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Annual Report for 2017

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Determination and Quantification of PBDEs and PCBs in Indian fish, their Human exposure and Health Risk Assessment using GC-MS

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1. Aim

Persistent organic pollutants (POPs) are of great environmental and health concern. Several polychlorinated biphenyls (PCBs) and Polybrominated diphenyl ether (PBDEs) have been targeted for restricted use or ultimate elimination by the Stockholm Convention on POPs which went into effect in 2004. Other groups of organic and emerging pollutants, including PBDEs and PCBs are considered the next generation of POPs to be included into the treaty due to their similarities to the banned chemicals in regard to health effects as well as their ubiquitous presence in the environment. Due to their performance and cost-effectiveness, polybrominated diphenyl ethers (PBDEs) have been used for many years as flame retardants in various commercial products, such as furniture, textiles, plastics, paints, and electronic appliances. The potential of these two groups of compounds (PBDEs and PCBs) to bioaccumulate has been detected in various environmental matrices. Recent studies noticed that concentrations of PBDES and PCBs have increased in the environment due to manmade activities. Hydroxylated polybrominated diphenyl ethers (HO-PBDEs) and methoxylatedpolybrominated diphenyl ethers (MeO-PBDEs), the biotransformation products of PBDEs have also been observed in tissues of fish and humans. Likewise PCBs metabolites were also found in several environmental and biotic samples. In this study, has been reported the levels of PBDEs and PCBs in fish samples from metro cities in south Indian rivers. Many POPs are persistent or pseudo-persistent (due to continuous emission) in the environment and toxic to non-target organisms. They also have the potential for bioaccumulation in organisms of different tropic levels.

1.1 Objective

- ✓ To collect the samples with background data and determine the quantification of PBDEs and PCBs flame retardants in fish samples which was already collected by the PI in Bangalore and Chennai cities of southern India, have been stored in es-bank until analysis.

- ✓ To find the hotspot of PBDEs and PCBs concentration in two cities Bangalore and Chennai. Calculate the human dietary risk level of PBDEs and PCBs using by fish concentration is based on the consumption of fish per day and daily intake of fish.

- ✓ Comparison of present data with globally who are all reported concentration levels of PBDEs and PCBs in fish samples and assessment of androgen and estrogen levels that are induced by organic pollutants such as PBDEs and PCBs, in fresh water fish collected from and near the sampling sites.

2. Extraction procedure for PBDEs and PCBs in fish sample:

Number fishes were collected in Bangalore and Chennai, in a Bangalore 2 types of fishes one was catfish (n=2) and tilapia (7). Likewise, Chennai city also 2 varieties of fishes mullet fish (n=13) and tilapia (n=8). Following extraction both PBDEs and PCBs has represents in Fig.1.

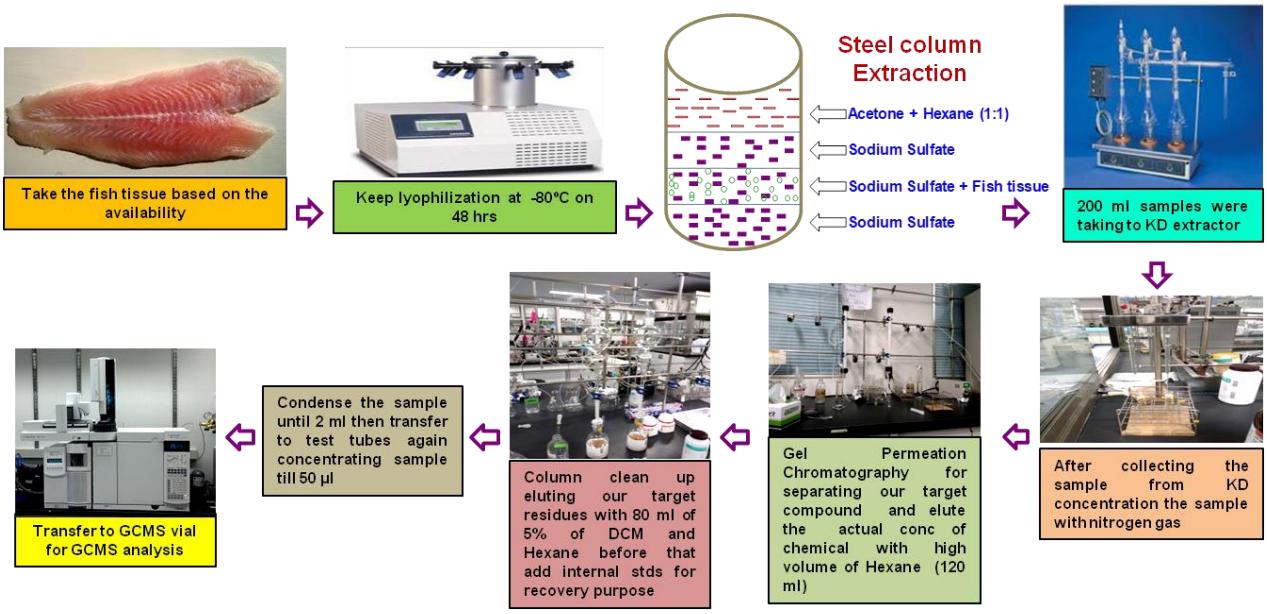

Fig.1. shows the extraction and analysis of PBDEs and PCBs in fish tissue

3. Result and discussion:

3.1 Levels of PBDEs in fish samples

PBDEs were quantified in the fresh water fish samples which are collected from the Chennai and Bangalore cities. In Chennai mullet and tilapia fishes were collected, it depends upon the sources and availability of fish species also. Levels of PBDEs, percentage and mean concentration have been represent in the Fig.2. Mean concentration of BDE 49, 47,155 and 154 are 0.62, 9.19, 6.44 and 2.26 (ng/g dw) respectively. In the levels of mean value was detected in the both mullet and tilapia varieties. Percentage wise both species were observed mullet 59 and tilapia 4. Among 43 congeners of PBDEs, detection of PBDEs only 4 congeners such as BDE 49, 47,155 and 154 comparing the 4 BDE 47 levels was high. In Bangalore based on the availability, have been collected 2 types of fish species (Cat fish and Tilapia). Same as above of Chennai, data are represents the concentration range, mean and percentage of PBDEs in fig.3.

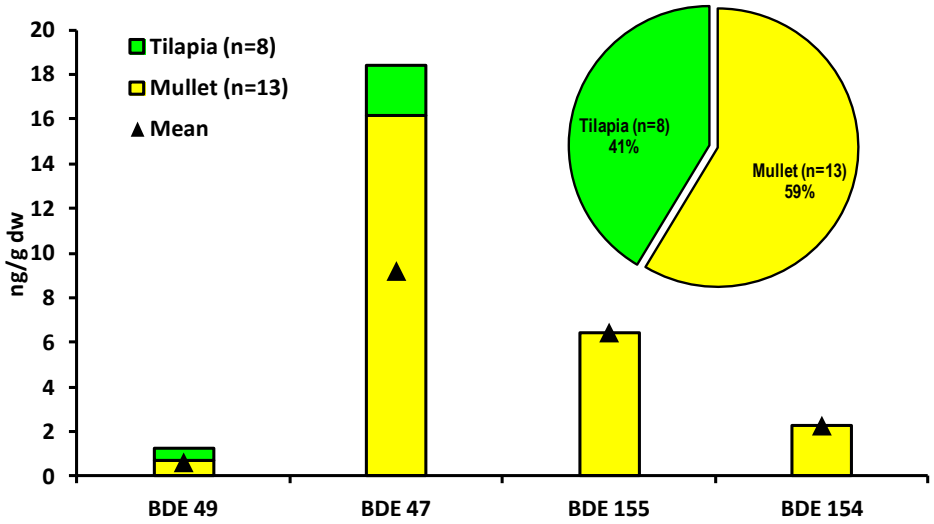

Fig.2 shows fish concentration range, mean and percentage of PBDEs in Chennai city

Among the 43 congeners of PBDEs, 14 congeners were detected in cat fish especially BDE 209 concentration 12.4 ng/g dw comparing others. Same way in tilapia species 4 congeners only observed it may because of the accumulation of species and nature of lipid content.

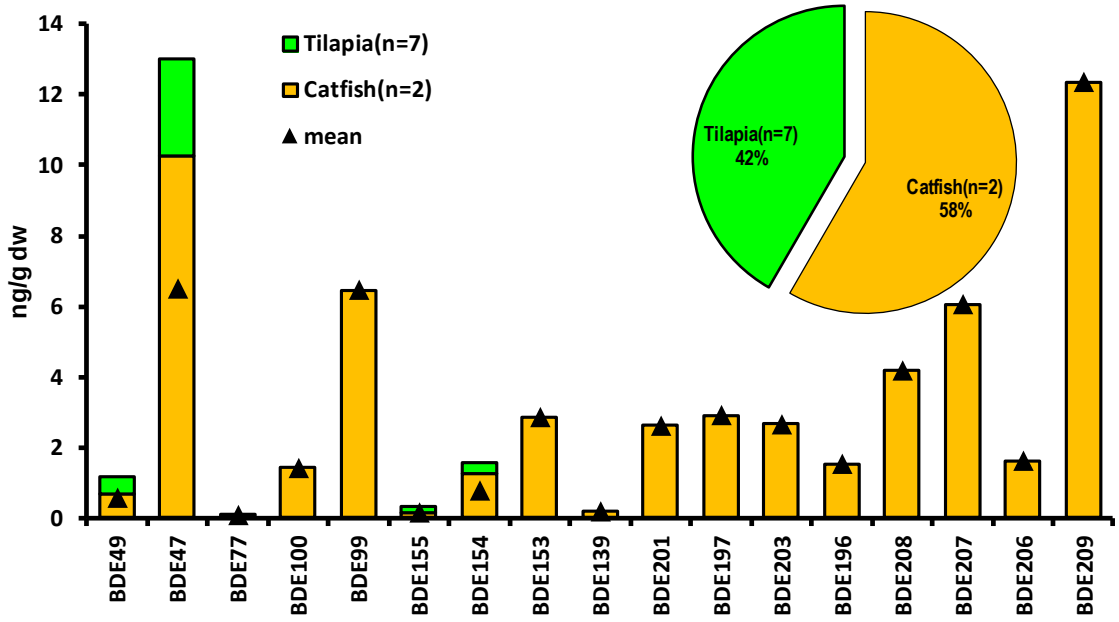

Fig.3 shows fish concentration range, mean and percentage of PBDEs in Bangalore city

PBDEs range observed in catfish and tilapia 0.1-12.4 ng/g dw and 0.2-2.8, respectively. Mean concentration of both species BDE 209 was higher than the other congeners and percentage wise catfish (58%) has observed high when comparing with tilapia (42%). Bangalore and Chennai both a cities

population wise are very high, but depends upon the PBDEs data Bangalore has been detected slightly higher than Chennai city. In the case still need to do more sampling in both cities fish samples in the species. Here interesting point noted tilapia fish levels have observed in same level in Bangalore and Chennai cities it may useful data for future studies.

3.2 Levels of PCBs in fish samples

PCBs levels are higher than the PBDEs; it was high in two cities of India such as Bangalore and Chennai. Concentration of fish ranged *MDL* – 1738 ng/g dw in Chennai included both mullet and cat fish. Among 61 congeners of PCBs, 41 congeners have been detected in all mullet fish and concentration was ranged 0.6-1738 ng/g dw and high concentration was observed in PCB 153 (1738 ng/g dw). In tilapia species, concentration ranged MDL – 354 ng/g dw high concentration was observed PCB 153 (354/g dw), respectively. High Mean and Percentage of PCBs were observed PCB 153 and Total percentage Mullet has been shows high comparing with tilapia species. (Fig.3).

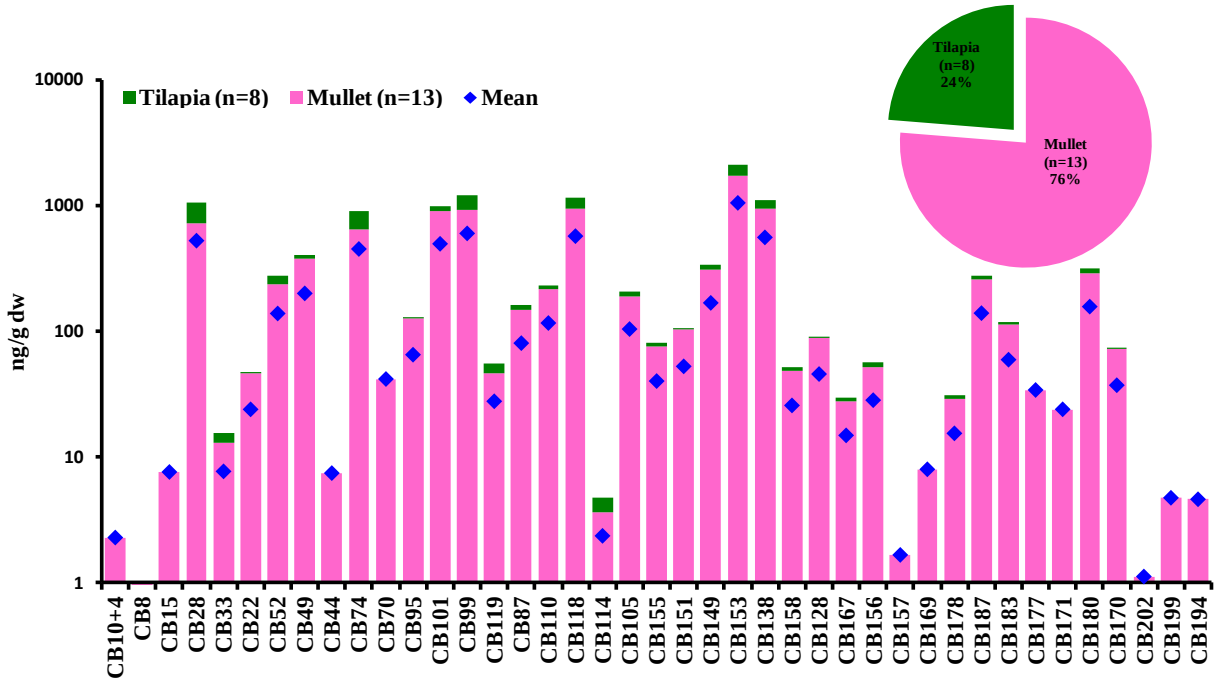

Fig.3 shows fish concentration range, mean and percentage of PCBs in Chennai city

Likewise, one more metro politician city Bangalore, concentration range for cat fish MDL-485 and tilapia MDL – 376 ng/g dw, respectively. Detection of PCBs among 61 congeners, 41 congeners detected in cat fish and 22 are tilapia. Even in mean level between all PCBs, PCB 28 was showed high concentration comparing with others (Fig.4). In percentage wise, Catfish (88%) shows higher than the tilapia (12%). Comparatively a Chennai and Bangalore city shows same levels as Concentration, mean and Percentage aspects. It may due to their low water solubility and high octanole-water partition coefficient; PCBs have strong potential to accumulate into the food chain and can be stored in fatty tissues.

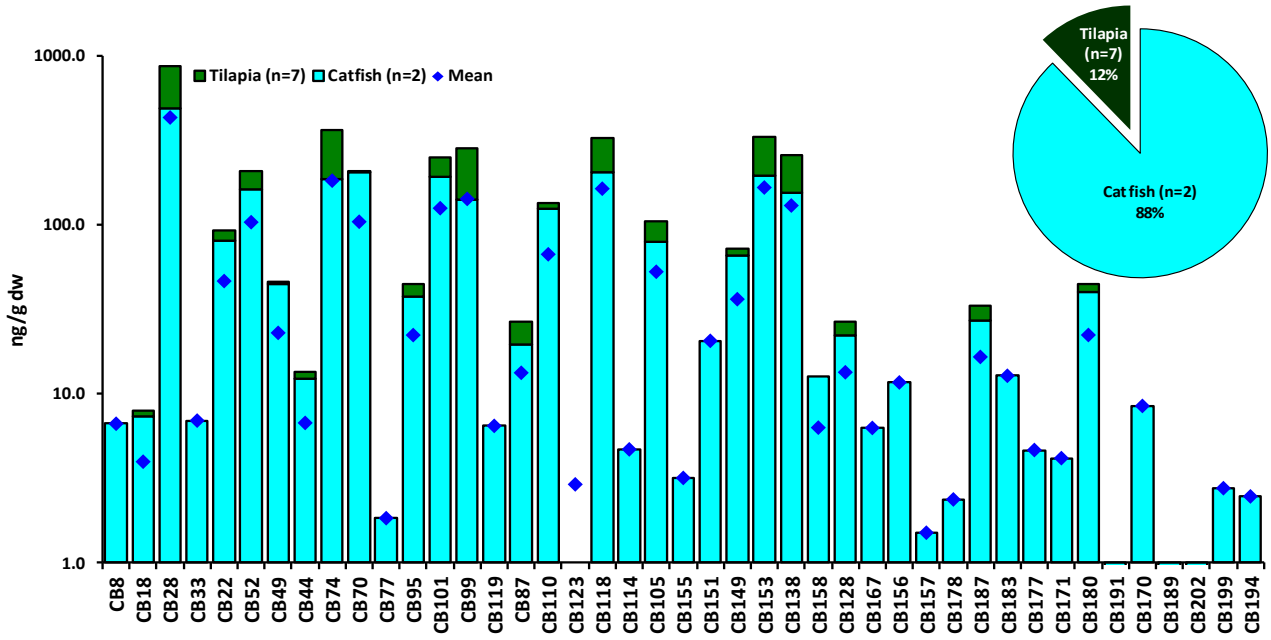

Fig.4 shows fish concentration range, mean and percentage of PCBs in Bangalore city

4. Human dietary health risk

Human risk levels were expressed followed by this formula; where, AE-Adult exposure (µg/kg bw); C_f-concentration of target compounds (C_{PBDEs} & $_{PCBs}$) in fish; FC per diem- fish consumption by Indian population (27 g per diem); BW-body weight (60 kg); and ADI acceptable daily intake (PBDEs 1671 µg/kg bw PCBs 49 µg/kg bw). HQ indicates the negligible/no risk at <1 and feasible risk at >1.

$$\mathbf{AE = (C_f * FC)/BW}$$

$$\mathbf{HQ_{human} = AE/ADI}$$

Fish is an important protein for human and also supplies in rich protein. PBDEs and PCBs are highly liphophic nature and harmful chemical to human it will cause so many hormone kind of problem to human. In this study sites, according to PBDEs level in Bangalore and Chennai shows very low risk based on the consumption of catfish and tilapia (Fig.5). Likewise, PCBs are shows maximum risk based on the consumption of mullet fish but in tilapia there is no risk.

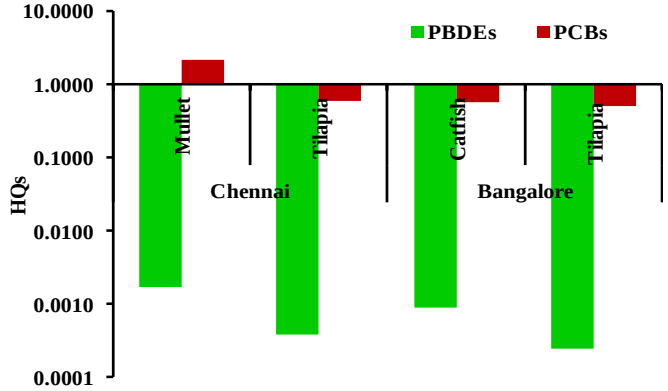

Fig.5 shows human dietary risk on PBDEs and PCBs in fish

Table 1. Comparison of PBDEs and PCBs in other country data

Location	Organism	PBDEs (ng/g ww)	PCBs (µg/kg ww)	Reference
Chennai River, India **Bangalore River, India**	**Mullet and Tilapia fish** **Cat fish and Tilapia**	**BDL – 7.29** **0.32-51.4**		**Present study**
Gironde Estuary, France	Eel	24-237		Tapie et al. (2011)
Eastern China Coastline	Yellow croaker and silver pomfret	1.11-5.28		Xia et al. (2011)
Northwestern Arabian Gulf	Mullet, tonguesole and yellowfin seaberam	2.80-190		Gevao et al. (2010)
Sydney Harbour, Australia	Flounder, tailor, yellowfin bream, luderick, fanbelly leatherjacket and sea muller	24-115		Losada et al.(2009)
Tokyo Bay, Japan	Japanese sea bass Ureogenic goby	ND-177		Mizukawa et al. (2009)
Georgia coast, USA	Anchovy, Flounder, Rock sea bass, Silver Perch, Spot and Spade fish	9.9-337		Sajwan et al.(2008)
Anoia and Cardenner River, Spain	Carp	29-744		Labandeira et al.(2007)
Hardley Lake, USA	Carp	760-2500		Dodder et al.(2002)
Virginia watershed, USA	Carp	5-47900		Hale et al. (2001)
Yakima River, USA	Carp	960		Johnson and Olson (2001)
Chennai River, India **Bangalore River, India**	**Mullet and Tilapia fish** **Cat fish and Tilapia**		**119-1584** **71-1784**	**Present study**
Campania Region, Italy	Fish muscle		25.4±39.6	Pacini et al.(2013)
Marche rivers, Italy	Fish muscle		4.1±0.4	Piersanti et al. (2012)
Taihu Lake, China	Fish muscle		0.16-2.13	Zhang et al.(2012)
Danube River, Serbia	Fish muscle		0.45-16.08	Jankovic et al. (2011)
Tiber River, Italy	Fish muscle		34.5-335	Miniero et al. (2011)
Slovak Republic, Various sites	Fish muscle		0.008-4.415	Salovicova and Zmetakova 2006
Catalonia River Basin area, Spain	Fish muscle		94.96±220.91	Pere-Trepat et al. (2006)
Sava River, Croatia	Fish muscle		8-177	Bosnir et al.(2005)

5. List of publication and Conference presentation

5.1 Publications:

1. R. Babu Rajendran, G. Preethi, R.K. Poopal, Nishikant Patil Nikhil**, K. Vimalkumar**, A. Subramanian, S. Krishna Kumar (2018). GC-MS determination of phthalate esters in human urine: a potential biomarker for phthalate bio-monitoring. *Journal of Chromatography B* 1079 (2018) 15–24 (**IF 2.603**).

2. **Vimalkumar K**, Arun E, Krishna Kumar S, Poopal R, N. N. Patil**,** Subramanian A, Babu Rajendran R. Occurrence of triclocarban and benzotriazole ultraviolet stabilizers in water, sediment, and fish from Indian rivers. *Science of the Total Environment* 625 (2018) 1351–1360 (**IF 4.900**).

3. Srimurali S, Krishna Kumar S, Govindaraj S, **Vimalkumar K**, Paromita C, Babu Rajendran R (2016). Evaluating Spatial Distribution and Seasonal Variation of Phthalates Using Passive Air Sampling in Southern India. *Environmental Pollution* 221 (2017) 407-417. (**IF 5.099**).

5.2 Book Chapter:

1. Nikhil Nishikant Patil, S. Krishna Kumar, **K. Vimalkumar**, E.Arun, *BabuRajendran, R*. Organochlorine pesticide contamination in the Kaveri (Cauvery) river, India: A review on distribution profile, status, and trends. In: Water Challenges and Solutions on a Global Scale (Ed. Satinder Ahuja), ACS Books, Washington, DC, 2015: 447p.

5.3 Conference presentation:

a) **Vimalkumar K***, E. Arun, S. Krishna Kumar, Nikhil Nishikant Patil, Rk. Poopal and R. BabuRajendran. Determination of Triclocarban (TCC) and Benzotriazole UV stabilizers (BUVSs) in surface water from South Indian Rivers. 19th International Conference Symposium on "Pollutant Responses in Marine Organisms" (PRIMO 19). (30th July – 3rd June, 2017) at Ehime University, Matsuyama, Japan.

b) **Vimalkumar K***, Govindaraj, S. Krishna Kumar, S. Srimurali, Nikhil NishikantPatil, E. Arun and R. BabuRajendran. Non steroidalanti inflammatory drugs (NSAIDs) in major rivers of Tamilnadu, India**.** International Conference on "Recent Trends in Bioscience". (07th – 09th February, 2016) at Alagappa University, Karaikudi, Tamilnadu, India.

c) **Vimalkumar K***, Bhuvaneswari R, Govindraj S, Arun E and Babu Rajendran R. Human and Environmental Risk Assessment of Organochlorine pesticides in Water and Fish from River Cauvery, Tamilnadu. Two days workshop on "Micro pollutants in water and their hazards" (12th – 13th January, 2015) at IIT, Madras, Tamil Nadu, India.

d) **Vimalkumar K***, Srimurali S, Krishna Kumar S, Govindaraj S, Babu Rajendran R. Determination of PCDDs, PCDFs and dioxin like PCBs in bovine milks and ash samples by using CALUX Assay in Tamilnadu, India. International Symposium on Halogenated Persistant Organic Pollutants (IEEP-2014) (January 16-17 2014) at CSIR-NEERI, Nehru Marg, Nagpur, Maharashtra, India.