

Form 3

Annual Report
LaMer, Ehime University

Date (08.02.2017)

To Director of LaMer

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Include the report on the result of the project/meeting in a separate sheet.

1. Project / Meeting title

Pharmaceutical and Personal Care Products (PPCPs) and Antibiotics in Aquatic ecosystem and Sewage Treatment Plants in South India and their Risk assessment – LC-MS/MS analysis

2. Members of project / meeting

Name	Affiliation	Position	Contribution part
PI Members			
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3 Contents (separate sheets)

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(1) Contents should be written in separate sheet, A4-size.

(2) Contents should be within 5 pages including figures and tables.

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(3) Contents should include "Title, members' names and affiliations, aim, procedure, result, perspectives in future, list of publication/conference presentation".

For category D,

(3) Contents should include "Title of conference, list of presenters and their affiliations, list of participants and their affiliations, aim, contents of presentations and discussions, result, perspectives in future". Attach the copy of additional products, i.e., abstract book and program, if available.

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Annual Report for 2016



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Pharmaceutical and Personal Care Products (PPCPs) and Antibiotics in Aquatic ecosystem and Sewage Treatment Plants in South India and their Risk assessment – LC-MS/MS analysis

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1. Aim:

Recently, the occurrence of “Emerging Contaminants” in the aquatic environment has become a worldwide issue; among these pharmaceuticals personal care products (PPCPs) are of great concern. PPCPs include a diverse collection of chemical substances used for human and animal diseases, as well as disinfectants used as personal care products and household chemicals for improving the quality of life. During the last decade, the focus on environmental research has been partly turned from the conventional priority pollutants to the so-called emerging contaminants among which Pharmaceutical Personal care Products (PPCPs) are particularly one of the most important groups of contaminants of emerging concern. PPCPs are generally only slightly transformed or even unchanged in the wastewater treatment plants (WWTPs) and then enter the aquatic environment. Other possible sources were attributed to the direct input by use of drugs in aquaculture facilities and the indirect input through application of manure during agricultural activities. Release from manufacturing sites, hospitals and nursing homes were other sources of PPCPs. PPCPs have been detected frequently throughout the world. They are of particular concern since some of them are produced and used in large quantities, and several investigations have indicated that many of them cannot be degraded during water treatment process. Many PPCPs 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 trophic levels.

1.1 Objective

1. To gather data on Pharmaceuticals and Personal Care Products (PPCPs) including antibiotics, pharmaceutical drugs and cosmetics in environmental and biotic samples from major cities in India which are contributing such compounds in considerable quantities to the Indian environment and also globally, wherefrom no data is available. The present sampling sites will be Bangalore and Chennai situated in Tamil Nadu, a south Indian state. The samples collected by the PI and also that are now archived at the *es-BANK* of Ehim University will be used.
2. To determine the PPCPs levels in surface water and compare with the concentration levels between the two major cities, Bangalore and Chennai from South India and also to compare the data with other countries' data.
3. Assessment of androgen and estrogen levels that are induced by organic pollutants such as PPCPs, in fresh water fish collected from and near the sampling sites.

2. Procedure:

2.1 Sampling location

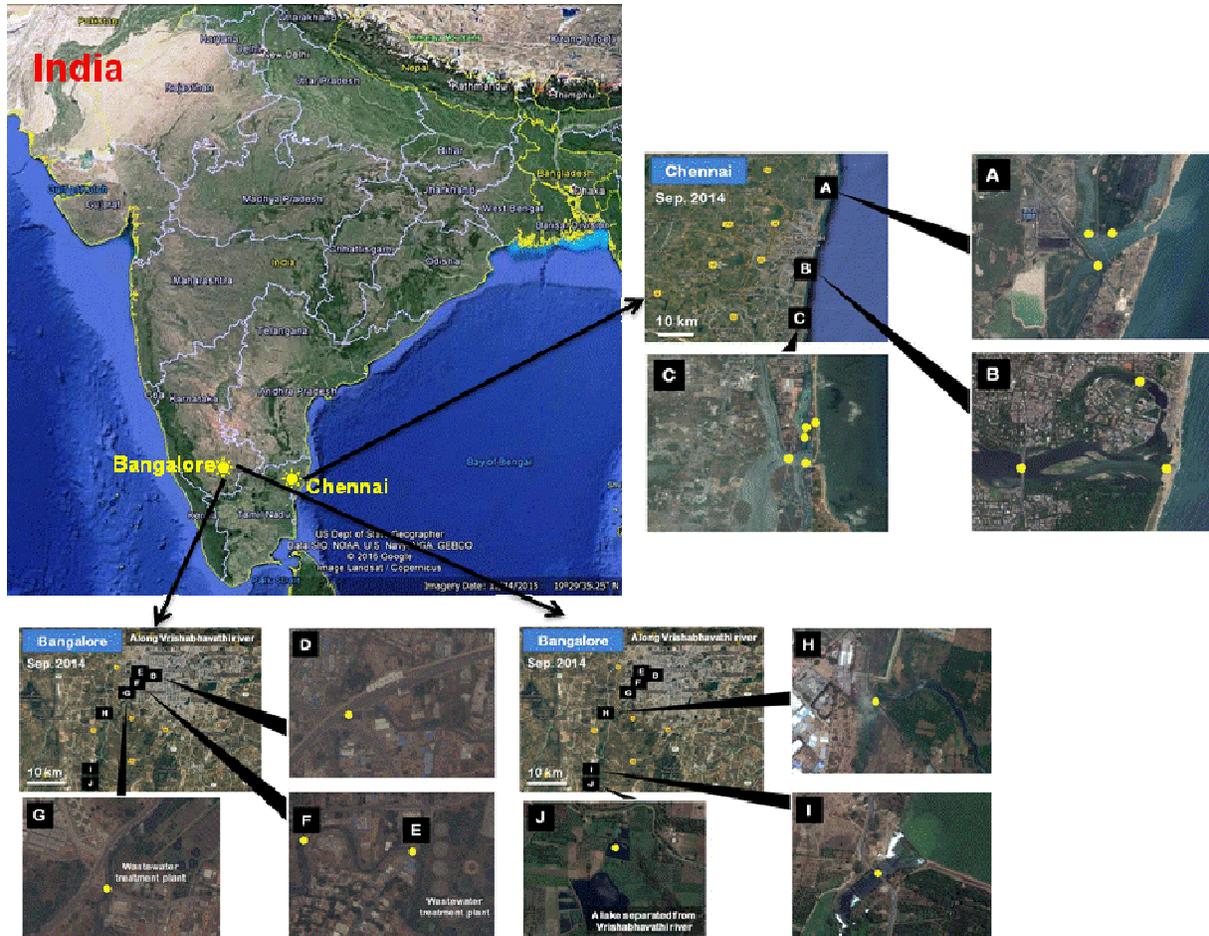


Fig.1: Location of the sampling points

Sample were collected from the Chennai (n=11) and Bangalore (n=8) including waste water treatment plants and an estuary.

Table.1 Target Analytes

S.No	Category of compounds	Name of the compounds	
1	NSAIDs	DF	Diclofenac
2		IND	Indomethacin
3		MF	Mefenamic acid
4		IBP	Ibuprofen
5	Antibiotics	SMXZ	Sulfamethoxazole
6		SMT	Sulfamerazine
7		EM	Erythromycin
8		RM	Roxithromycin
9	Hypertensive agent	DIL	Diltiazem
10		PRP	Propranolol
11		LS	Losartan
12	Antiepileptic agent	CBZ	Carbamazepine
13		HLP	Haloperidol
14	Antihyperlipidemic agent	BZF	Bezafibrate
15	Fenofibrate metabolite	FA	Fenofibric acid
16	Antihistamine agent	DPH	Diphenhydramine
17	Anti-itch agent	CTM	Crotamiton
18	Anticoagulate agent	WAR	Warfarin
19	Antimicrobial agents	TCS	Triclosan
20		TCC	Triclocarban
21	Preservative agents	MeP	Methyl paraben
22		EtP	Ethyl paraben
23		PrP	Propyl paraben
24		BuP	Butyl paraben
25	Insect repellent	DEET	N,N-diethyl-3-toluamide

2.2 Extraction method for Surface water

20 ml of water sample with added internal standard was filtered and the pH was adjusted to be between 6-8. Using solid phase extraction technique water samples were filtered through Oasis HLB cartridge. 3 mL 5% methanol in milli-Q water (7:3) was passed through the cartridge for washing. The sample was concentrated and reconstituted with 2ml of Milli-Q water and the syringe spike was added. Finally samples were injected in to LC-MS/MS.

3. Results and Discussion

3.1 Monitoring of Pharmaceutical Personal Care Products (PPCPs):

Pharmaceuticals were determined in surface water samples from Chennai and Bangalore. Among 20 pharmaceutical drugs tested (Table 1) 16 have been detected (Table 2). Those which were below detection levels were sertaline, nonsertaline, sulfamethazine and sulfamerazine. Mean concentration of the detected chemicals ranged between 400 ng/L and 1100 ng/L. Ibuprofen was detected at high concentration in both cities probably because of anthropogenic activity *via* usage of drugs in the hospitals that related through the sewage water to the rivers. The highest concentrations were 392.7 ng/L at Chennai and 1079.5 ng/L in Bangalore (Fig.2). High concentration in Bangalore may be due to its higher population and more anthropogenic activities. Moreover, Bangalore has many hospitals and other medical facilities, thus having more of pharmaceuticals in its environment. Moreover, the people of Bangalore are more aristocratic using more of personal care products thus increasing their levels in the environment.

Levels of Personal Care Products (PCPs) such as Antimicrobial agents, preservatives and insect repellents were detected at levels 48.8 ng/L, 81.4 ng/L and 152.6 ng/L, respectively at Chennai. At same time, in Bangalore city Triclosan and Triclocarban 592.3 ng/L, Methyl Paraben, Ethyl Paraben, Propyl Paraben and Butyl Paraben were at levels 592.3 ng/L and 101.3 ng/L, 490.4 ng/L, 105 ng/L, 217.5 ng/L and 11 ng/L, respectively. Bangalore has higher levels of detergents, cosmetics, etc. because of their higher usage by the more affluent people there than at Chennai where still people use more of natural products.

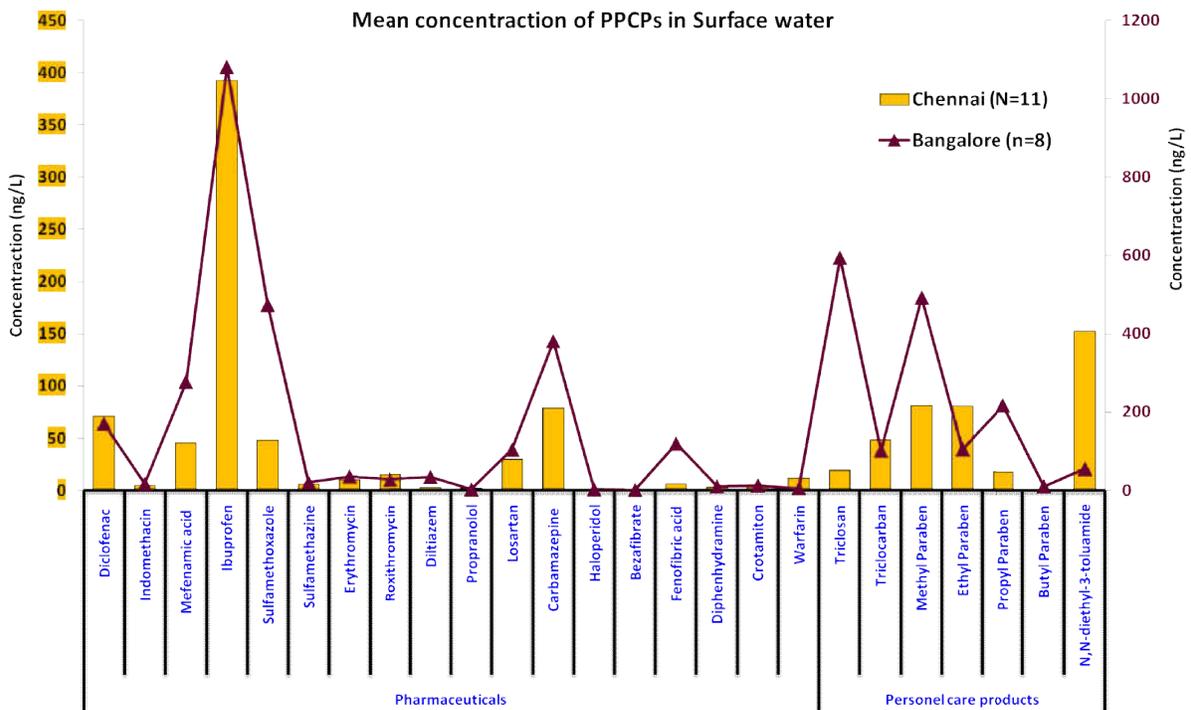


Fig.2. Mean concentrations of PPCPs determined in the surface water samples in South India

Pharmaceutical and personal care products were globally found in the surface and waste water influent and effluent samples at various concentration levels in China, Korea, UK, Romania, Japan, Germany, Italy, etc. (Table.1). Compared with the present study, higher concentrations were observed in UK (surface water) and Germany (influent). It was shown that ibuprofen levels were lower in these cities when compared with both cities of the present study (Chennai and Bangalore) and the levels in other Asian countries such as Korea and Japan are high.

Among the 16 compounds Ibuprofen, Carbamazepine, Mefenamic acid have been observed more because in daily life these drugs are freely available in India and people consume them even for small ailments. Likewise PCPs are used in many cosmetic products especially the Antimicrobial agents (TCC and TCS) and as preservatives (MP, EP, PP and BP). Antimicrobial agents are commonly used in all shampoos, soaps and detergents as ingredients and preservative chemicals are widely added to food materials. According to global data (**Bu et.al, 2013**) mainly surface water samples from China contained such compounds up to milligram levels. For example, the mean levels of personal care products in the present study ranged from ND to 592.3 ng/L whereas in China they were detected up to <LOQ – 2142ng/l (**Bu et.al, 2013**).

Pharmaceuticals (ng/L)																			
Sampling Name	DF	IND	MF	IBP	BZF	FA	DPH	CBZ	HLP	DIL	PRP	LS	CTM	WAR	SMXZ	SMTZ	EM	RM	
Other Countries																			
Surface water, Korea, 2007		ND-33.5	ND-326	ND-414				ND-595			ND-40.1							ND-137	
Surface water, UK, 2004			<50-366	<20-5044							<10-215							<10-1022	
Surface water, Romania, 2003				LOQ-115.2															
Surface water, Italy, 2000				20.0				175.3										4.5	
STP influent, Japan, 2006		45.1	157	339				9.17			1.93								
STP influent, Germany, 2007				3400±1700				2000±1300			510±350							830±270	
Present study (Mean)																			
Coovam River and lake, Chennai, India	71.1	4.8	45.9	392.7	N D	6.3	3.5	79.2	ND	3	2.3	29.8	3.7	11.8	48.6	6	10.7	15.2	
Vrishabhavathi river and WWTP, Bengalore, India	171	17.37	277	1079.5	1	119 .1	10.4	379.7	2.6	34.4	2.2	103.6	12.9	5.3	473	20.6	36.2	28.5	

Table.2 Comparison of Pharmaceutical drugs levels with other countries data

DF- Diclofenac, IND – Indomethacin, MF – Mefenamic acid, IBP – Ibuprofen, BZF – Bezafibrate, FA- Fenofibric acid, DPH – Diphenhydramine, CBZ – Carbamazepine, HLP – Haloperiol, DIL – Diltiazem, PRP – Propranolol, LS – Losartan, CTM – Crotamiton, WAR – Warfarin, SMXZ – Sulfamethoxazole, SMTZ – Sulfamethizole, EM – Erythromycin, RM - Roxithromycin

Table.3 Comparison of PCPs levels with other countries data

Personal Care Products (ng/L)							
Sampling Name	TCC	TCS	MP	EP	BP	PP	DEET
China							
Pearl river, Guangdong, 2008	4.9-155	7.7-218	0.9-66.1	0.2-23.1	<0.1-5.3	1.2-86	
Liuxi river, Guangdong, 2010	<LOQ-13.9	<LOQ-26.2					
Zhujiang river, Guangdong, 2010	4.5-46.2	6.5-31.1					
Shijing river, Guangdong, 2010	68.3-388	90.2-478					
Victoria Harbor, Hong Kong, 2007		31.9-99.3	<LOQ-1062		ND	<LOQ-2142	
Other countries							
Effluent, Spain, 2010			25	40	ND	4.8	
Effluent, Hong Kong, 2011			6.9-7.1	1-1.1	ND	3.3-6.8	
Effluent, France, 2013			10-13	<LOQ-7	<LOQ	<LOQ-6	
Effluent, USA, 2014			0.14-1.73	0.14-1.47	0.36-3.55	0.36-4.90	
River water, Spain, 2011	4	1	119	16	14	145	
Present study							
Coovam River and lake, Chennai, India	48.8	19.4	81.4	80.3	ND	18.3	152.6
Vrishabhavathi river and WWTP, Bangalore, India	101.3	592.3	490.4	105	11	217.5	55.7

TCC – Triclocarban, TCS – Triclosan, MP – Methyl Paraben, EP – Ethyl Paraben, BP – Butyl Paraben, PP – Propyl Paraben, DEET – N, N – diethyl – 3 – toluamide

4. Perspectives for the future:

The present study and the past data clearly indicate the widespread occurrence of PPCPs in Chennai and Bangalore, the two metropolitan cities in southern India. Some of those compounds do occur in higher levels when compared with some other Asian and European countries. Among these two cities, Bangalore, the more aristocratic city with an affluent population has more of many of these compounds than Chennai where the people use more of natural products as preservatives and beauty-care products showing the quality and way of life as one of the major way of entry of such compounds in to the environment and non-target organisms. This indicates the necessity for switching over more to natural products of PPCPs in future and also for continued survey of PPCP chemicals in the entire major cities of India as well as other developing countries wherefrom such data are meagre.

5. List of publication and Conference presentation

5.1 Publications:

1. Srimurali .S, Krishna Kumar, S., Govinda Raj.S, **Vimalkumar.K**, Paromita Chakraborty and *R.BabuRajendran* (2015). Evaluating spatial distribution and seasonal variation of phthalates using passive air sampling in southern India. *Environmental Pollution* 1-11 (**IF. 4.839**).
2. Nikhil Nishikant Patil, S. Krishna Kumar, **K. Vimalkumar**, E.Arun, *Babu Rajendran*, 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

3.

5.2 Conference presentation

1. **K. Vimalkumar**, S. Govindaraj, S. Krishna Kumar, S. Srimurali, Nikhil NishikantPatil, E. Arun and **R. BabuRajendran**. Nonsteroidal anti-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.
2. **Vimalkumar K**, Bhuvaneshwari 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” (12th – 13th January, 2015) at IIT, Madras, Tamil Nadu, India.
3. **Vimalkumar K**, Srimurali S, Krishna Kumar S, Govindaraj S, **BabuRajendran 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 Persistent Organic Pollutants (IEEP-2014) (January 16-17 2014) at CSIR-NEERI, Nehru Marg, Nagpur, Maharashtra, India.
4. **Vimalkumar K**, Buvaneshwaran C. Study on effect of elevated CO₂ on growth and nutrient accumulation in important indigenous in the International Symposium on Environmental Risk Assessment (ISERA - 2011) (17 – 19 October, 2011) at Bharathiyar University, Coimbatore, Tamil Nadu, India