Determination and identification of flame retardants in soil collects from E-waste industries and End of Life vehicles (ELV) from major cities of South India

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1. Aim

Polychlorinated biphenyls (PCBs) are a group of commercially synthesized and widely used in numerous industrial applications, such as chemical stability, high thermal conductivity, and electrical insulation properties. PCBs are stable under extreme temperature and pressure. Hence, PCBs are used as additives in dielectric fluids in transformers and capacitors, heat transfer fluids and hydraulic fluids in partially closed-industrial systems, furthermore, this can be used as additives in lubricants, casting waxes, surface coatings, adhesives, plasticizers, and inks (UNEP, 1999; WHO, 2000; Erikson and Kaley II,2011).

Many literatures reported the variety of hazardous substances found in concerning levels in ELVs, in which approximately 90 million ELV units had been produced in all over the world in 2014 only (Niinipuu, 2013; Korea Statistical Information Service, 2015). Among those variety of hazardous substances, PBDEs are become great concern in international community, because of its persistence and toxicity in the environment (Gearhart and Posselt, 2006; Sakai et al.,2006; lagalante et al.,2011; Jiang and Li, 2016). PBDEs are used for variety of manufactured products (foam, cushioning in furniture and plastics in television and computers). Three of the PBDE commercial mixtures have been produced, like deca-BDE, octa-BDE and penta-BDE. Deca BDDE is used as flame retardant in certain types of plastics, including electric products (vehicles, airplanes and certain building materials). Penta BDE was used in polyurethane foam, furniture, mattresses, carpet padding and automobile seats and Octa BDE was used in high impact plastics, such as fax machine, certain electric and electronic devices (telephones and kitchen appliances) (USEPA, 2010). Wide usage of PCBs, PBDEs and PCDD/Fs consequence on the severe environmental pollution and affects the human health, due to its persistence and bioaccumulative profile. Three major PBDEs are commercially used, like penta (BDE-47, -99, and -100), octa- (BDDE-194 to BDE-205), and deca BDE (BDE-209 with minor nanoBDE and octaBDE congener impurities).

Fast growing urbanization and motorization in developing and newly industrialized countries are generating large volume of end-of-life vehicles (ELVs) (Sakai et al.,2014). Likewise, waste electric and electronic equipments are recovered and reused in ELVs if the proper handling is followed. Many contaminants were released from the ELVs such as heavy metals, persistent organic pollutants (POPs) (PCBs)

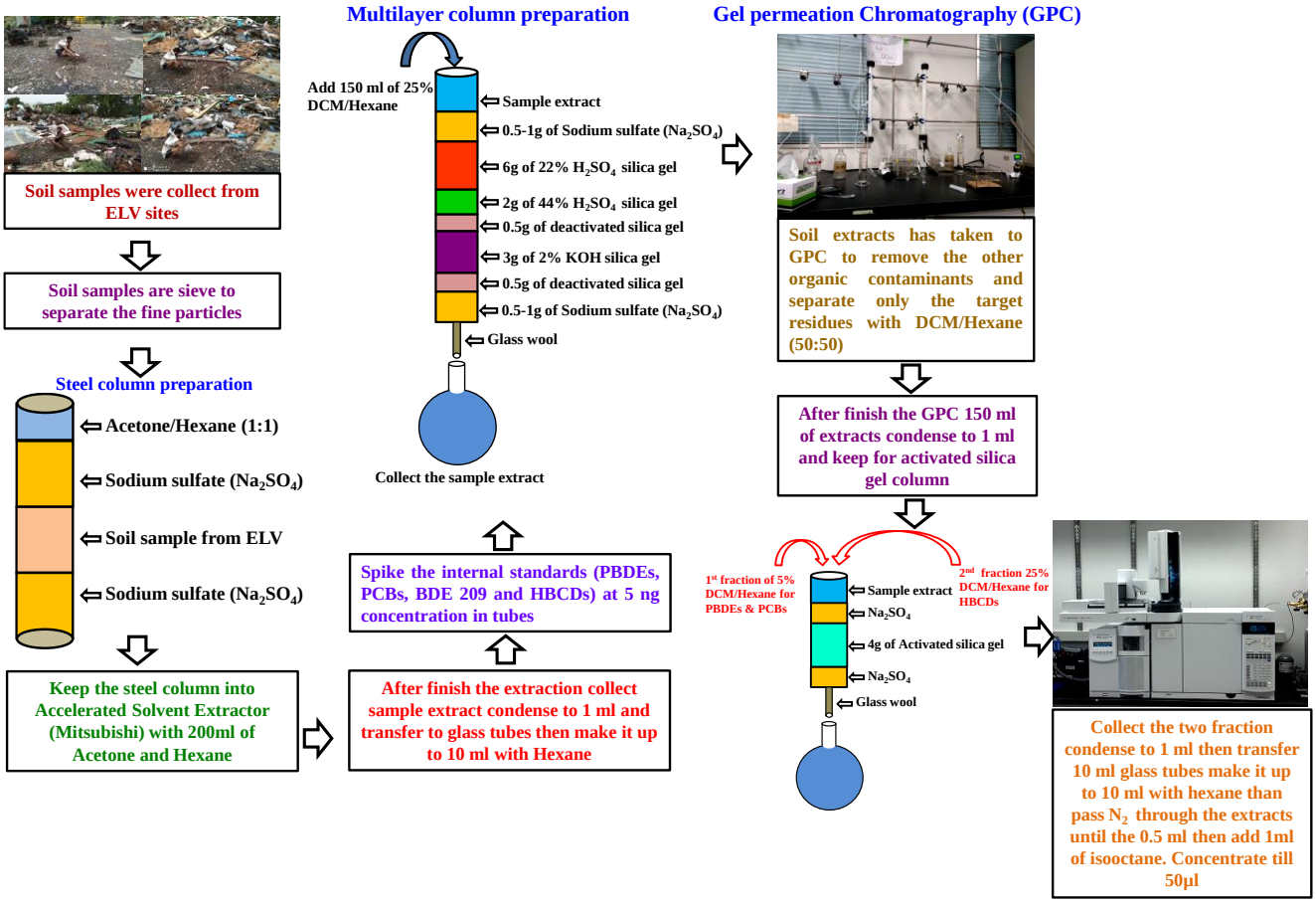
halogenated/phosphorus flame retardants and organotin stabilizers in plastics and foams (Sakai et al.,2007; Osada et al.,2008; Abdullah et al.,2008).

The present study has revealed to determine and quantify PCBs, PBDEs and their biotransformation products in End of Life Vehicles soil samples from major cities of Tamil Nadu state in India. The current study was focused on the levels of PCBs and PBDEs in soils from ELV sites and their distribution based on the activity at particular site locations. Further, this study was noticed the levels of 56 PCB and 31 PBDEs congeners, and their concentration range, maximum, and minimum level of PCBs at specific sites. Number of studies are available on the PCB contamination in industrial area, urban area, rural area and e-waste recylcing sites (Chakraborty et al.,2016; Sohail et al.,2018; Wang et al.,2013; Tue et al.,2013). But this is the first report of PCBs and PBDEs level in End of Life Vehicle sites in India specifically in South India (Tamil Nadu).

2. Objectives

- ✓ To collect the background data and main sources of PBDEs and PCBs in E-waste industry, and End of Life Vehicles (ELVs).
- ✓ To find the distribution and concentration of PBDEs and PCBs in E-waste and End of Life Vehicles (ELV) in soils samples from various locations and also to find out the hotspots of PBDEs and PCBs contaminated sites.
- ✓ To evaluate the PBDEs and PCBs using the already available data on environmental levels from the study area and the data to be obtained in this study.

3. Methodology for PBDEs and PCBs extraction in soil samples



4. Result and Discussion

4.1 Level of PBDEs in End of Life Vehicles (ELV) sites in Chennai, Coimbatore and Tiruchirappalli

Concentration of PBDEs in soil from ELV sites in Chennai, Coimbatore and Tiruchirappalli were shown in Table 1. PBDEs concentration in Chennai was ranged from 9.4 to 160 ng/g dw, followed by Coimbatore (13.1- 565.2 ng/g dw) and Tiruchirappalli (39.5-162.2ng/g dw), respcetively. Higher PBDEs concentration was found in Coimbatore (MP5) (Fig.2) ranged as 565.2 and 171.6 ng/g dw followed by Tiruchirappalli (TPJ1) (Fig.3) (162.2 ng/g dw) and Chennai (C3) (Fig.1) (160 ng/g dw). Scrabing of truck engines and dismandling consequence on the higher level of PBDEs at MP5and MP2, may due to engine oils had released PBDEs at higher concantration. In Tiruchirappalli, tyre removal and storage site (TPJ1) was found with higher concantrationof PBDEs, PBDEs could be used in tyre to prevent from high temperature and some kind of tyres were made up of tetiles to handle the tyre easily. The major sources of PBDEs in automobiles are seat foam, rigid insulation, automobile trim, insulations, carpet foam pads, cable insulation,

textile coating, headliners and stereos. Hence, the automobile residues could releases large amount of PBDEs in environment (Jeff Gearhart and Hans Posselt, 2006). In the present study, engine dismandling and scrabing sampling sites showed higher level of PBDEs than those of other ELV sites. The present study was not corroborate with other research reports, because of lack of information about PBDEs released by automobile engines.

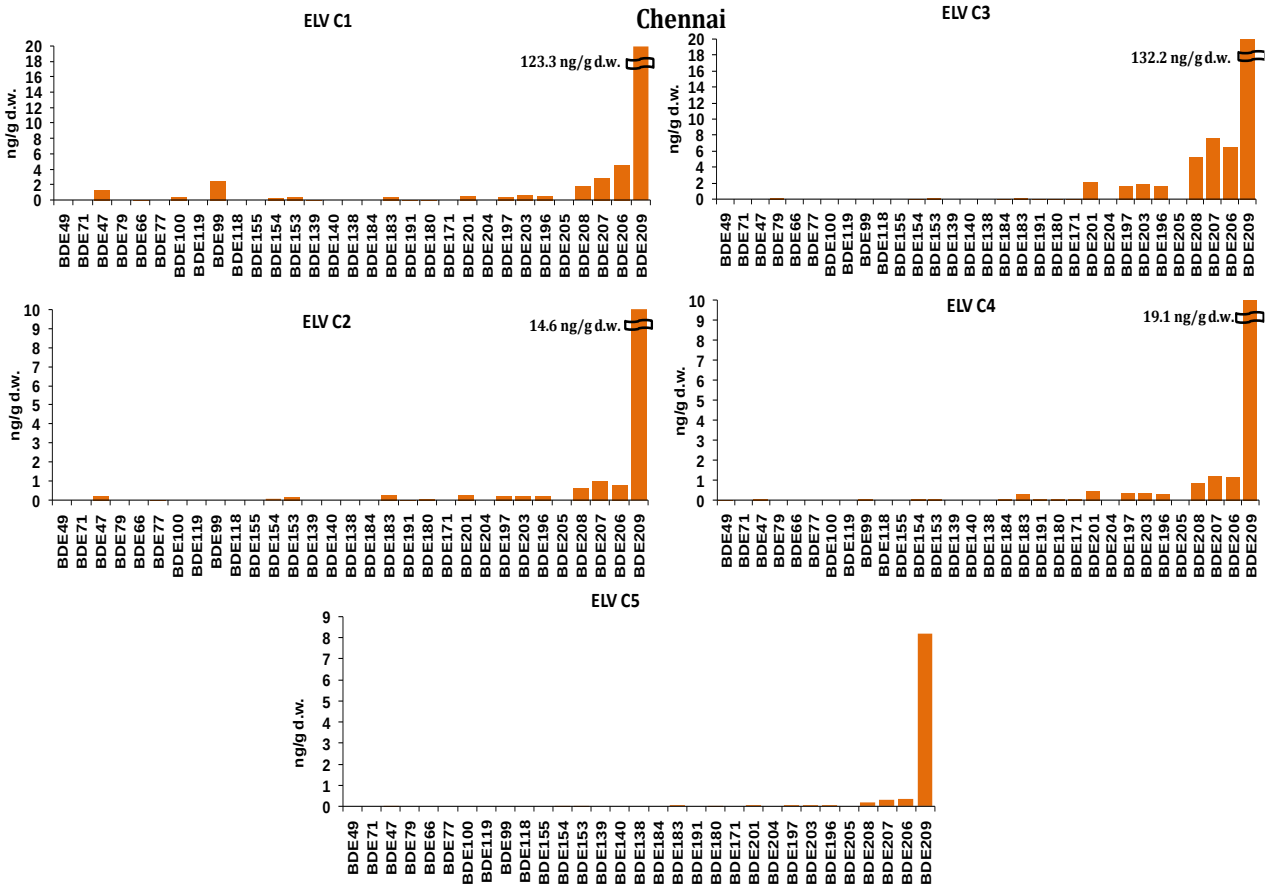


Fig.1 Levels of PBDEs in ELV sites from Chennai city, India

Choi et al.(2017) reported the PBDEs concentration in automobile shredded residues (218 to 2710 mg/kg), seat fabrics (25158 to 65842 mg/kg) and other interior components such as interior light cover, floor cover, and headliner and seat belt (<1 to 10865 mg/kg). PBDEs could be released into the atmosphere in their life cycle, for as approximately 627 ton of PBDEs fromautomobiles were enter into the domestic market through manufacturing (1743 ton), export (119 ton) and import (74 ton). An automobile in use stage had approximately 7748 ton of PBDEs and at the final stage (ELVs) about 285 ton of PBDEs were generated. In incineration approximately 208 ton of PBDEs were released from ELVs, 23 ton of PBDEs in ELVs were emitted inenergy recovery and 16 ton were landfilled. A study conducted in Japan showed high PBDE concentration in interior materails and cabin dust of ELVs results in saet fabrics had PBDEs ranged from

55000 to 78000 mg/kg, likewise seat foam had 52000 mg/kg of PBDEs and other interior components had 6600 to 8200 mg/kg of PBDEs (Kajiwara et al.,2014). The seat fabrics had the predominat level of PBDEs in most of the studies (Choi et al.,2017). Niinipuu, (2013) reported the PBDEs in two samples (Sample A- 1400 mg/kg; Sample B- 570 mg/kg) from ELVs in Sweden.

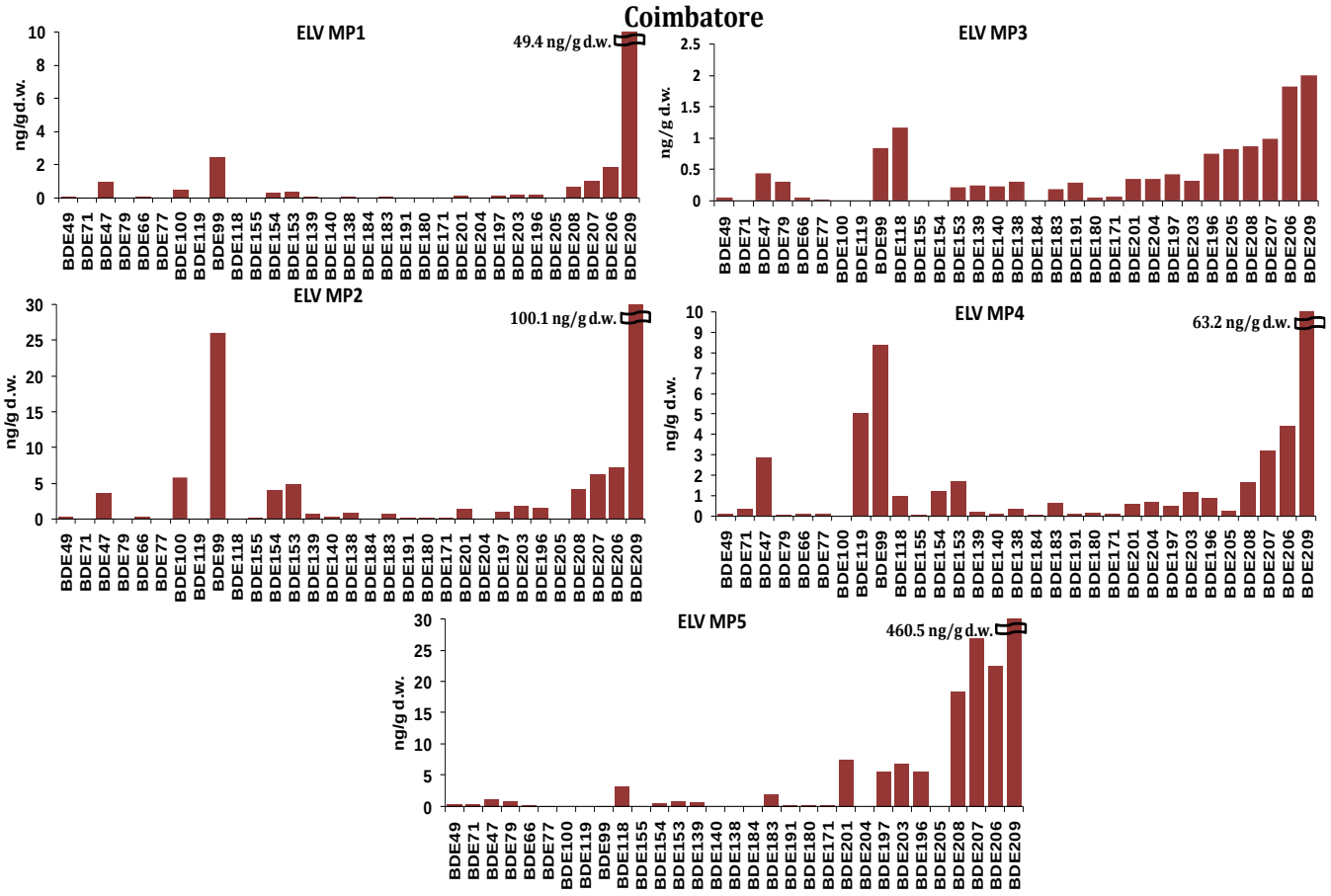


Fig.2 Levels of PBDEs in ELV sites from Coimbatore (Mettupalayam (MP)), India

BDE-209 was found higher concentration at all sampling sites in Chennai (C3-132.2ng/g dw), Coimbatore (MP5-460.5 ng/g dw) and Tiruchirappalli (TPJ1-138.6 ng/g dw), respcetively. In Chennai, higher level of BDE-209 was found at C3 (132.2ng/g dw) followed by C1(123.3ng/g dw); BDE-207 (7.69 ng/g dw) and BDE-206 (6.44ng/g dw) concentration was lower than the BDE-209. Likewise,in Coimbatore except MP3(BDE-206-1.8 ng/g dw) and MP5 (BDE-207-26.8 ng/g dw) the other sampling sites (MP1- 2.4 ng/g dw; MP2- 26.1 ng/g dw and MP4-8.4 ng/g dw) were found with higher BDE-99 concentration however this was lower than that of BDE-209. BDE206 and BDE183 were higher in ELVs from Tiruchirappali, but not higher than BDE-209. TPJ1 (6.5 ng/g dw) and TPJ2 (2.9 ng/g dw) sampling sites showed higher BDE-206

Table 1 Total concentration, Maximum, Minimum, Mean and median of PBDEs in ELV site soils from Tamil Nadu, India

Locations	**Chennai**					**Coimbatore**					**Tiruchirappalli**			
Sample sites	C1	C2	C3	C4	C5	MP1	MP2	MP3	MP4	MP5	TPJ1	TPJ2	TPJ3	TPJ4
ΣPBDEs (ng/g d.w.)	141	19	160	25	9.4	58.2	171.6	13.1	98.7	565.2	162.2	50.7	60.9	39.5
Maximum	123.4	14.6	132.6	19.1	8.2	49.5	100.2	2	63.2	460.5	138.6	34	30	11.5
Minimum	0.04	0.01	0.02	0.02	0.01	0.02	0.05	0.02	0.003	0.14	0.03	0.06	0.09	0.14
Mean±SD	7±27.4	1.2±3.7	10±32.7	1.4±4.4	0.7±2.3	2.8±10.7	6.9±20.2	0.5±0.5	3.3±11.5	24.6±95.3	7.7±30	2.7±7.6	2.3±5.6	1.4±2.3
Median	0.5	0.2	0.9	0.2	0.1	0.2	0.9	0.3	0.5	0.8	0.5	0.8	0.8	0.5

concentration and TPJ3 (5.6ng/g dw) and TPJ4 (5.7 ng/g dw) showed higher BDE-183 concentration next to BDE-209. BDE-209 waspredominatly used congener (≥97%) than other congeners like nano-BDE (0.3-3%). Hence the dis tribution rate of BDE-209 was higher compared to other PBDEs (Penta and octa-BDE) (UNEP, 2014). Debromination of higher brominated congeners results in lower brominated congeners like BDE-47, BDE-183 and BDE-154due to photolytic and thermal debromination.

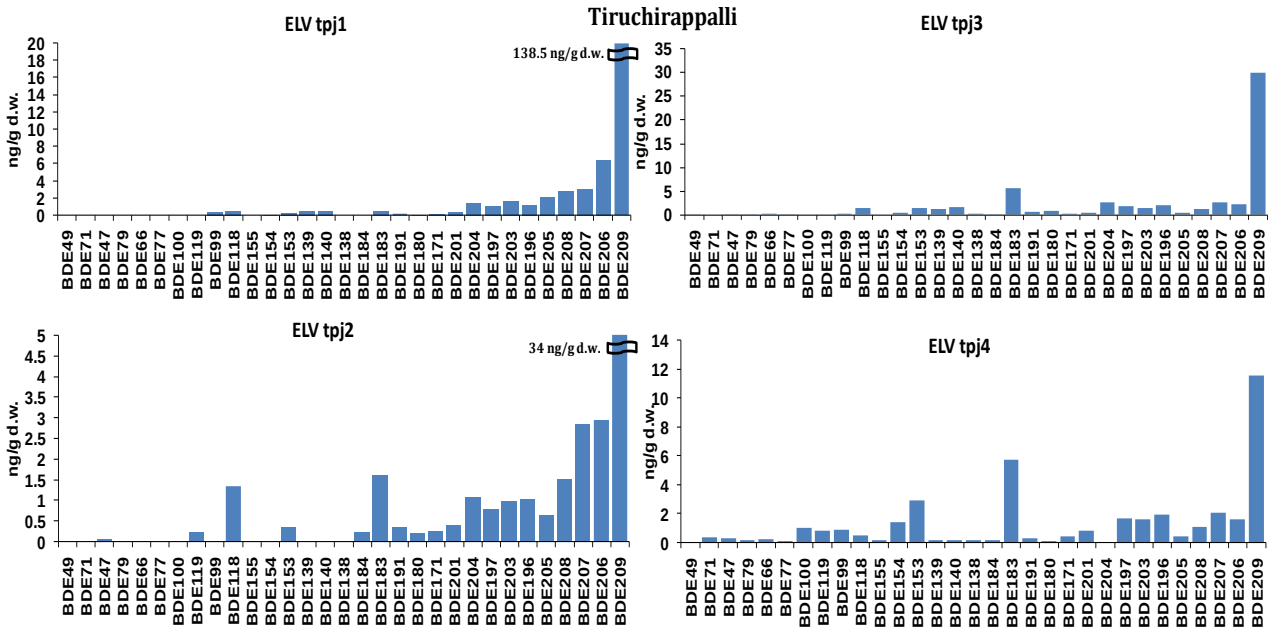


Fig.3 Levels of PBDEs in ELV sites from Tiruchirappalli, India

4.2 Level of PCBs in End of Life Vehicles (ELV) sites in Chennai, Coimbatore and Tiruchirappalli

Concentration of PCBs in soil from Chennai, Coimbatore and Tiruchirappalli were given in Table 2. PCBs concentration in Chennai was ranged from 61.9 to 5429.6 ng/g dw followed by Coimbatore (1.6- 18901ng/g dw) and Tiruchiruppalli (5.2-127.6ng/g dw), respectively. Higher concentration of PCBs was found at C3 in Chennai, MP5 in Cimbatore and TPJ2 in Tiruchirappalli. PCBs are widely used in capacitors, electromagnets and miscellanous electrical equipment, whereas dielectric fluids, hydraulic fluids, break fluid, igition coils and lubricants used to avoid friction inengins. These could be the reason for the higher release of PCBs. The Higher abundance of PCBs at MP5 (18901.4 ng/g dw) (truck engine scraping) may due to the presence of PCB- containing materials like electrical capacitors and transforners. Moreover, some other sources also led to higher amount of PCBs depend upon the PCB usage in closed system, and heat transfer fluids (transformers, capacitors, fluoroscent light ballasts) (60%), plasticizers (25%), hydraulic fluids and lubricants (10%) and miscellanous uses (5%). Followed to Coimbatore, Chennai C3 site had higher PCB concantration, where truck engines were dismandled. Depend upon the activity the contamination level also varied, like MP1 was detected lower PCB concentration because engine spares were stored other than this ELV site in tiruchirappalli had storing and dismandling the vehicle spares. Moreover, coating materials are sources for lower PCB concentration.

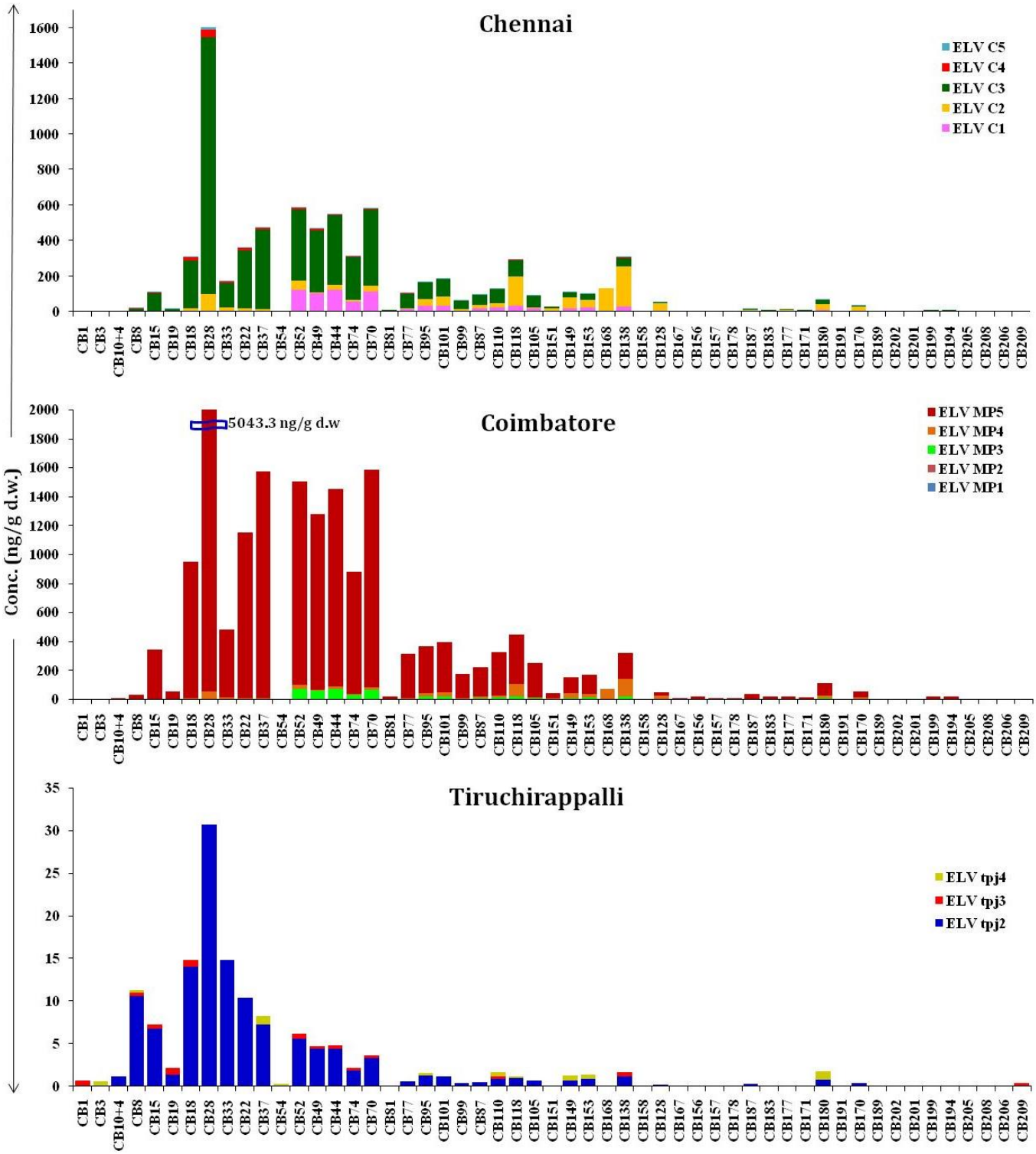


Fig.4 Levels of PCBs in ELV site soils from Chennai, Coimbatore and Tiruchirappalli cities, India

PCBs concentration in floor dust from an informal ELC recycling site in northern Vietnam was ranged from 19 to 2200 ng/g (Takahashi et al.,2016). The author and colleages were found the major groups of PCB homologue profiles were PeCBs and HxCBs, which were found in house dust from the urban site of Hanoi. PCBs were found in different dust samples collected from industrial, urban and rural areas, in this case industrail and urban samples were detected with higher level of PCB concenration than that of rural areas. The reason behid this was samples collected near to diesel engine manufacturing company, central area of the industrail park, comprising numerous factories could results in significantly higher PCB concentration. In Hanoi (Urban area), the samples were collected from the city center with several automobile workshops, and road crossing busy and chotic bus station (Anh et al.,2019). Higher PCB concentratio was reported in the street dusts in the surrounding of the e-waste recycling facility (760-16000 ng/g) and industrail sites (3600-63000 ng/g) in Norh Rhine- Westphalia,Germany (Klees et al.,2017; Klees et al.,2015). These reported concentratio was several order of magnitude higgher than the present study.

Table 2 Total concentration, Maximum, Minimum, Mean and median of PCBs in ELV site soils from Tamil Nadu, India

Locations	**Chennai**					**Coimbatore**					**Tiruchirappalli**		
Sample sites	C1	C2	C3	C4	C5	MP1	MP2	MP3	MP4	MP5	TPJ2	TPJ3	TPJ4
ΣPCBs (ng/g d.w.)	798.3	1243.9	5429.6	159.5	61.9	1.6	3.6	464.8	676.6	18901.4	127.6	6.3	5.2
Maximum	123.5	228.8	1448.7	43.5	14.9	0.2	0.8	71.9	124.5	5043.3	30.7	0.8	1
Minimum	0.1	0.1	0.1	0.3	0.1	0.04	0.1	0.05	0.04	0.5	0.2	0.3	0.2
Mean±SD	23.5±37	31.1±47.7	110.8±234.8	5.7±8.6	2.1±3.2	0.1±0.1	0.3±0.2	13.7±21.5	16.9±26	385.7±817.5	4.4±6.6	0.5±0.2	0.5±0.3
Median	4.4	17	11.7	1.7	0.6	0.1	0.2	2.6	9.2	40.9	1.2	0.4	0.5

The total detected PCBs congeners were 50 out of 56 in Chennai, followed by 51 samples out of 56 in Coimbatore and 20 out of 56 in Tiruchirappalli. PCB-28 was detecd in all the sampling sites at higher concentration followed by PCB37, PCB70, and PCB52 in Chennai and Coimbatore, respectively (Fig 1). This was corroborate with Anh et al.(2019), reported that PCB28 and PCB-52 were significantly more abundant in industrial street dust from Thai Nguyen. Furthermore, PCB28 was the predominant compound inoutdoor dusts from Guangzhou and Hong Kong, China (Wang et al.,2013). The possible source of PCB could be oil leakage in electric equipment and lubricating oils inmotor vehicles (Hoi et al.,2010; Toan et al.,2007). According to Cetin, (2016) and Chakraborty et al.(2016) the six lightly chlorinated congeners (PCB28, PCB52,

PCB44, PCB70, PCB49 and PCB74) were emitted from metallurgical plants in industrail area and the PCBs were used inpaints, surface coatings and plastic additives. Hence, body panels, interior items and frames could release lower level of PCBs.

The PCBs and PBDEs concentration were higher at MP5 sampling site in Coimbatore, the other sites showed different pattern, whereas PCBs and PBDEs concentration were higher at C5 and C3 in chennai. In tiruchirappalli, TPJ2 and TPJ1 showed higher PCBs and PBDEs concentration. Engine scrabing was the major source for PCB and PBDEs contamination in soil from ELVs.

Table.3 Background activity of Soils samples in different ELV sites

S.No	ELV sites	Sample ID	Sources of scrapped vehincels	Date of collection
1	Chennai	CH1	Engine dismantle and dumped	17.09.2018
2		CH2	Lorry engine dismantle and storage	
3		CH3	Large types of truck engine dismantle and oil spilied noticed	
4		CH4	Bus engines was dismantle and spares was dumped	
5		CH5	Bus and Van body scrapped and burned (soil contained some ash)	
6	Coimbatore	MP1	Bunk of car engines are stored	26.08.2018
7		MP2	Car bodies are scraped and dumpped	
8		MP3	Vehicle interior spares are dumped	
9		MP4	Car bodies dismantle and storage	
10		MP5	Truck engines are dismantled and scraped	
11	Tiruchirappalli	TPJ1	Tyres are removed and dumped	16.092018
12		TPJ2	Vehicle interior spares are dismantle	
13		TPJ3	Alloy wheel dismantle and storage	
14		TPJ4	Car engines are dismantled and scraped	

5. List of publication and Conference presentation

5.1 Publications:

1. **K. Vimalkumar**, S. Sangeetha, A. Pugazhendhi (2019). Fate of Triclocarban (TCC) in aquatic and terrestrial systems and human exposure. *Journal of Chemosphere* 230 201-209(**IF 5.108**).

2. R. BabuRajendran, G. Preethi, R.K. Poopal, NishikantPatil 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 15–24(**IF 2.813**).

3. **K.Vimalkumar,** E. Arun, S.Krishna Kumar,R.K. Poopal,N, N,Patil.A.Subramanian,R.BabuRajendran(2018). Occurrence of triclocarban and benzotriazole

ultraviolet stabilizers in water, sediment, and fish from Indian rivers. *Science of the Total Environment*625 1351–1360 (**IF 5.589**).

4. S. Srimurali, S.KrishnaKumar, S.Govindaraj, **K.Vimalkumar**, C.Paromita, R.Babu Rajendran (2017). Evaluating Spatial Distribution and Seasonal Variation of Phthalates Using Passive Air Sampling in Southern India. *Environmental Pollution* 221 407-417 (**IF 5.714**).

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 Presentation:

1. **Vimalkumar K***, Tue Minh Nguyen, Shin Tanabe and Tatsuya Kunisue entitled Contamination levels of PCBs and PBDEs in fresh water fish from Chennai and Bangalore cities in India and their toxicological risk. 39th International Symposium on Halogenated Persistent Organic Pollutants (DIOXIN 2019). (26th – 30th, August 2019) at Kyoto International Conference Center, Kyoto, Japan.

2. Babu Rajendran R, **Vimalkumar K**, Patil Nikhil Nishikant, Arun E and Poopal RK entitled Perfluorinated compounds (PFCs) in Indian environment. 27th Symposium on Environmental Chemistry. (22-25, May 2018) at Okinawa, Japan.

3. **Vimalkumar K*,** Srimurali S, Krishna Kumar S, Govindaraj S, Paromita C, BabuRajendranRentitled Spatial Distribution and Seasonal Variation of Phthalates from atmospheric air using Passive Air Sampler in Southern India. International conference on Biodiversity and Sustainable Resource Management (ICBSRM 2018) (12th – 13th March, 2018) at Madras University, Chennai.

4. **Vimalkumar K***, E. Arun,S. Krishna Kumar, Nikhil NishikantPatil, RK. Poopal and R. BabuRajendranentitled 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.

5. **Vimalkumar K*,** E. Arun,S. Krishna Kumar, Nikhil NishikantPatil, RK. Poopal and R. BabuRajendranentitled Toxicity of metal and metal oxide nanoparticles to the Asian common Toad *DuttaphrynusMelanostictus*. 19th International Conference Symposium on "Pollutant Responses in Marine Organisms" (PRIMO 19). (30th July – 3rd June, 2017) at Ehime University, Matsuyama, Japan.

6. Subramanian A, BabuRajendran R, Takafumi Matsushita, **Vimalkumar K***, Tatsuya Kunisue and Shinsuke Tanabe entitled PCDD/Fs, DL-PCBs and PBDEs in the dumping site soils of

Tiruchirappalli town, South India. 19th International Conference Symposium on "Pollutant Responses in Marine Organisms" (PRIMO 19). (30th July – 3rd June, 2017) at Ehime University, Matsuyama, Japan.

7. **Vimalkumar K***,Govindaraj, S. Krishna Kumar, S. Srimurali, Nikhil NishikantPatil, E. Arun and R. BabuRajendranentitledNonsteroidalanti 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.

8. **Vimalkumar K***, Bhuvaneswari R, Govindraj S, Arun E and BabuRajendran R entitled 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.

9. **VimalkumarK***, Srimurali S, Krishna Kumar S, Govindaraj S, BabuRajendran R entitledDetermination 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.

10. **Vimalkumar.K*** present paper entitled "Study on effect of elevated CO_2 on growth and nutrient accumulation in important indigenous tree species" in International Symposium on Environmental Risk Assessment at Department of Zoology, School of Life Sciences, Bharathiar University, Coimbatore, Tamil Nadu, India (17th – 19th October, 2011)**.**

***Presenter**