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Heavy metal analysis in selected water bodies of Sivakasi town, Tamil Nadu during different seasons

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Abstract
The present study was undertaken in Periyar colony and Thiruthangal water bodies in Sivakasi town for analysis of seasonal variations in heavy metals such as lead (Pb), cadmium (Cd), silver (Ag) and copper (Cu). Heavy metal analysis was carried out for a period of two years from June 2014 to May 2016 in four seasons as pre-monsoon, monsoon, early post monsoon and late post monsoon. Concentration of heavy metals Pb, Cd, Ag and Cu were determined by continuous flame method using atomic absorption spectrophotometer. High level of Cd was reported in Thiruthangal water body (0.0220 ppm± 0.72) during monsoon season and during late post monsoon (0.2522 ppm ± 1.43) in Periyar colony. High level of Pb was reported during monsoon (0. 0510 ppm ± 0.93) and low during late post monsoon (0. 0089 ppm ± 0.90). High level of Cu was recorded during late post monsoon (0.0116 ppm ± 0.98) in Periyar colony and during pre-monsoon (0.0159 ppm ± 0.45) season in Thiruthangal water body. Our study revealed that, accumulation of heavy metals such as Cd, Ag, Pb and Cu showed slight variation between the years 2014-2015 and 2015-2016. However, concentrations of some metals are higher during summer season. Concentrations of most of heavy metals in water are observed during monsoon season and this may be mainly due to the addition of heavy metals by run off during monsoon season.

Keywords: heavy metals; parameters; pollution; sivakasi; water bodies

1. Introduction
Heavy metals are metallic elements which have high atomic weight and density much greater than water. There are more than 20 heavy metals which affects the environment. In which four heavy metals, lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) are of particular concern to human health. Adsorption and accumulation of these elements depend on their concentration, physio-chemical properties of water, distribution in body and physiological effects of metals [1]. Metals like As, Cd, Pb and methylated mercury have been reported to have no known importance in human biochemistry and physiology, and consumption even at very low concentrations can be toxic. Toxicity of heavy metals cause death of various organisms or it shows effect on development, feeding, activity, reproduction and general physiology [2].
The physical and chemical forms of heavy metals in the fresh water ecosystem are governed by environmental variables such as temperature, salinity, pH, biological activities and metal properties [3]. Bio-accumulation of heavy metals by living organisms is often a good integrative indicator of exposure and has been extensively used to assess contamination levels of heavy metals in polluted ecosystems [4]. Even for those that have bioimportance, dietary intakes have to be within regulatory limits as excess may result in toxicity [5].
People in Tamil Nadu consume a large amount of fishes. Prominent amount of fishes sold in market are captured from local small rivers, dams and other water bodies. Sivakasi is reported to have more number of printing industries, match factories and fireworks factories. It is very likely that the metals present in water of these industrial effluents in and around the water bodies of Sivakasi town may get deposited in sediment and incorporated in the fish and through the food-chain may enter the human and threaten their health. Thus it is very important and urgent to study the level of heavy metal concentration in those edible fishes which are captured from the water bodies of Sivakasi town to meet the requirement of the people of study areas. In view of this, level of heavy metals such as cadmium, silver, lead and copper were analysed for a period of two years in two water bodies (Periyar colony and Thiruthangal) located in Sivakasi town.

2. Materials and Methods
2.1 Study Area and Climatic Conditions
The water bodies selected for the study of heavy metals with reference to seasons are located in and around Sivakasi town, Virudhunagar District, Tamil Nadu, India. The district has a hot tropical climate with a maximum temperature rarely above 43°C and the minimum temperature seldom below 18°C. Sivakasi is a well-known place all over India, since it contributes nearly 90% of the total fireworks products, 70% of the total matches and 60% of the offset and litho printing products in India. In Sivakasi town alone there are nearly 300 fireworks, thousands of litho works and offset units, 750 match units and 80 other industries including textile, dye, printing ink, chemical manufacturing and other industries. Hence these industrial effluents, which are discharged without any treatment, cause environmental degradation.
The depth of each water body is about 12 feet and covered by different types of vegetation and is also being used by the local people for bathing and washing purposes. All the selected water bodies are rainfed and receiving sporadic

rainfall during south-west and north-east monsoons and hold water throughout the year. The average rainfall varies from 20-300 mm per year. The rainfall is confined to the month of October, November and December and is very irregular and uncertain. The study for heavy metal analysis was carried out for a period of two years from June 2014 to May 2015 and June 2015 to May 2016 in four seasons as pre-monsoon (June - August), monsoon (September - November), early post monsoon (December - February) and late post monsoon (March - May).

2.2 Sample Collection
Sites for the collection of water samples are the discharge points of the various industries. Surface water samples were collected using clean plastic container for estimation once in a month at morning hours of the day (~7 AM). The collected water samples were immediately brought to the laboratory for the analysis of heavy metals.

2.3 Analytical Procedure
Experimental samples were digested in a mixture of analytical grade nitric acid and per-chloric acid (2:1 v/v). The volume of digestion mixture was 10 times the sample mass in gram. After digesting the specimens in the mixture, it was kept for overnight at room temperature. The mixture was gradually heated to 2000^0C in a sand bath over a period of 3 hours. Digestion was then continued until no fumes were observed and the mixture became pale yellow. Mixture was then diluted to 25ml with double distilled water and filtered the samples. Blanks (super pure nitric acid and perchloric acid (2:1 v/v) and ultrapure distilled water) and standard (known volume) solutions were run with sample.

Concentration of heavy metals lead (Pb), cadmium (Cd), silver (Ag) and copper (Cu) were determined by continuous flame method using Shimadzu AA-6300 atomic absorption spectrophotometer (AAS). The Cd measurement was carried out at 253.3 nm and the flame type Air-C_2H_2 flame was used. The Cu measurement was carried out at 324.8 nm and the flame type Air-C_2H_2 flame was used. The Pb measurement was carried out at 283.3 nm and the flame type Air-C_2H_2 was used. The Ag measurement was carried out at 213.3 nm and the flame type Air-C_2H_2 flame was used. The major advantage of flame AAS is that, under usual conditions, the relative error is of the order of 1 to 2%.

A calibration curve was created by recording the absorption of monochromatic light by standard solutions. Then, absorption of monochromatic light by each sample was measured and concentration of each metal ion was determined from the calibration curve.

3. Results
3.1 Variations in Heavy Metals Level during 2014-15
The seasonal changes of heavy metals content in Periyar colony and Thiruthangal water bodies located in Sivakasi town during the study period 2014-2015 were enumerated in table 1 and 2 respectively. During monsoon period high level of Cd was reported in Thiruthangal water body (0.0220 ppm± 0.72). In water body of Periyar colony, high level of Cd was reported during late post monsoon (0.2522 ppm ± 1.43) and low level during early post monsoon (0.0047 ppm ± 0.78). In Thiruthangal water body, low level of Cd was reported during early post monsoon (0.0044ppm ± 0.26) and high during late post monsoon (0.3793 ppm ± 0.26).

The low Pb level was reported in Periyar colony water body (0.0122 ppm ± 0.67) during late post monsoon. The low level of Pb was reported in in Thiruthangal water body (0.0070ppm ± 0.34) during late post monsoon. In Periyar colony water body, high level of Pb was reported during monsoon period (0. 0510 ppm ± 0.93) and low during late post monsoon (0. 0089 ppm ± 0.90). In Thiruthangal water body, high level of Pb was reported during pre-monsoon period (0. 1223 ppm ± 0.43) and low during late post monsoon (0. 0089 ppm ± 0.90).

During early post monsoon concentration of Cu was observed as low in Periyar colony water body (0.0026 ppm ± 0.78) and high level during late post monsoon (0.0116 ppm ± 0.98). In Thiruthangal water body, high level of Cu was reported during pre-monsoon (0.0159 ppm ± 0.45) and low during early post monsoon period (0.0046ppm ± 0.53). The high level of silver was reported in Thiruthangal water body during pre-monsoon period (0.0329 ppm ± 0.78).

Table 1: Seasonal variations of heavy metals in selected water body of Periyar colony, Sivakasi town during different seasons of 2014-2015

Heavy metals analysed	Study seasons			
	Premonsoon	Monsoon	Early post-monsoon	Late post-monsoon
Cadmium (ppm)	0.0192± 0.32	0.0216± 0.49	0.0047± 0.78	0.2522± 1.43
Silver (ppm)	0.0249± 0.53	0.0112± 1.24	0.0210± 0.76	0.0116± 0.65
Lead (ppm)	0.0122± 0.67	0.0510± 0.93	0.0355± 0.82	0.0089± 0.90
Copper (ppm)	0.0028± 0.67	0.0090± 1.87	0.0026± 0.78	0.0116± 0.98

Pre-monsoon - June to August, 2014; Monsoon - September to November, 2014; Early post-monsoon - December to February, 2015; Late post-monsoon - March to May, 2015

Table 2: Seasonal variations of heavy metals in selected water body of Thiruthangal near Sivakasi town during different seasons of 2014-2015

Heavy metals analysed	Study seasons			
	Premonsoon	Monsoon	Early post-monsoon	Late post-monsoon
Cadmium (ppm)	0.0167± 0.46	0.0220± 0.72	0.0044± 0.26	0.3793± 0.26
Silver (ppm)	0.0329± 0.63	0.0163± 0.57	0.0214± 0.98	0.0251± 0.54
Lead (ppm)	0.1223± 0.43	0.0969± 0.76	0.0666± 0.67	0.0070± 0.34
Copper (ppm)	0.0159± 0.45	0.0120± 0.75	0.0046± 0.53	0.0129± 1.37

3.2 Variations in Heavy Metals Level during 2015-16

The seasonal changes of heavy metals content in Periyar colony and Thiruthangal water bodies located in Sivakasi town during the study period 2015-2016 were enumerated in table 3 and 4 respectively. During early post monsoon, high concentration of Cd has been observed in Periyar colony water body (0.0287ppm ± 0.70). In Periyar colony water body, high level of Cd was reported during late post monsoon (0.0384 ppm ± 0.56) and low during monsoon period (0.0089 ppm ± 0.86). In Thiruthangal water body, high level of Cd was reported during post monsoon (0.0433 ppm ± 1.37) and low during monsoon (0.0070 ppm ± 0.90).

During monsoon season, high level of Ag was reported in Thiruthangal water body (0.0251 ppm ± 0.18). In Periyar colony water body, high level of Ag was reported during early post monsoon (0.0634 ppm) and low during monsoon (0.0116 ppm ± 0.65). In Thiruthangal water body, high level of Ag was reported during early post monsoon (0.0799 ppm ± 1.70) and low during monsoon period (0.0251 ppm ± 0.18).

The low level of Pb was reported in Periyar colony water body (0.0119 ppm ± 0.33) during pre-monsoon period. During pre-monsoon period, high level of Pb was reported in Thiruthangal water body (0.1241 ppm ± 0.45) and low in Periyar colony water body (0.0119 ppm ± 0.33). In Periyar colony water body, high level of Pb was observed during early post monsoon (0.3544 ppm ± 0.76) and low during pre-monsoon (0.0119 ppm ± 0.33). In Thiruthangal water body, high level of Pb was observed during monsoon (0.3793 ppm ± 0.56) and low during pre-monsoon (0.1241 ppm ± 0.45).

Low level of Cu was reported in Periyar colony water body (0.0025 ppm ± 0.26) during pre-monsoon period. In Periyar colony water body, high level of Cu was reported during late post monsoon (0.2203ppm ± 0.72) and low during pre-monsoon (0.0025ppm ± 0.26). In Thiruthangal water body, high concentration of Cu was reported during late post monsoon (0.1831ppm ± 0.62) and low during monsoon (0.0129ppm ± 0.32).

Table 3: Seasonal variations of heavy metals in selected water body of Periyar colony, Sivakasi town during different seasons of 2015-2016

Heavy metals analysed	Study seasons			
	Premonsoon	Monsoon	Early post-monsoon	Late post-monsoon
Cadmium (ppm)	0.0196± 1.10	0.0089± 0.86	0.0287± 0.33	0.0384± 0.56
Silver (ppm)	0.0240± 1.34	0.0116± 0.34	0.0634± 0.57	0.0551± 0.70
Lead (ppm)	0.0119± 0.33	0.2522± 0.87	0.3544± 0.76	0.2816± 1.27
Copper (ppm)	0.0025± 0.26	0.0116± 0.62	0.0044± 0.55	0.2203± 0.72

Table 4: Seasonal variations of heavy metals in selected water body of Thiruthangal near Sivakasi town during different seasons of 2015-2016

Heavy metals analysed	Study seasons			
	Premonsoon	Monsoon	Early post-monsoon	Late post-monsoon
Cadmium (ppm)	0.0169± 0.28	0.0070± 0.90	0.0232± 0.53	0.0433± 1.37
Silver (ppm)	0.0320± 0.85	0.0251± 0.18	0.0799± 1.70	0.0493± 1.25
Lead (ppm)	0.1241± 0.45	0.3793± 0.56	0.1636± 0.43	0.2721± 0.78
Copper (ppm)	0.0160± 0.23	0.0129± 0.32	0.0177± 0.36	0.1831± 0.62

4. Discussion

In the present study, seasonal changes of heavy metals such as cadmium, silver, lead and copper for a period of two years (2014-2015 & 2015-2016) in two water bodies located in and around Sivakasi town were studied. Heavy metals are the natural components of the Earth's crust, they cannot be degraded or destroyed and dangerous, because they tend to bio-accumulate. It can be enter to a water supply by industrial and consumer waste or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater.

Cadmium (Cd) has carcinogenic properties as well as a long biological half-life leading to chronic effects as a result of accumulation in the liver and renal cortex [6]. It can also cause kidney damage and produce acute health effects resulting from over exposure to high concentrations. Chronic exposure to low doses of cadmium causes damage to the renal tubules, followed by proteinuria, pulmonary lesions and arterial hypertension [7]. It stated that, Cd was highly accumulated during late monsoon period and low in monsoon period. Cd can be considered as most poisonous high weight elements, it is found widely in nature and present in air, all soils and aquatic systems. Considerable amount of Cd get continuously flowed in water bodies due to anthropogenic activities. Concentration of Cd was high during post monsoon season at Coromandel Coastal region of Bay of Bengal [8].

According to the results of present study, Ag was mostly accumulated during pre-monsoon period in two study sites during 2014-2015 and it was high during post late monsoon in 2015-2016, but it was low as compared to the study period 2014-2015, because of seasonal variation like high rainfall or less pollutants. In general, metal concentrations were highest in early rainy season, next highest during dry season and lower in late rainy season. In general, levels of Pb in drinking water are low, normally in the range of 10-20 µg/L. In places where water is extremely soft, has acidic pH and Pb plumbing and lead-lined storage tanks are commonly used and concentrations of Pb can be as high as 300µg/L [9]. Pb in environment exists almost in inorganic form except small amounts of organic Pb which results from the use of leaded gasoline and from natural alkylation processes that produce methyl lead compounds. Lead is a commutative poison and a possible human carcinogen [10].

It revealed that higher concentration of Pb was observed during early post monsoon period. From the results of present investigation, it was revealed that high level of Pb was

observed during the early post monsoon period of 2015-2016 than the period of 2015-2016. It indicates that concentration of Pb was increased due to human activities. Common sources of Pb are mainly from mining and industrial wastes, vehicles emission, lead-acid batteries, fertilizers, paints, treated woods, ageing water supply infrastructure. Copper is an essential element for plants and animals [11]. So plants and animals must absorb Cu by eating, drinking and breathing. Copper sulfate use represents 13% of releases to water and urban runoff contributes 2% [12]. In the absence of specific industrial sources, runoff is the major factor contributing to elevated Cu levels in river water as well as other water bodies [13]. Domestic waste water is the major anthropogenic source of Cu in waterways [14]. The toxicity of copper depends on alkalinity of water.

Although Cu is an essential nutrient to humans, its presence in high concentration in drinking water is indicated to cause liver cirrhosis in patients, anemia, liver and kidney damage. The results of present study indicated that highest concentration was monitored during late post monsoon season. Comparison between the study period of 2014-2015 and 2015-2016, concentration of Cu was high in early post monsoon during both study periods. But in 2014-2015, more amount of Cu was recorded than in 2015-2016 because of the accumulation of firearms training grounds.

5. Conclusion

The present study revealed that, accumulation of heavy metals such as Cd, Ag, Pb and Cu showed slight variation between the years 2014-2015 and 2015-2016. Heavy metals can enter into water via drainage, atmosphere, soil erosion and all human activities by different ways. With increasing heavy metals in the environment, these elements enter the biogeochemical cycle and they enter from contaminated water into fish body by different routes and accumulate in them. It is observed that there is no much seasonal variation in concentrations of heavy metals in fish samples. However, concentrations of some metals are higher during summer season. Concentrations of most of heavy metals in water are observed during monsoon season and this may be mainly due to the addition of heavy metals by run off during monsoon season. Concentrations of heavy metals in sediment are also observed during post-monsoon season and this may be due to deposit of heavy metals from the water.

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