“4 Research Report”

Occurrence, spatial distribution, and health status risk of emerging Contaminants in marine water, sediment and biota samples in Bay of Bengal, India

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1. Introduction

Synthetic musks are organic compounds produced in large quantities and extensively used in various consumer products, especially cosmetics and personal care products (PCPs) (Mottaleb et al., 2012; Nakata, 2005). Polycyclic musks (PCMs - galaxolide and tonalide) are widely applied in various PCPs and additives in cigarettes and fish baits (Homem et al., 2015). They can cause oestrogenic/anti-oestrogenic effects in humans and other organism (Huang et al., 2016; Hu et al., 2011). Synthetic musks are currently found in most surface aquatic systems and atmosphere (Lange et al., 2015; Nakata et al., 2012; Lee et al., 2014). They enter the aquatic environment through direct means like swimming and bathing in rivers and beaches, and indirect discharges, like effluents from wastewater treatment plants (WWTPs) (Homem et al., 2015; Groz et al., 2014). Synthetic musks are lipophilic, persistent and highly bio accumulative. They easily adsorb onto organic matter and accumulate in the soil, sediments and marine organisms (Huang et al., 2016; Wang et al., 2013; Chen et al., 2014). Galaxolide and tonalide were frequently observed in the effluents of domestic WWTPs and fish tissues from aquatic environments close to urban centres of Germany and China (Lange et al., 2015; Zhang et al., 2013; Klaschka et al., 2013; Reiner and Kannan, 2011). Nakata et al. (2012) found synthetic musks contamination in mussels from coastal areas in Asian countries. Contamination studies on freshwater fish by emerging contaminants were scarcely reported. Nevertheless, monitoring of synthetic musks in marine samples (Water, Sediment and Biota) was not investigated in India. Hence, the current study was carried out to explore the fate of synthetic musks (Galaxolide, tonalide and Musk Ketone) in marine water, sediment and biota samples.

1.1. Objective

- ✓ To collect the samples with background data and determine the quantification of Galaxolide, tonalide and MK in Marine samples which was already collected by the PI in Bay of Bengal, southern India.
- ✓ To determine the levels of synthetic musks (Galaxolide, tonalide and MK) in the appropriate samples from marine water, sediment and biota, and their bioaccumulation factors in biota samples will be measured and human and environmental risk assessment will be calculate based on this RQ = MEC/PNEC. (RQ- Risk Quotient, MEC-Measured Environmental Concentration, PNEC-Predicted No Environmental Concentration).

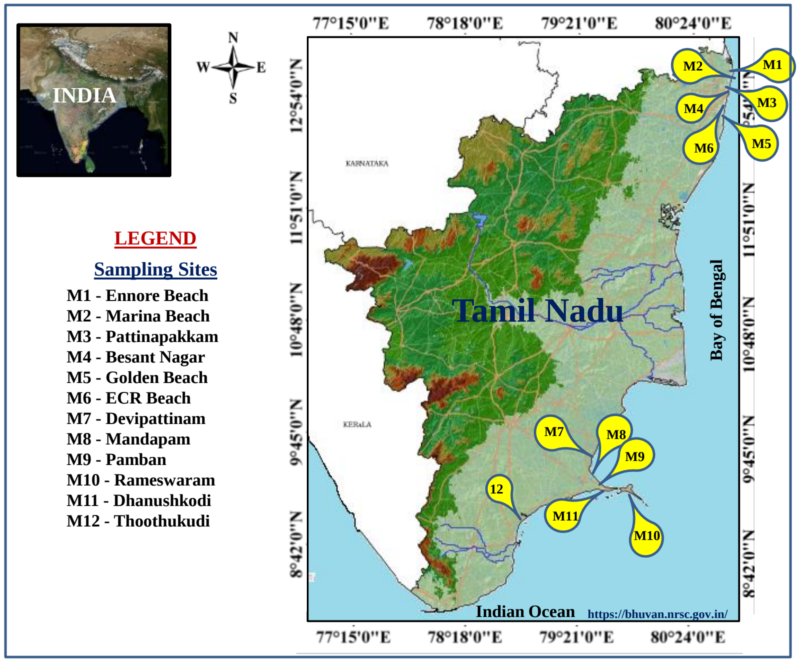


Fig. 1 Map of the study area with all sampling locations marked.

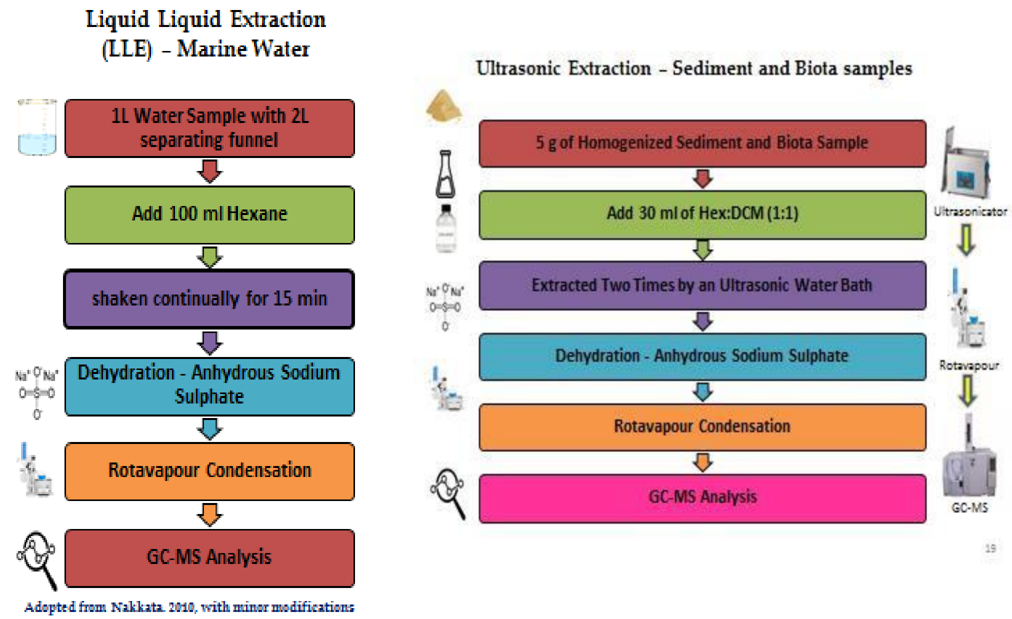


Fig.2 shows the extraction and analysis of Synthetic Musk

2. *Extraction procedure for Synthetic Musk in Marine Samples*

Number samples were collected Marine water (12), Sediment (12), Biota (8) in Chennai metro pollutants area and Gulf of Mannar Bioreserve (GMB).

3. *Result and discussion*

3.1 Occurrence of Synthetic musks in Marine water

The concentration (mean and median) and detection frequency of synthetic musks (Galaxolide, Tonalide and MK) in marine water were summarised in Table 1. The concentrations of galaxolide, tonalide and MK in marine water from the Bay of Bengal in southern, India, were ND - 3.08 (ng/L), ND-0.84 (ng/g), and ND - 5.58 (ng/g), respectively (Fig. 3). The detection frequency of synthetic musks are observed in the order of Musk Ketone > Galaxolide > Tonalide). Musk Ketone was found high in Gulf of Mannar region and compare with that metro pollutant area is very lowest concertation detected at M1 and M3. The municipal sewage, industrial wastewater, and hospital wastewaters were directly or indirectly discharged into the Gulf of Mannar region, which leads to a higher concentration of SMs in the marine water. The major source of SMs Contamination in these Gulf of Mannar may be due to the leak of sewage treatment systems and the Human activities had been the predominant source for SMs in the Gulf of Mannar region, specifically M8, M9, M10, M11 and M12 (fig.2).

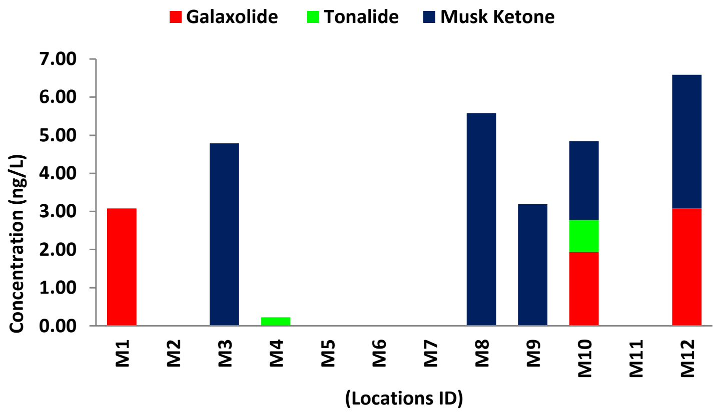
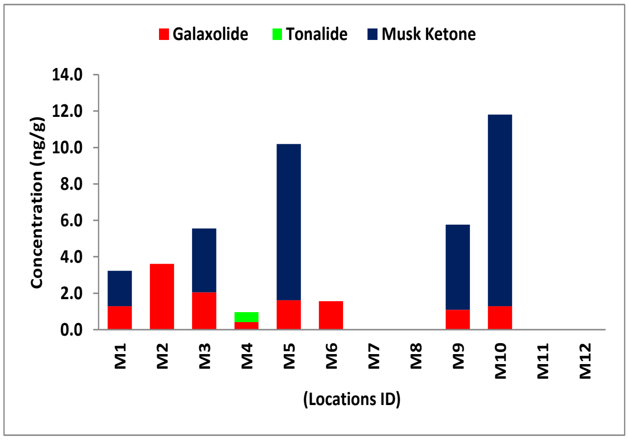


Fig. 3 Concentrations (ng/L) of Synthetic Musk in seawater from the Bay of Bengal, India

Similarly, of from M8 to M10 sampling sites were human activities (bathing, washing etc.) were high. These reasons would imply higher SMs concentration in the Mannar regions. Chemical transformation (i.e., oxidation) mechanism may play a significant role in eliminating SMs from sewage (Lv *et al.,* 2010). The present observation of SMs corroborates with our earlier studies on pharmaceutical and personal care products (Triclosan, Triclocarban, Benzotriazole UV Stabilizers, Parabens, NSAIDS and Carbamazepine) and plasticisers (phthalates and phenolics) as found higher levels in the riverine system reported (Ramaswamy et al., 2011; Selvaraj et al., 2015; Vimalkumar et al., 2018; Shanmugam et al., 2014). The concentration of galaxolide and tonalide in Haihe River in China ranged from 3.5 to 32 ng/L and 2.3 to 26.7 ng/L, respectively. However, synthetic musk levels observed in this study were 1–2 orders of magnitude lower than reported in the Arctic, the North Sea and Northern Germany (galaxolide 0.012–2.03 ng/L and tonalide 0.003–0.965 ng/L) (Xie et al., 2007). Lee et al. (2014) investigated the contamination of SMs in the Nakdong River in Korea, and total SMs were two to three orders of magnitude (150–16,720 ng/L) greater than the present study. Further, it indicates that the consumption of fragrances containing SMs in Korea was high.

3.2 Occurrence of Synthetic musks in Marine sediment

Phthalate concentration (mean and range) and their prevalence in sediment from southern Indian Bay of Bengal are given in Table 1. The concentrations of galaxolide and MK in marine sediment from the Bay of Bengal were ND - 3.61 (ng/g) and ND - 10.53 (ng/g), respectively (Fig. 4). In sediment samples, the galaxolide and Musk Ketone detection rates were 67 % and 42 % and tonalide not detected at in any sediment samples. Galaxolide and MK were also dominated SMs in sediments of the Pearl River Delta (China) (Zeng et al., 2008), Macao coastal region (China) (Wang et al., 2014) and Lake Michigan (USA) (Peck and Hornbuckle, 2004) respectively. The lipophilic properties of galaxolide and tonalide lead to their absorption onto particles during seawater and sediment partitioning (Lange et al., 2015). In the present study, SMs concentration in sediment was higher than the water samples from the bay of Bengal regions. This could be due to the surface runoff of synthetic musk from its potential sources, i.e. leaching from land, and treated/non-treated domestic wastewater. Vimalkumar et al. (2020) reported higher concentrations of synthetics musks in the particulate phase than in the dissolved phase of wastewater from Savannah, Georgia, USA reported PPCPs and Musks. In water, PPCPs and suspended particulate matter (SPM) relate with each other and accumulate in the sediment and this could elevate the concentration of PPCPs in water and sediment (Zhao et al., 2013). Higgins et al. (2011) and Wang et al. (2014) stated that personal care products (PCPs) persist in the sediment because of their high affinity towards organic carbon. Moreover, PPCPs has a low solubility and high no octanol-water partition coefficient; this could be a possible reason for its accumulation in matrices like sediment (Lv et al., 2014). Synthetic Musks has high affinity to organic carbon (Guna et al., 2014) and this could be used as a reliable indicator for organic contamination in the aquatic ecosystem.



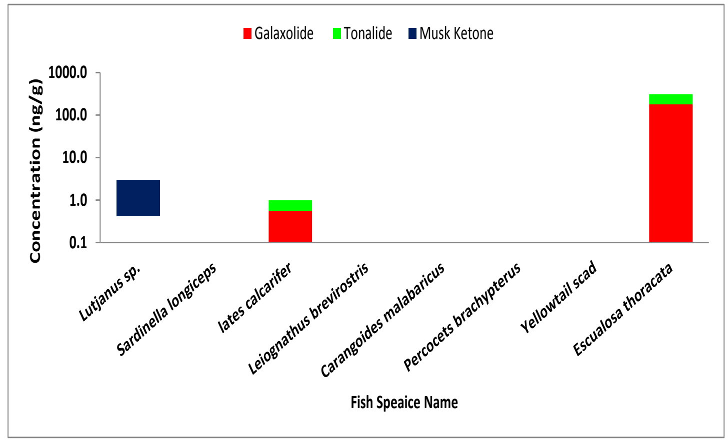


Fig. 4 and 5 Concentrations (ng/g(dw & ww)) of Synthetic Musk in sea sediment and Fish from the Bay of Bengal, India

3.3 ***Occurrence of Synthetic musks in Marine Biota samples***

The levels of synthetic musks in eight species fish samples collected Bay of Bengal are shown in Fig. 1. Galaxolide, tonalide and MK in fish ranged as ND - 178, ND - 134 and ND - 2.5 ng/g (ww). Whereas as the highest concertation at detected at Galaxolide and Tonalide in *Escualosa thoracata (spic)* respectively (Fig.5). The higher octanol – water partition coefficients (Log_{Kow}) for galaxolide (5.9), tonalide (5.7) and MK (4.3) (Chen et al., 2015) reflecting their residual burden in biota. A clear seasonal distribution pattern of SMs was noticed in this study. Kannan et al. (2005) USA reported lower concentrations of galaxolide and tonalide in the *Atlantic salmon* (1–3.2 ng/g ww; 1–1.6 ng/g (ww), *Atlantic sharpnose shark* (4.6–5.2 ng/g (ww); 1.4–1.7 ng/g (ww) and *smallmouth bass* (4.3–5.4 ng/g (ww); 1.6–1.9 ng/g (ww) However, the concentration of in present study higher concertation of Galaxolide in the species of *Escualosa thoracata,* . Galaxolide concentration in the liver of marine hammerhead shark *(Sphyrnidae)* in Japanese coastal waters was ranged from 16 to 48 ng/g (ww), which is lower than the fish in the Gulf of Mannar region.

4. *Human health risk assessment*

The human Hazard Quotient (HQ_{human}) was calculated from Adult Exposure (AE) rates through fish and the acceptable daily intake (ADI) for SMs.

$$1.\quad AE = (Cf * FC)/BW \quad 2.\ (HQ_{human} = AE/ADI)$$

A human exposure risk assessment by fish consumption was assessed as per Yao et al. (2018). The acceptable daily intake for SMs galaxolide, tonalide and MK are 150, 5 and 15 mg/kg BW, respectively (Block, 2003; P. Prevention, 2014; Worth and Patlewicz, 2007). Yao et al. (2018) and Boonsaner and Hawker (2013) assessed human exposure of PCPs and found no risks. The present investigation concludes that human exposure of SMs by fish consumption is negligible, and there are no human health risks in GFM regions (Fig.7).

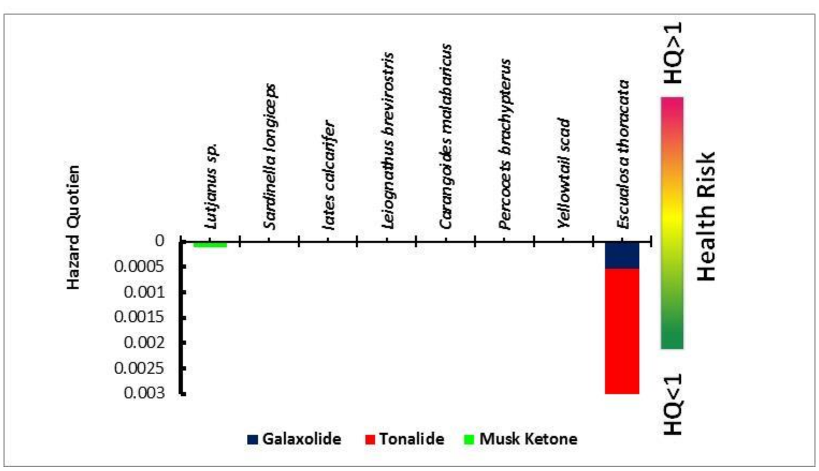


Fig.6. Human health risk assessment

Table. 1 Synthetic musk concentration (range, mean ± SD, and detection frequency) in seawater, sediment and fish samples from Tamil Nadu Coastal

Marine Environment									
	Water (12)			Sediment (12)			Biota (8)		
Synthetic Musks	**Range**	**Mean ± SD**	**Df (%)**	**Range**	**Mean ± SD**	**Df (%)**	**Range**	**Mean ± SD**	**Df (%)**
Galaxolide	nd-3.0	0.6 ± 1.2	25	nd-3.6	1.0 ± 1.08	67	nd-178	22.3 ± 62.9	25
Tonalide	nd-0.8	0.08 ± 0.2	17	nd-0.5	0.04 ± 0.15	8	nd-134	16.9 ± 47.5	37
Musk Ketone	nd-5.5	1.5 ± 2.1	42	nd-10.5	2.4 ± 3.7	42	nd-2.5	0.3 ± 0.9	12

Past achievement related to this project or meeting (article, conference presentation, award, patent, etc. by PI and members)

Articles (Joint research publication):

1. ***BabuRajendran, R.,***J.W. Kim,T. Isobe,K.H. Chang, A. Amano, T.W. Miller, F.P.Siringan, S. Tanabe (2011). Determination of preservative and antimicrobial compounds in fish from Manila Bay, Philippines using ultra high performance liquid chromatography tandem mass spectrometry, and assessment of human dietary exposure. *Journal Hazardous Materials* 192: 1739-1745 (**IF 4.114**).
2. Kim, J.W., T. Isobe, ***R. BabuRajendran***, K.H. Chang, A. Amano, T.W. Miller, F.P.Siringan, S. Tanabe (2011). Contamination and bioaccumulation of benzotriazole ultraviolet stabilizers in fish from Manila Bay, the Philippines using an ultra-fast liquid chromatography-tandem mass spectrometry. *Chemosphere* 85: 751-758 (**IF 3.253**).
3. Kim, J.W., ***R. BabuRajendran***, K.H. Chang, T. Isobe, S. Tanabe(2011). Multiresidueanalytical method for the determination of antimicrobials, preservatives, benzotriazole UV stabilizers, flame retardants and plasticizers in fish using ultra high performance liquid chromatography coupled with tandem mass spectrometry. *Journal of Chromatography A* 1218:3511-3520 (**IF 4.101**).
4. Minh, N.H., T.B.Minh, N.Kajiwara, T.Kunisue, A.Subramanian, H.Iwata, T.S.Tana, ***R.BabuRajendran***, S.Karuppiah, P.H.Viet, B.C.Tuyen, S.Tanabe (2006). Contamination by Persistent Organic Pollutants in dumping sites of Asian developing countries: implication of emerging pollution sources. *Archives of Environmental Contamination and Toxicology* 50 (4): 474-481 (**IF 1.864**).
5. Kunisue, T., M. Watanabe, H. Iwata, A. Subramanian, I. Monirith, T.B. Minh, ***R. BabuRajendran***, T.S. Tana, P.H. Viet, M. Prudente, S. Tanabe (2004). Dioxins and related compounds in human breast milk collected around open dumping sites in Asian developing countries: Bovine milk as a potential source. *Archives of Environmental Contamination and Toxicology* 47: 414-426 (**IF 1.864**).

A.N. Subramanian

1. **Annamalai Subramanian**, Tatsuya Kunisue, Shinsuke Tanabe. 2015.Recent Status of Organohalogens, Heavy Metals and PAHs Pollution in Specific Locations in India. Chemosphere, 137:122-134.
2. Lee HuuTuyen, Nguyen Minh Tue, Shin Takahashi, Go Suzuki, Pham Hung Viet, **Annamalai Subramanian**, Kesav A. Bulbule, PeethambaramParthasarathy, AlagappanRamanathan, Shinsuke Tanabe. 2014. Methylated and unsubstituted polyaromatic hydrocarbons in street dust from Vietnam and India: Occurrence,

distribution and *in vivo* toxicity evaluation. Enviro.Pollu., 194: 272-280.

3. HazukiMizukawa, Kei Nomiyama, Tatsuya Kunisue, Michi X. Watanabe, **Annamalai Subramanian**, Hisato Iwata, Mayumi Ishizuak, Shinsuke Tanabe. 2015. Organohalogens and their hydroxylated metabolites in the blood of pigs from an open waste dumping site in south India: Association with hepatic cytochrome P450. Environ. Res., 138: 255-263.

❖ **Book Chapters:**

1. Patil, N. N., **Arun. E.**, Vimalkumar, K., & Ramaswamy, B. R. (2022). Phthalate Esters and Their Ecotoxicological Risks from the Rivers of India. In Organic Pollutants (pp. 153-176). Springer, Cham.
2. Nikhil NishikantPatil**,** S. Krishna Kumar, K. Vimalkumar, **Arun. E**, *BabuRajendran, R*. Organochlorine pesticide contamination in the Kaveri (Cauvery) river, India: Water Challenges and Solutions on a Global Scale (Ed. Satinder Ahuja), ACS Books, Washington, DC, 2015: 447p.

❖ **Conference Presentation:**

1. K. Vimalkumar, S. Govindaraj, Nikhil Nishikant Patil, **E. Arun** and **R. BabuRajendran**. Non steroidalanti inflammatory drugs (NSAIDs) in major rivers of Tamilnadu, India**.** International Conference on “Recent Trends in Bioscience”. (07^{th} – 09^{th} February, 2016) at Alagappa University, Karaikudi, Tamilnadu, India.

2. Vimalkumar K, Bhuvaneswari R, Govindraj S, **Arun E** and **BabuRajendran R**. Human and Environmental Risk Assessment of Organochlorine pesticides in Water and Fish from River Cauvery, Tamilnadu. Two days workshop on “ Micropollutants in water and their hazards” (12^{th} – 13^{th} January, 2015) at IIT, Madras, Tamil Nadu, India.