludge	500–15,600	Supercritical fluid extraction	GC-MS	McAvoy et al. (2002)
Lake sediment	37–53	Extraction (PLE)	LC-ES-MS-MS ion trap	Aguera et al. (2003)
Marine sediment	0.27–130.7	PLE-solid phase extraction (SPE)		
Sludge	400–8,800	Soxhlet extraction-SPE	GC-MS	Bester (2003)
Sludge	418–5400	Microwave extraction-SPE	GC-MS-MS	Morales et al. (2005)
River sediment	4.4–35.7			
River sediment	310–800	LLE	LC-ESI-MS Triple	Miller et al. (2008)
Soil	69–833	PLE-SPE	GC-MS	Kinney et al. (2008)

Table 2: Concentration of triclosan in sediments from Valliyar estuary, expressed in ng g⁻¹ dry weight (d.w.) ± SD

Sampling sites	Triclosan	Distance from seashore in metres
TJ-1	275 ± 20 (n = 3)	100
TJ-2	132 ± 15 (n = 3)	100
TJ-3	265 ± 17 (n = 4)	200
TJ-4	573 ± 20 (n = 3)	400
TJ-5	496 ± 25 (n = 3)	400
TJ-6	811 ± 27 (n = 3)	500
TJ-7	711 ± 30 (n = 3)	600
TJ-8	973 ± 32 (n = 4)	700
TJ-9	962 ± 27 (n = 3)	700
TJ-10	976 ± 28 (n = 3)	800
TJ-11	935 ± 2310 (n = 3)	900
TJ-12	2569 ± 29 (n = 3)	1000
TJ-13	1309 ± 39 (n = 4)	1200
TJ-14	2473 ± 40 (n = 3)	1500
TJ-15	3073 ± 28 (n = 3)	1500
Range	132-3073	

n = number of samples considered in average

**Figure 3: GC chromatogram with MS detection and full scan mass spectra of standard triclosan (a) and sample triclosan (b).**

the mucosa in the mouth and intestinal tract when administered via dental care products (Sandborgh, 2006). Furthermore, human health would be seriously threatened by food and water contamination with triclosan. Therefore, monitoring of triclosan in developing countries is essential to determine its impacts on the environment.

The concentrations of triclosan detected in this study were higher than the acute toxic levels reported in previous studies (Bhargava, 1996; Orvos, 2002). This might be due to the heavier usage of triclosan in residential household as commercial products for antibacterial mouth rinse and hand wash. The household wastewater was found to be discharged to the river Valliyar. Among the 15 sampling stations, highest concentration of triclosan was detected at TJ-15 which is far away from the sea and the lowest concentration was detected at TJ-2 which is very near the seashore area (Figure 4). The analytical results obtained in this study clearly shows that the concentrations of triclosan in the sediment samples have depended on the distance from the seashore. The level of triclosan increases when the sampling points were moving from seashore to the river direction. This may be due to stagnation of water for several days as well as the high organic matter content in the sediment at the inner area of the estuary. The estuaries are more polluted because enormous quantities of pollutants are transported by floods due to monsoon rains.

To our knowledge, our data represents the first report of TCS concentrations in the estuarine sediments of present study area. We found higher concentration of TCS in most of the sampling sites (132–3073 ng g⁻¹ d.w.). A similar trend of higher TCS concentration (90–7060 ng g⁻¹ d.w.) was observed recently in agricultural soils following land application of biosolids (biosolids from wastewater treatment plants) (Cha, 2009).

Episodic events may also play a role in the overall concentration of triclosan within the estuary. Large storms may cause overflow in the numerous combined sewage overflows. This overflow would result in pulse inputs of sewage being released into the estuary untreated.

The concentration of triclosan obtained in the water samples collected from the Tane Canal, Japan (Nishi, 2008) was very low (11 to 32 ng L⁻¹) compared to our present study. The observation was may be due to the hydrophobic nature of triclosan. Wu (2007) also observed the low range of (31.9 to 99.3 ng L⁻¹) triclosan in wastewater treatment. However, triclosan is a hydro-phobic compound and has a high potential for

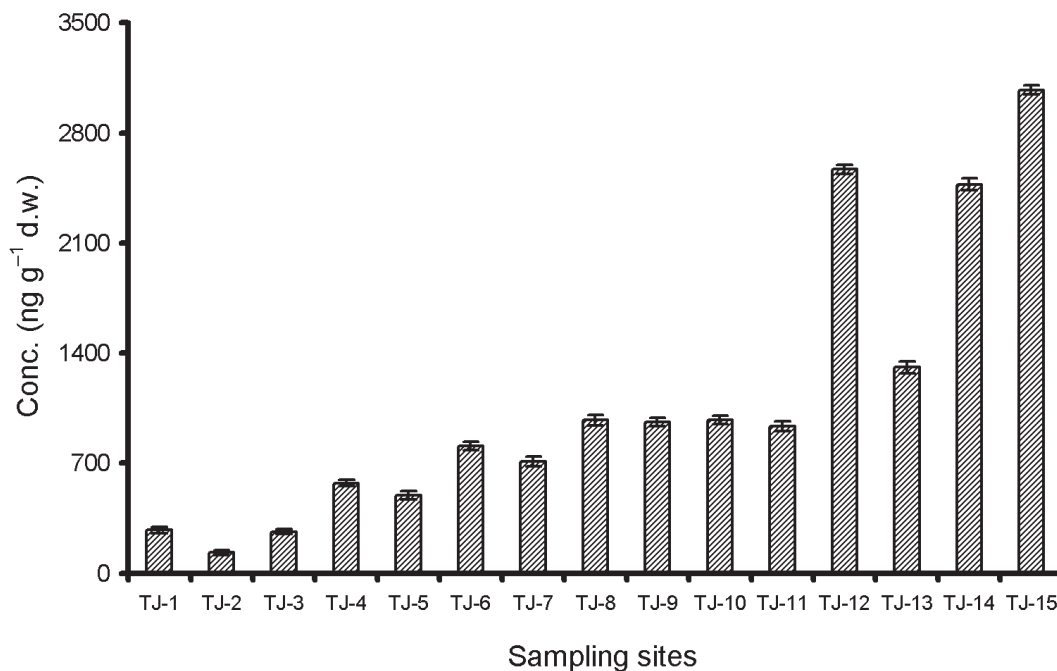


Figure 4: Distribution of triclosan in the sediments of Valliyar estuary.

bioaccumulation. The value of the bioaccumulation factor was 4157 in zebra fish when the triclosan concentration of the test solution was 3 mg L⁻¹ (Orvos, 2002). The risk of chronic study due to exposure to very low concentration of triclosan remains unclear. Furthermore, the formation of methyl triclosan, chlorinated triclosan and dioxin from triclosan has already been reported (Miyazaki, 1984; Latch, 2003). Methyl triclosan is more hydrophobic than triclosan and has been detected in fishes (Miyazaki, 1984). Chlorinated triclosans are relatively unstable compounds and easily degraded to 2,4-dichloro-phenol and 2,4,6-trichlorophenol, which are well known for their toxicity and endocrine-disrupting activity (Canosa, 2005). It has been reported that in aquatic environments, 2,8-dichlorodibenzo-*p*-dioxin might be generated from triclosan (Kobayashi, 2003; Kiguchi, 2007). Therefore, it still appears necessary to monitor triclosan and its various derivatives in various aquatic environments and soil sediments of estuary.

Conclusion

The study revealed that the sediments in the estuarine environment of Valliyar river are heavily polluted by triclosan. Samples were collected from fifteen sites of the study area near Arabian Sea. The quantitative analysis of triclosan have been done by GC-MS technique. The results have shown that the triclosan in the sampling

stations are higher than those of literature values. The concentrations varied from 132.2–3073 ng g⁻¹ d.w. Among the 15 sampling stations, highest concentration of triclosan was detected at TJ-15 which is far away from the sea and the lowest concentration was detected at TJ-2 which is nearer to the seashore area. Municipal sewages were the original sources for TCS. Due to the accumulation of triclosan in the sediments of Valliyar estuary, sediments could be a sink for TCS, but also a source for release back into the surface water. Further research should be performed to investigate the toxicological effects of triclosan in sediments water and pore water from estuarine area of Valliyar river.

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