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Empreinte géochimique urbaine dans la mégapôle de Chennai sur les sédiments de rivière : gradient amon-aval, sources et résilience

Geochemical urban footprint of Chennai megacity onto river sediment: upstream – downstream gradient, sources and resilience

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Résumé en français

Les zones urbaines sont des lieux importants pour le développement de la culture, de la société et de l'économie des sociétés. Les mégapôles au développement rapide sont fortement touchées par de multiples sources de contamination, les effets de cette pollution se superposant dans l'espace et dans le temps.

En Inde, il y a de nombreux réseaux fluviaux urbains qui approvisionnent en eau une immense zone de service. Au cours des dernières décennies, l'explosion industrielle et la surpopulation humaine ont aggravé l'état écologique des cours d'eau. Ces réseaux fluviaux sont donc menacés par l'urbanisation et l'industrialisation, parfois de manière irréversible. Ils doivent donc être protégés pour assurer la ressource en eau nécessaire aux générations futures.

La gestion de l'eau dans les mégapôles est donc un défi mondial majeur. La seconde révolution industrielle a entraîné une dégradation majeure des plans d'eau, de sorte que les années 1970 sont la décennie la plus polluée de l'histoire de l'Europe occidentale et de l'Amérique du Nord. Aujourd'hui, les pays émergents sont confrontés au même problème, amplifié par une démographie exceptionnelle : les fleuves urbains des grandes mégapoles indiennes sont parmi les plus pollués au monde mais peu d'études scientifiques ont permis de préciser (i) les niveaux de contamination, (ii) la nature des traceurs d'une activité urbaine, (iii) les niveaux de perturbateurs endocriniens et (iv) l'empreinte géochimique de la ville sur les ressources en eau. Ces travaux de recherche sont particulièrement novateurs puisque c'est la première fois que de nouveaux indices sont mis en œuvre pour expliquer la pollution des eaux de surface en Inde. D'autre part, une comparaison unique est faite avec d'autres mégapoles où les niveaux de pollution ont été étudiés. Cette recherche est originale et souligne la question de l'astysphère et de l'empreinte géochimique des villes sur les ressources naturelles.

Dans cette étude, l'état actuel de la pollution des rivières Adyar et Cooum (Chennai – Inde), a été déterminé. Ce sont les deux rivières importantes parmi les six

voies navigables principales de cette mégapole du Tamil Nadu qui a connu une urbanisation importante au cours des trois dernières décennies. La population urbaine métropolitaine de Chennai est de plus de 10,26 millions de personnes au début de 2017 (Demographia, avril 2017). La caractérisation des sources et le transfert des contaminants dans ces 2 systèmes fluviaux a été entreprise, l'objectif principal étant d'établir l'empreinte géochimique des mégapoles sur les sédiments fluviaux. La caractérisation amont - aval du système fluvial, y compris l'influence des apports par les drains urbains a été menée. De nombreuses causes peuvent être attribuées à l'état actuel des rivières, telles que l'explosion de la population, le rejet direct des eaux usées domestiques non traitées et les effluents industriels, la formation de barres de sable à l'embouchure de la rivière, etc.

Un échantillonnage très resserré des sédiments de surface et des laisses de crue a été effectué à plus de 18 stations dans les deux rivières et 6 grands canaux. Les sédiments ont été prélevés à une profondeur de 0 à 15 cm à l'aide d'un dispositif de carottage Uwitec en février 2015 et 2016 (avant et après l'inondation centennale de 2015). Les échantillons ont été prélevés de l'amont vers l'aval, les sites ayant été choisis en fonction des sources ponctuelles potentielles (effluents industriels et urbains) et de leur accessibilité. Les échantillons ont été immédiatement transférés dans des sacs plastique à l'aide d'une pelle en plastique et stockés à 4ºC dans une glacière. En laboratoire, après avoir enlevé les fragments de coquilles et organismes visibles, les sédiments ont été séchés à 60ºC dans un four bien ventilé. Les concentrations de plusieurs éléments traces ont été déterminées dans la fraction sédimentaire inférieure à 63 µm. Ces échantillons ont été analysés pour les éléments traces et les composants organiques au laboratoire national CNRS-SARM, à Nancy (France) et au laboratoire LERES de Rennes (France) respectivement.

Les concentrations en éléments traces (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) ont été évaluées à l'aide de l'indice de géoaccumulation (I_{geo} ; Muller 1969) et du nouvel indice d'empreinte géochimique urbaine (GUFI - geochemical urban footprint index). La qualité des sédiments de Chennai a également été comparée à la pollution de mégapoles mondiales à l'aide des recommandations pour la qualité des sédiments

(Sediment Quality Guideline) et un nouveau classement des mégapôles par leur niveau de pollution a été établi. De même, les composants organiques des sédiments fluviaux étudiés ont été estimés à l'aide de rapports de concentrations des hydrocarbures aromatiques polycycliques (HAP) et des Polychlorobiphényles (PCB), polybromodiphényléthers (PBDE) et les phtalates ou alkylphénols. Les résultats sont discutés de façon générale dans trois chapitres pour définir le plus globalement possible ce que peut être l'empreinte géochimique urbaine.

Les résultats de l'index de géoaccumulation indiquent que les concentrations d'éléments traces de sédiments dans les rivières de Chennai sont fortement polluées. Des traceurs comme l'argent (Ag), le cadmium (Cd) et le mercure (Hg) sont les plus pertinents pour établir le gradient spatial de la contamination urbaine (Saravanan et al., 2015 ; 2019 soumis). La présence de concentrations de chrome (Cr) confirme une contamination par les tanneries qui inclut d'autres éléments traces tels que As, Cu, Ni, Pb et Zn dans la mégapole de Chennai. Les résultats de l'index GUFI varient d'un niveau de contamination modérée à extrême, en particulier dans les tronçons en aval des deux rivières. Cette tendance spatiale est liée à diverses pollutions ponctuelles qui sont identifiées à des stations d'échantillonnage précises et à l'absence de zones tampons identifiables (Desmet et al., 2018). Selon la comparaison mondiale des polluants dans les mégapoles, Chennai est classé cinquième.

Concernant les données de contaminants organiques, seules les concentrations en HAP sont quantifiées. Les concentrations de HAP augmentent depuis l'amont vers l'aval pour les deux rivières. La concentration totale des Σ13 HAP dans les sédiments de la rivière Cooum est supérieure à celle de la rivière Adyar, ceux de poids moléculaires plus élevés (4 à 6 cycles) étant plus prédominants dans les sédiments que ceux de poids moléculaire faible (moins de 3 cycles). Considérant différents rapports de HAP tels que FLA/(FLA+PYR), ANT/(ANT+PHE), BaA/(BaA+CHR) et IcdP/(IcdP+ BghiP) , les sources sont multiples telles que les émissions des véhicules et combustion d'herbe, de bois et de charbon. Les concentrations en PCB, PBDE et phtalates sont très faibles voire inférieures aux

limites de détection sauf pour le PCB 101 et les phtalates (DiNP et DBP) dans quelques échantillons.

La mousson exceptionnellement intense de décembre 2015 a déclenché d'énormes inondations à Chennai. Le bassin urbain de Cooum a été inondé et le niveau d'eau de la rivière Adyar a augmenté en raison d'un rejet élevé d'un grand réservoir situé en amont. La qualité des sédiments de février 2016 a été comparée à celle de février 2015 pour comprendre la résilience des rivières après de telles inondations. Les résultats de l'index de géoaccumulation calculé sur les sédiments post-mousson révèle que les concentrations en éléments traces sont similaires qu'avant l'inondation de 2015 en amont d'Adyar et en aval de Cooum. Toutefois, le niveau de pollution pour le cadmium (Cd) et le mercure (Hg) a significativement diminué, passant d'extrême à modéré en aval de la rivière Adyar. Selon le GUFI, les stations en amont des deux rivières sont trés peu contaminées alors que les stations en aval ont une contamination modérée dans la rivière Adyar et une contamination forte à élevée dans la rivière Cooum.

Pour les HAP, la diminution de leurs concentrations est bien marquée en aval des deux rivières par rapport à la campagne de 2015. Les différents rapports de HAP montrent que le risque a été réduit après la mousson de 2015. Pour les PCB, ils sont uniquement détectés dans les stations aval de la rivière Cooum en raison du niveau plus élevé d'activités commerciales, résidentielles et industrielles. Pour les phtalates, les concentrations en DEHP sont 16 fois plus élevées et celles du DiNP 5, cinq fois plus par rapport aux niveaux de 2015 avant la mousson en aval de la rivière Adyar. Les PBDE ne sont détectés nulle part dans les rivières de la mégapole de Chennai.

Mots clés : mégapole, sédiments, métaux lourds, activité urbaine, contamination, perturbateurs endocriniens.

Abstract

Urban areas are extremely important for the development of culture, society and economy. Fast developing cities are highly affected by multiple sources of contamination, the effects of these pollution overlap in space and time. In India there are many urban river systems supplying water to huge service area. In the recent decades due to the industrial explosion and human overpopulation has aggravated pollution. These hydrosystems are in endangered situation including the impact on the ecosystem in those rivers. Urbanisation and industrialization put deep and irreversible impact on aquatic systems. These aquatic systems need to be protected for sustainability of future generation.

The management of water resources in megacities is a major global challenge. In the western world, the second industrial revolution led to a major degradation of the water bodies so that the 1970s is the most polluted decade in the history of western Europe and the North America. Today, emerging countries are facing the same problem, amplified by exceptional demography : since then, the urban rivers of the great Indian megacities have become the most polluted in the world and it is necessary to outline (i) the contamination levels, (ii) the most present trace elements, (iii) the tracers of an urban activity, (iv) endocrine disruptor levels and (v) the geochemical footprint of the city onto the water resources. This research is particularly innovative since it is the first time that new indexes have been implemented to explain the pollution of water bodies in India. On the other hand, a unique comparison is made with other megacities where the pollution levels in water bodies have been investigated. This research is particularly original and highlights the issue of the astysphere and the geochemical footprint of cities on natural resources

In this study an attempt is made to ascertain the present pollution status of the Adyar and Cooum rivers, which are two important rivers among the six main waterways in the megacity of Chennai, Tamil Nadu, India. This megacity has experienced extensive urbanisation over the last three decades and provoked serious concerns in modifying the chemical composition of a river system / water bodies. The

Chennai metropolitan urban population has crossed, over 10.26 million in early 2017 (Demographia, April 2017). An intensive study is also conducted to find out the sources and transfer of the pollution by trace elements and organic component across the river stream. The main aim of this study is to be establish a Geochemical footprint of megacities onto river sediments using an upstream-downstream characterization of the fluvial system, including influents and drains of identifying potential agricultural, industrial and urban sources of incoming pollution. Many reasons can be attributed to the present condition of the river such as population explosion, discharge of untreated domestic sewage and industrial effluents, sand bar formation at the river mouth etc.

An intensive surface sediment and flood deposit survey was carried out over 18 locations from both rivers and 6 locations from some major drains. The sediment samples were collected at a depth of 0 – 15 cm using uwitec coring device during the February post monsoon season of 2015 and 2016 (before and after the 2015 flood). The samples were retrieved from upstream to downstream and sampling sites were selected on the basis of potential point sources (industrial effluents and urban sewages) and accessibility. The samples were immediately transferred to plastic-sealed bags using plastic scoop and stored at 4ºC in an icebox. In the lab, after removing the coarse shell fragments and visible organisms, sediments were dried at 60ºC in a well-ventilated oven. Concentrations of multi trace elements were determined in sediment fraction of <63 µm. These samples were analysed for the trace elements and organic components at the national CNRS-SARM laboratory, Nancy, France and LERES laboratory Rennes, France.

The trace element concentrations (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) for Chennai megacity were assessed using the geoaccumulation index (I_{geo}) (Muller 1969) and the new Geochemical Urban Footprint Index (GUFI). The sediment quality of Chennai was also compared to worldwide megacity pollution using Sediment Quality Guidelines (SQGs) and a new megacity pollution ranking was determined. Similarly, the organic components of the river sediments were estimated using diagnostic ratios of Polycyclic Aromatic Hydrocarbons (PAHs) and other endeavor source levels by Polychlorinated Biphenyls (PCBs), Polybrominated Diphenyl Ethers (PBDEs) and

phthalates or Alkylphenols. The results are discussed broadly in to three components such as geochemical urban Footprint, endocrine disruptor occurrence and influence of 2015 flood hazard.

The I_{geo} results indicate that the trace element concentrations of sediment in Chennai Rivers are polluted strongly to extreme. The tracers such as silver (Ag), cadmium (Cd) and mercury (Hg) are the most significant tracers of urban contamination (Saravanan *et al.* 2015 & 2019). The presence of chromium (Cr) concentrations confirms an industrial contamination which includes other trace elements such as As, Cu, Ni, Pb and Zn in the Chennai megacity rivers. The GUFI result ranges from moderate to extreme contamination, particularly in the downstream stretches of the two rivers. This spatial trend is related to various point source pollutions which are identified at specific sampling stations and a lack of identifiable buffer zones (Desmet *et al.* 2018). According to the worldwide comparison of pollutants in megacities, Chennai is ranked fifth.

The endocrine disruptors result shows that the concentration varies less to high from upstream to downstream station of both rivers. The total sediment concentration of Σ13 PAH in Cooum River is more than the river Adyar. The higher molecular weights of PAHs (4-6 rings) were more predominant in the sediment sample than the Lower molecular weight of PAHs (3 rings). Considering the different diagnostic ratios of PAHs (such as FLA/(FLA+PYR)), (ANT/(ANT+PHE)), (BaA/(BaA+CHR)) and (IcdP/(IcdP+ BghiP))) revels that the sediments samples were likely attribute mixed pyrogenic sources (vehicular emission and grass, wood and coal combustion) in downstream of both rivers. Similarly, PCBs and phthalates concentration in sediments are found to be very low or below the detection limits as per the international standards, except PCB 101 and phthalates (DiNP and DBP) are found in few sediment samples. Also, PBDEs concentrations are not detectable in the sediment samples from both rivers.

The unusually intense monsoon in December 2015 triggered huge flood events in Chennai. The Cooum urban basin was flooded and water level of the Adyar River increased due to high discharge from a major upstream reservoir. The February

2016 sediment survey was compared to the previous survey in February 2015 to understand the resilience of rivers after the flood events. The I_{geo} result of 2015 post flood reveals that the sediment concentrations in sampling stations are same as before the 2015 flood in upstream of Adyar and downstream of Cooum. However, the cadmium (Cd) and mercury (Hg) pollution level is decreased from extreme to moderate in the downstream of river Adyar and silver (Ag) in the upstream of river Cooum (Saravanan *et al.* 2017). According to the GUFI, the upstream stations of both rivers have extremely low contamination, downstream stations have moderate contamination in Adyar river and strong to high in Cooum river (Saravanan *et al.* 2018). This spatial trend is related to availability or non-availability of open lands within the urban area.

Similarly, the endocrine disruptor of PAHs shows that the decline in concentrations of sediments in the downstream of both rivers when compared to pre-flood of 2015 which is due to the tidal influence. The diagnostic source ratio of PAHs comparison of 2015 flood hazard on river sediment pollution and toxicity level are reduced. Correspondingly, PCBs congeners are not deducted in Adyar river and detected in downstream stations of Cooum river due to higher level of commercial, residential / industrial activities. Also, phthalates congeners of DEHP is increased 16 times and DiNP 5.5 times than the 2015 pre-flood levels in downstream station of Adyar river and the sediment concentration of PBDEs congeners are not detected anywhere in the rivers of Chennai megacity. This study concludes that the developed new GUFI is useful to quantify the pollution severity status of any Megacity river over the I_{geo} which is influenced by the emerging contamination due to urbanisation.

Keywords : geochimistry, megacity, sediments, urban activity, contamination, endocrine disruptor.

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CHAPTER 1

INTRODUCTION



Outline of the river quality in Chennai megacity

CHAPTER 1
INTRODUCTION

1.1 GENERAL

Rapid urbanization and industrial development over the past four decades have impacted in waterbodies, especially in megacities (Miguel *et al.* 2005; Lyons & Harmon 2012; Giri *et al.* 2013; Shafie *et al.* 2014; Yoshimura *et al.* 2014; Islam *et al.* 2015). Large towns and cities affect the natural landscape (Miguel *et al.* 2005; Khadse *et al.* 2008; Mohiuddin *et al.* 2011; Lyons & Harmon 2012). Fast developing cities are affected by multiple sources of contamination, the effects of these pollution overlap in space and time. Urbanization and industrialization put deep and irreversible impact on our aquatic systems (Kaushik *et al.* 2009). In urban areas, anthropogenic activities are continuously modifying the chemical composition of river systems. Urban rivers are an important part of the urban system, which act as a carrier of pollutants that transfer into the surrounding environment. With population increase and the urban expansion, the amount of surface runoff, sewage and industrial effluent have increased dramatically (Walker *et al.* 1999; Khadse *et al.* 2008; Zhuo *et al.* 2017; Huang *et al.* 2017). For a long time, urban rivers have been associated with increase in pollution level due to discharging of untreated domestic and industrial wastes (Walker *et al.* 1999; Khadse *et al.* 2008; Venugopal *et al.* 2009; Veerasingam *et al.* 2012).

The trace elements and organic compounds are present in urban river water and sediments due to anthropogenic sources of domestic and industrial effluents. These are major quality issues in many urban areas (Macfarlane & Burchett 2000; Purushothaman & Chakrapani 2007; Raju *et al.* 2012; Sheykhi & Moore 2013; Mourier *et al.* 2014; Van Metre *et al.* 2015). The occurrence of trace elements in water and biota is not necessarily indicative of an existence to the anthropogenic sources. However, the occurrence of certain trace elements and in certain concentrations may indicate the presence of anthropogenic sources such as domestic and industrial

effluents (Homady *et al.* 2002; Wang *et al.* 2011; Xu *et al.* 2017). Depending on concentration levels of trace elements are known to be harmful for both environment and human health. The overall trace element behaviour in aquatic environment is strongly influenced by the association of metals with various mineralogical phases in sediments (Grosbois *et al.* 2011; Islam *et al.* 2015). However, the high concentrations of trace elements in river sediments of megacity have been reported in India and the pollution of surface water bodies has been attracting substantial public attention over the past few decades.

In India, the indiscriminate industrialization and urbanization have significantly influenced the quality of surface water resources (Singh & Singh 2007; Singare *et al.* 2012). The pollution of surface water bodies has been attracting substantial public attention over the past few decades. High levels of trace elements were observed in sediments of many urban rivers in India, such as the Ganges, Yamuna, Hindon, Narmada, Mithi, Kanini River etc. (Singh 2001; Singh *et al.* 2002; Jain 2004; Jain *et al.* 2005; Hejabi *et al.* 2011; Lin *et al.* 2013) although most of the urban population still depends on river water sources for their day to day consumption purpose (Kaushik *et al.* 2009).

Hence, the sediment quality is assessed to evaluate the environmental risk, latter extended to water resources and food chain (Loring & Rantala 1992; Perkey 2006; Silva *et al.* 2013; Xu *et al.* 2017). River sediments are an important sink but also a source for assessing heavy metal pollution in rivers: (i) It present a great affinity for the solid fraction (Luoma & Bryan 1981; Howari *et al.* 2001; Adekola *et al.* 2002; Lai *et al.* 2013; Lin *et al.* 2013; Chambers *et al.* 2016). (ii) Have a long residence time (Muller *et al.* 1979; Subramanian 2004; Olivares-rieumont *et al.* 2005; Taylor & Owens 2009). Trace element pollution is then a serious environmental concern for an influence of toxic metals such as Ag, Cd, Cr, Cu, Ni, Pb, Zn etc., (Szefer *et al.* 1996; Perkey 2006; Rath *et al.* 2009; Marshall *et al.* 2010; Yoshimura *et al.*2014).

The organic pollutants cause an adverse effect in the environment and human health. These are ubiquitous and highly persistent in the environment, as they are found in soils, sediments, air or biota (Boll *et al.* 2008; Radice *et al.* 2008). Metals are accumulating into sediments at levels that are several orders of magnitude higher than the natural geochemical background (Akcay *et al.* 2003; Cheung *et al.* 2003; Sharma & Subramanian 2010; Connor *et al.* 2014). Upstream-downstream sediment study is then an appropriate approach to assess the gradient and sources of contamination.

Moreover, large amount of organic pollutant is transported to receiving waters and accumulated into the sediments. Sediments constitute one of the main compartments of the aquatic environment where organic contaminants can be accumulated. Some pollutants may be associated with fine sediment particles causing gradual or instant deterioration of the aquatic system (Boll *et al.* 2008; Dos santos *et al.* 2018). Hence, a better understanding of the fate of endocrine disruptors is required and is ultimately essential for managing organic contaminant levels in the urban environments.

1.2 NEED FOR THE STUDY

Chennai megacity is the one of the most comprehensive industrial and commercial metropolitan cities in India (Krishnamurthy & Desouza 2015), which experienced an intense process of land use change and the human impact. The Adyar and Cooum River, which are the two important rivers among four rivers in Chennai megacity, Tamil Nadu, India and greatly influenced by urbanisation in the past three decades and is a classic example of the pollution problem. Adyar river and Cooum river, play a vital role in flood control, drainage, water supply and irrigation (once upon a time), but today they act as carriers of urban waste and sewage water (Veerasingam *et al.* 2012; Jayaprakesh *et al.* 2012). Past one decade, these rivers have been polluted extremely by the urban discharge of untreated sewage and industrial effluent. In addition, the land use in Chennai river basin have significantly changed due to the rapid urbanization (Achyuthan & Thirunavukarasu 2009). Hence, these rivers are considered for the present study.

Chennai Metropolitan Area (CMA) falls in three Districts of Tamil Nadu state encompassing 1189 km^2. There are two main waterways crossing the Chennai city which Adyar and Cooum rivers, are natural rivers flowing towards east direction to the Bay of Bengal. These urban rivers are seasonal, and the main flow is due to the North-East monsoon during October to December. The surplus water (due to heavy rain) of Chembarambakkam tank can cause flood in Adyar river. Especially 2015 flood event is a historical record in Chennai city. Portion of upstream side of the two rivers will be dried during non-monsoon period. Then, both the rivers receive less quantum of flow. It carries waters from domestic and industrial wastes outflows to the rivers via drains. Also, the estuary of these rivers are influenced by sea tide, which allow saline water entering mouth of the rivers.

Many reasons can be attributed to the present condition such as, (i) population explosion along with the unplanned growth of the city (ii) discharge of untreated domestic sewage and industrial effluents; (iii) formation of sand bar at the mouth of the river; (iv) indiscriminate pumping of groundwater leading to reduced base flow in the upstream part of the river; (v) accumulating large volumes of organic sludge; and (vi) encroachment along the river banks. So, Chennai's polluted waterways have become both an eyesore and a source of disease in the city especially along the downstream side of the river. Hence, a study taken as to the pollution by trace elements and organic component across the river stream using sedimentological characteristics.

1.3 OBJECTIVES

The main objectives of this research are designed into 3 parts,

(i) Trace element of urban footprint onto river sediments in megacity

a) To establish an upstream-downstream characterization of the fluvial system including influents and tributaries

b) To estimate the impact of anthropogenic inputs with new urban tracer specially dedicated to Chennai megacity

c) To identify polluting hotspot from disentanglement for various urban and industrial sources of incoming pollution

d) To compare Chennai contamination level to worldwide megacity pollution level

(ii) Endocrine disruptor occurrence: Preliminary study for PAHs, PCBs, Phthalates and PBDEs

a) To identify spatial distribution of organic contaminants (PAHs, PCBs, Phthalate and PBDEs)

b) To identify and assess pollution emission sources using PAHs diagnostic ratios

c) To endeavor sources, concentrations and hazard levels of PCBs, PBDEs and Phthalates in the surface sediments

(iii) Influence of 2015 floods onto trace elements and organic component pollution level with regards to the quality of the two main rivers

a) Geochemical and organic composition of river sediments after the 2015 flood in Chennai

b) To investigate the sediment quality and flood influence on the urban tracer level

c) To compare the state of sediment contamination of special index Geochemical Urban Footprint Index (GUFI)

d) To evaluate the pollution and toxicity levels of organic contaminants (PAHs, PCBs, Phthalates and PBDEs)

1.4 ORGANIZATION OF THESIS

In this thesis, the findings of the research works carried out are summarized and conclusion emerging from the study is presented. The scope for further research in this direction is also outlined. The thesis is organized into eight chapters and a brief detail of each chapter is given below.

Chapter 1 gives an introduction, specifies the need for the study, summarizes the objectives and briefly outlines the content of the thesis.

Chapter 2 discusses the salient features and fluvial system of the study area.

Chapter 3 includes Methodology and techniques adopted in this study.

Chapter 4 includes trace element urban footprint of megacity onto river sediments.

Chapter 5 covers endocrine disruptor occurrence: preliminary study for PAHs, PCBs, Phthalates and PBDEs.

Chapter 6 contains an influence of 2015 flood hazard onto trace elements and organic component pollution level with regards to the quality of the two main rivers.

Chapter 7 covers the summary and conclusion of the thesis by highlighting the salient features of methodology and the contribution of the thesis work and the recommendation for future work are also indicated.

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CHAPTER 2

STUDY AREA



CHAPTER 2
STUDY AREA

2.1 GENERAL

This chapter provide a brief description of the city's location, administration, demographics, economy, geology, land use pattern and fluvial system.

2.2 BACKGROUND: OVERVIEW OF HISTORICAL DEVELOPMENT

The study area is Chennai (Madras) has a long history, and its beginning can be traced back to the British East India Company. Under the direction of Mr. Francis Day, the East India Company acquired a grant to build a fort near the Coromandel Coast in 1640. The company began the construction of St. George Fort on March 1, 1640. The construction was completed in 1653. The East India Company encouraged merchants and artificers to settle around the fort, and the city of Chennai began to grow (Chennai Corporation). The city of Chennai played a critical role in India's struggle for independence. After independence was achieved, most Indian cities were reorganized based on the linguistic identities of the local people groups; for Chennai, this was the Tamil. While Chennai quickly emerged as one of the fastest growing cities in India, due to the dominance of the Tamil (Darvidian heritage), the city maintained an orthodox and conservative outlook (Arabindoo 2011). Over past several decades, the city of Chennai has forced the spatial expansion of the city and transformed into corporation then CMA (Chennai Metropolitan Area).

2.3 LOCATION

Chennai is located between 12°50'49" and 13°17'24" North latitude and 79°59'53" and 80°20'12" East longitude on the Coromandel coast in southern India and the capital of Tamil Nadu (India) (Figure 2.1). Chennai lies close to the equator and has a tropical monsoon climate. Maximum temperatures of around 40°C occur in late May to early June. The minimum annual temperature is 20 °C in early January. The predominant

wind direction is from south-east to north-west and the average annual rainfall is around 1,400mm, falling mainly during the rainy season in October to December.

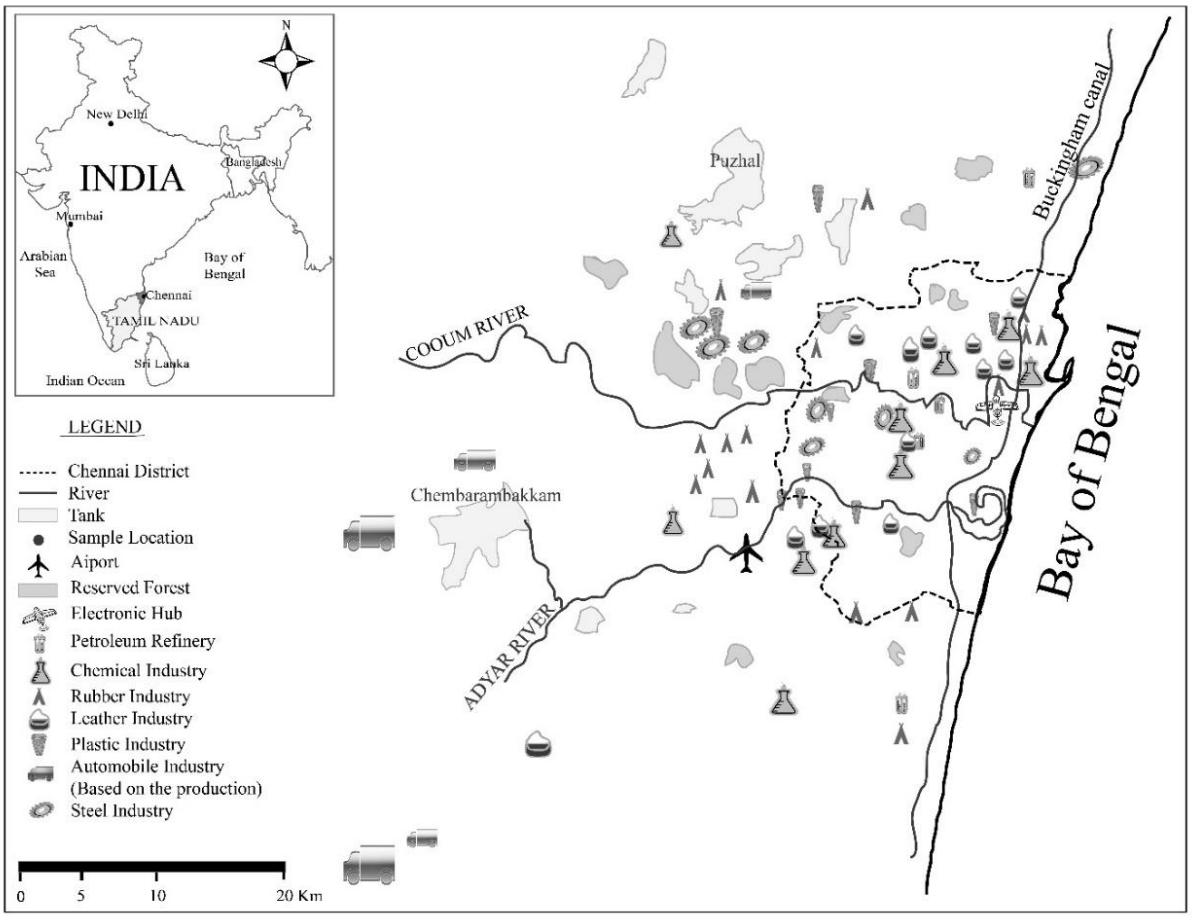


Figure 2.1 Location and associated urban activities in the study area

2.4 ADMINISTRATIVE STRUCTURE

Chennai falls within the Chennai Metropolitan Area (CMA), being the fourth most populous and fifth largest metropolitan area in India. At the world scale, Chennai is the 22nd most populous city in Asia and the 40th most populous city in the world (Census of India 2011). Chennai Metropolitan Area (CMA) is spread in three districts of Tamil Nadu state, which includes sixteen municipalities, 20 town panchayats and 10 panchayat unions (comprising 214 villages) and an area encompassing 1189 km^2.

2.5 DEMOGRAPHICS

Chennai has a tremendous growth in population in and around the city with a population increase from 7.04 million in 2001 to 8.65 million in 2011 as per census (www.cenus2011.co.in). Figure 2.2 shows population of Chennai Metropolitan Area (CMA).

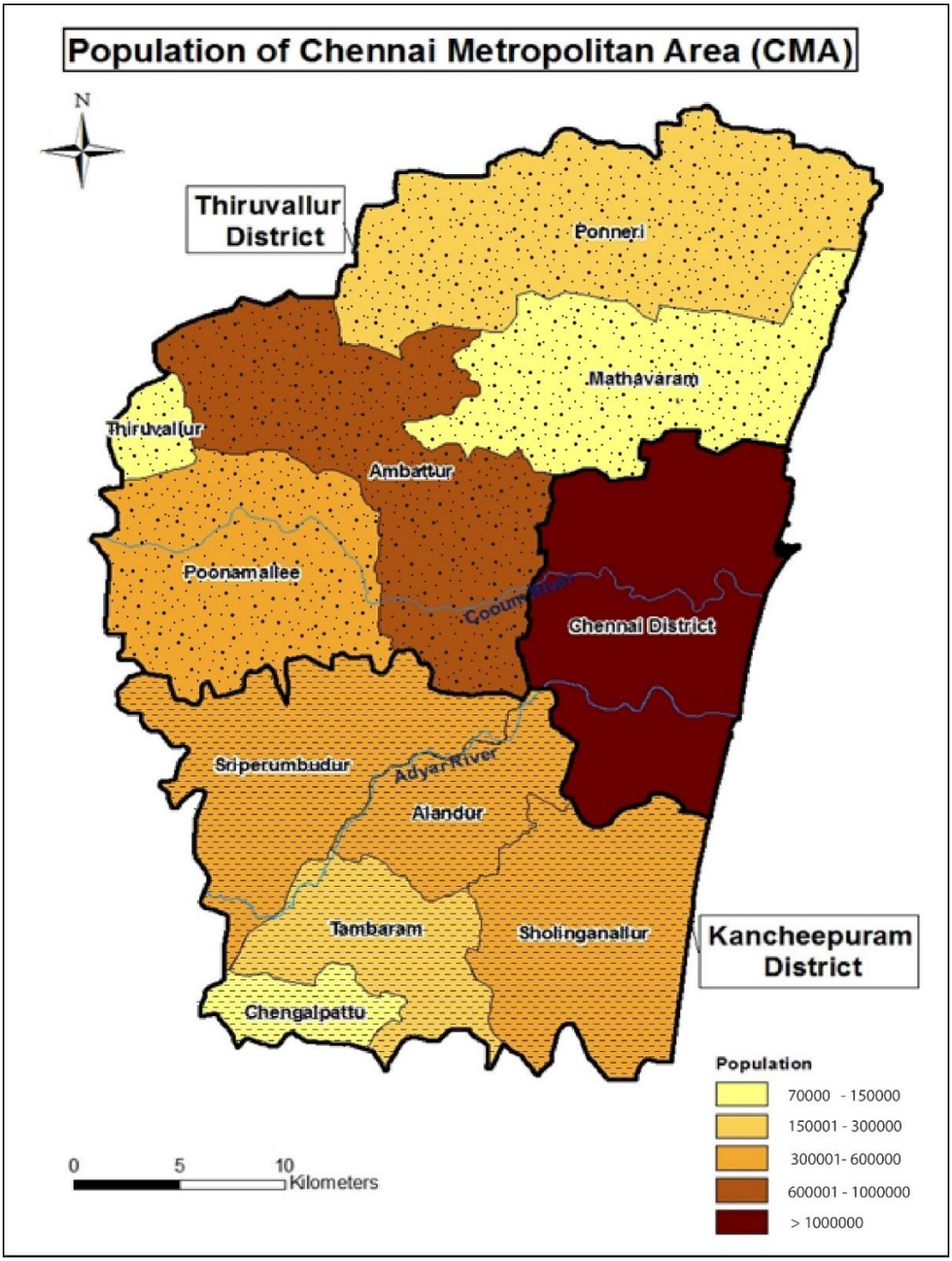


Figure 2.2 Population of Chennai Metropolitan Area (CMA)

The urban population in CMA has crossed, over 10.26 million in early 2017 (Demographia, April 2017) and it is estimated to be 11.12 million by 2021 (Population projection given by CMA). Various factors have contributed to the growth in population, which include large scale investments from Multinational Companies (MNCs), growth within the automobile and manufacturing industries, the presence of foreign embassies and the growth of educational and cultural institutions (Achyuthan & Thirunavukarasu 2009; Krishnamurthy & Desouza 2015).

2.6 ECONOMY

The economic activities in Chennai constitute the largest industrial commercial centre in south India, often referred to as the "Detroit of India" and the "Gateway to South India" (U.S. International Trade Commission 2007). In recent decades, large industrial facilities have been established in Chennai suburbs resulting in large-scale population growth (Krishnamurthy & Desouza 2015). The city is home to a large range of companies, including petroleum, chemical, rubber, leather, plastic, steel, automobile and manufacturing industries. In addition, Multinational Companies (MNCs) have set up in the city and include Information Technology (IT - software services and hardware manufacturing), non-residential complexes (hotels, cinemas and shopping malls), and also medical and health care (CMDA 2008).

2.7 GEOLOGY

Geology of the study area is mostly ferricrete surfaces (Achyuthan & Thirunavukarasu 2009; Deepa *et al.* 2017; Seenirajan *et al.* 2017). Adyar watershed lays on charnockites, Cooum watershed falls into an alluvium and coastal alluvium (Figure 2.3). The charnockite bedrock formed due to more or less fragmental decomposed matter drifted by wind, water or other sources of erosion. Almost the entire area is covered by Pleistocene/ Recent alluvium, deposited by the two rivers. This alluvium is consisting of mainly clays, sands, sandy clays and occasional boulder or gravel zones. Sandy areas are found along their banks. Igneous/ metamorphic rocks are found in the Adyar river. The river sediments containing clay, silt, sands originating from alteration of

charnockite rocks and reworked alluvium deposits. A thin layer of laterite is also found at some places and well-rounded pebbles have been encountered at several locations at varying depths (Veerasingam *et al.* 2012).

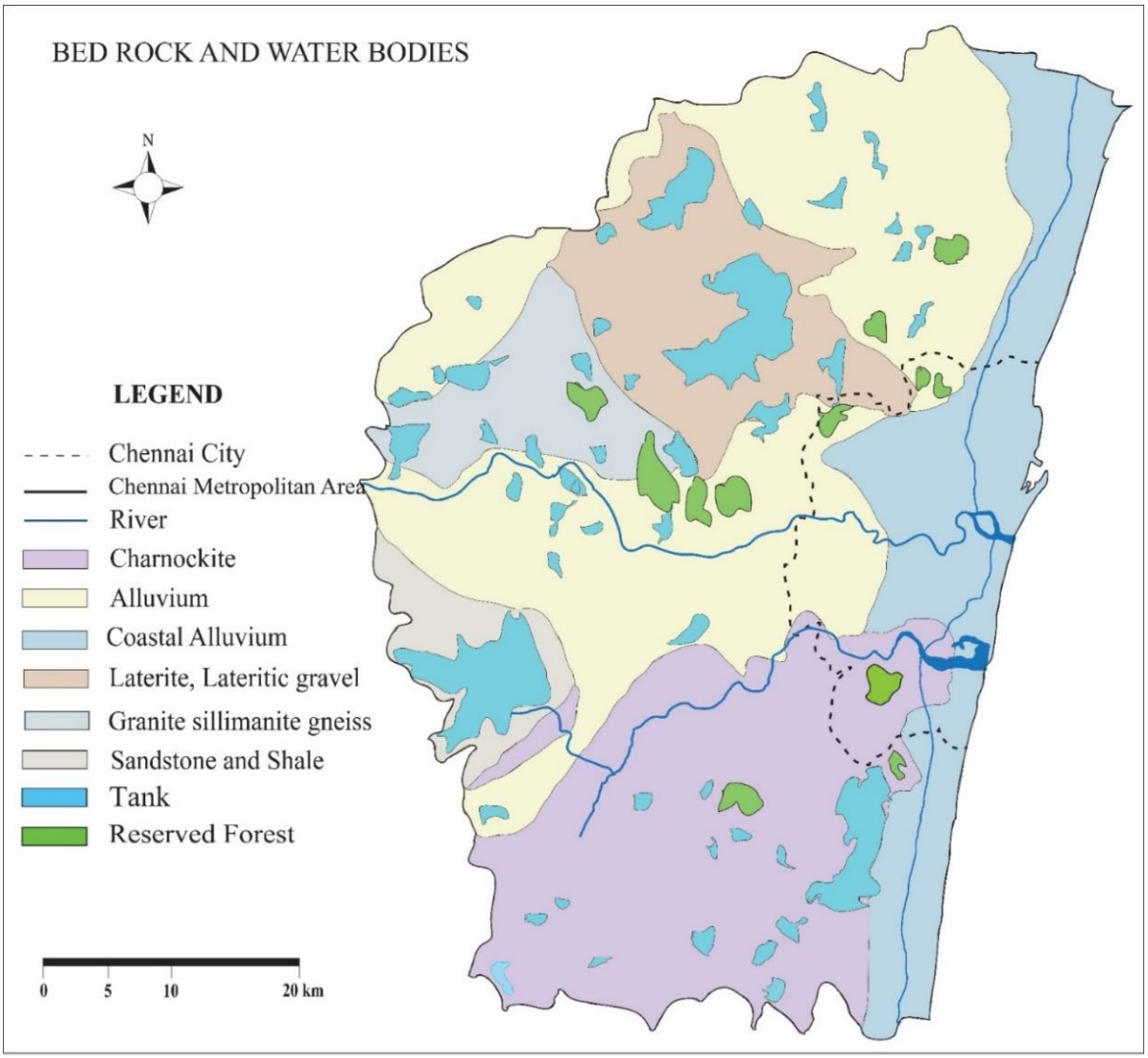


Figure 2.3 Geological map of Chennai Metropolitan Area (CMA)

2.8 LAND USE PATTERN

The land use pattern of Chennai megacity is influenced by anthropogenic activities. Land use pattern classification was done in the year of 2016 (LISS data) as shown in Figure 2.4. In Chennai city over past decades, the agricultural land is

completely converted into residential, institutional or industrial structures. This is indicating the high rate of urbanization in Chennai megacity.

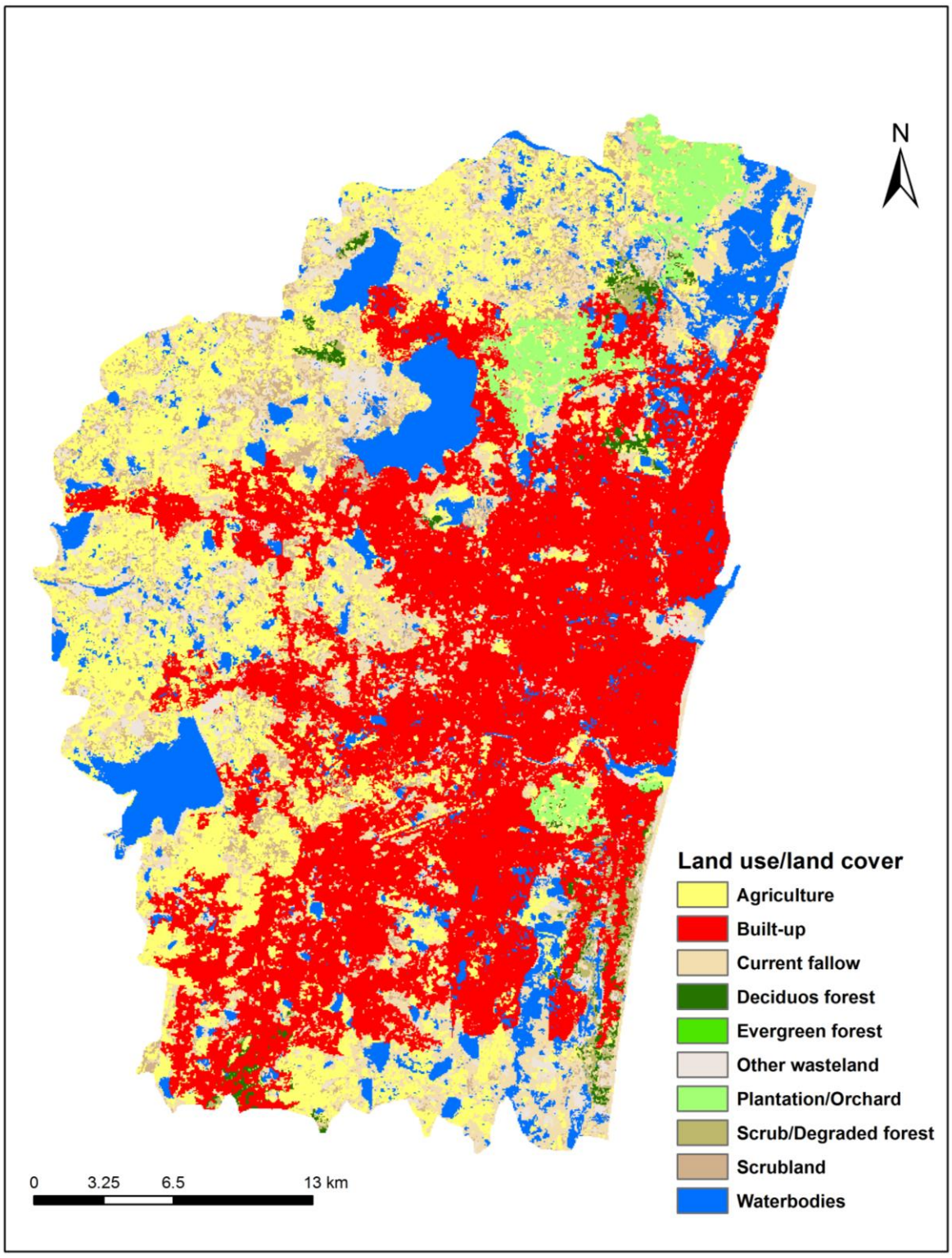


Figure 2.4 Land use pattern of Chennai Metropolitan Area (CMA)

2.9 FLUVIAL SYSTEM

This study focused on the fluvial system of megacity rivers (Adyar and Cooum rivers) and some of their major drains in CMA (Chennai Metropolitan Area). In CMA Adyar and Cooum rivers are main waterways and crossing the Chennai megacity (Figure 2.1). Adyar and Cooum rivers are natural and flowing towards east to the Bay of Bengal. Both the Adyar and Cooum rivers are seasonal, and their main flow is due to the North-East monsoon from October to December.

The upstream portions of the two rivers are dry during the non-monsoon period (Jayaprakesh *et al.* 2012), thus they both mostly act as channels for city sewage in their respective upstream reach (Veerasingam *et al.* 2012). Sewage and wastewater outflows enter the rivers via drains which are connected to different networks and collect all kinds of urban and industrial waste from the city (Jayaprakesh *et al.* 2012). As river slopes are very low, sediment transport is also reduced (Gowri & Ramachandran 2008) and dilution by various water nor particle inputs is not very effective. The mouths of these rivers open into the Bay of Bengal. The most downstream part of the Adyar river experiences a tidal influence, which allows salt water to enter the mouth (Achyuthan & Thirunavukarasu 2009; Jayaprakash *et al.* 2010; Veerasingam *et al.* 2012). Similarly, Buckingham Canal (Figure 2.1) is man-made waterways, which runs from north to south intersecting both rivers. The Buckingham canal is a 796 km long fresh water navigation canal in the north part and connects most of the natural backwaters along Andhra Pradesh to Marakkanam (Gowri & Ramachandran 2008).

2.9.1 Adyar River

Adyar River starts from Malaipattu tank (12.93° North latitude and 80.00° East longitude) near Manimangalam village in Sriperumbudur Taluk at about 15 km west of Tambaram near Chennai. The river flows through Kancheepuram, Tiruvallur and Chennai districts for about 42 km length and the catchment area is 860 km^2 before joining the Bay of Bengal in Adyar, Chennai. The surplus water from the Chembarambakkam reservoir can result in this river flooding. A historical flood event

was recorded in Chennai in 2015. The river forms a backwater near the mouth known as “Adyar Creek” due to the formation of sandbar at the mouth. This Creek is a natural channel which carries tidal water back into the sea.

2.9.2 Cooum River

The Cooum river, originates from “Cooum” or “Koovam” in Tiruvallur district adjoining Chennai. It flows parallel to the south. The river trifurcates the city and separates Northern Chennai from Central Chennai. The total catchment area is 290 km^2 and the length of this river is 65 km with about 18 km within the Chennai limits, which flows through three corporation zones namely Kilpauk, Nungambakkam and Triplicane. Surplus from about 75 tanks in the catchment reaches Cooum river.

2.9.3 Drains

There are a number of other smaller drains or macro drainage (Burma colony, YMCA or Mambalam drain, etc.) draining into these main waterways. These macro drains are connected from different network (Figure 2.5) and collect all kind of urban and industrial waste from the city. 84% of these macro drains carry sewage (www.cmdachennai.gov.in/ smps/smps.html) while, the rest carry storm water. In Chennai megacity, Adyar and Cooum rivers are almost stagnant and not carrying enough water except during monsoon session. These rivers are playing major role during floods. The surplus water of Adyar is three times more than the Cooum River (Gowri & Ramachandran 2008).

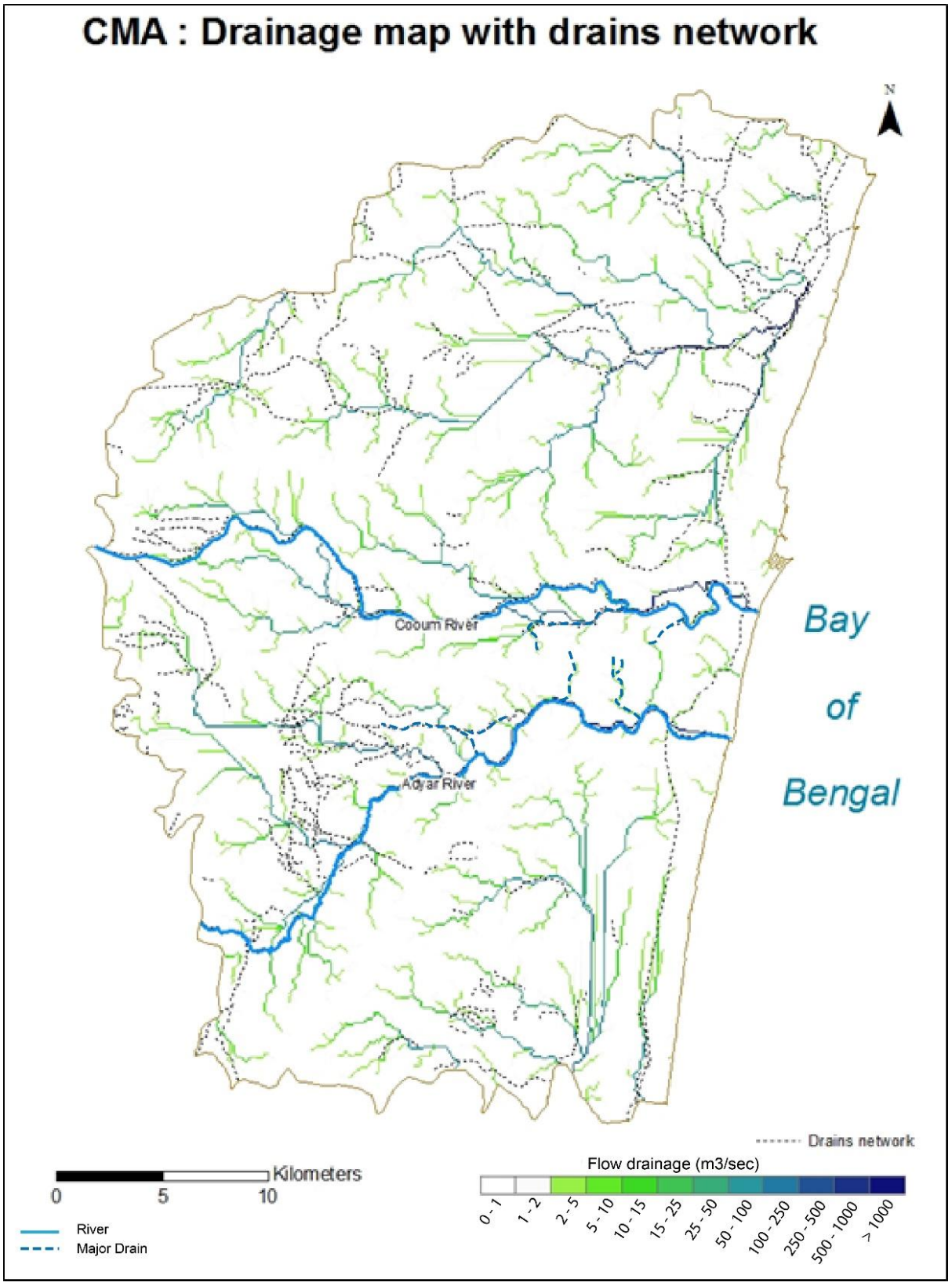


Figure 2.5 Drainage map with drains network

2.9.4 History and Present Scenario of the Rivers

Once upon a time the Adyar and the Cooum were in pristine condition with balanced eco-systems and beautiful environments. A mural at the Adyar Poonga exhibition centre shows the wealth of fauna of the original Adyar estuary. As late as the 1960s people boast of fishing and bathing in the rivers. Also, recreational boating was attracted tourists. The river is described as a "languid stream" which carries little water except during the monsoon.

Presently, the river is highly polluted and malodorous and can be said to have become 'dysfunctional'. Nowadays in Chennai metropolitan area, the two rivers are the major sources of pollution from domestic and industrial wastes (Jayaprakesh *et al.* 2010). Sewage and wastewater outflows come from the two studied rivers via drains. Cooum river is one of the most severely polluted rivers in India (Jayaprakash *et al.* 2012; Veerasingam *et al.* 2012).

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CHAPTER 3

METHODOLOGY



CHAPTER 3
METHODOLOGY

3.1 GENERAL

This chapter describes the methodology adopted to analyse the present pollution status of the Adyar and Cooum rivers in Chennai megacity. Methodology include works carried out in field, laboratory and interpretation phases.

3.2 METHODOLOGY

The prime objective and target of the research is to develop the geochemical urban footprint of the contamination level in Chennai megacity onto river sediments. The detailed methodology flow chart is designed and utilized in this research work is shown in Figure 3.1. The proposed methodology is broadly divided into the following sections, which include data collection, geochemical analysis and organic component analysis, identification of urban tracer, pollution sources and hazards level in the Chennai megacity.

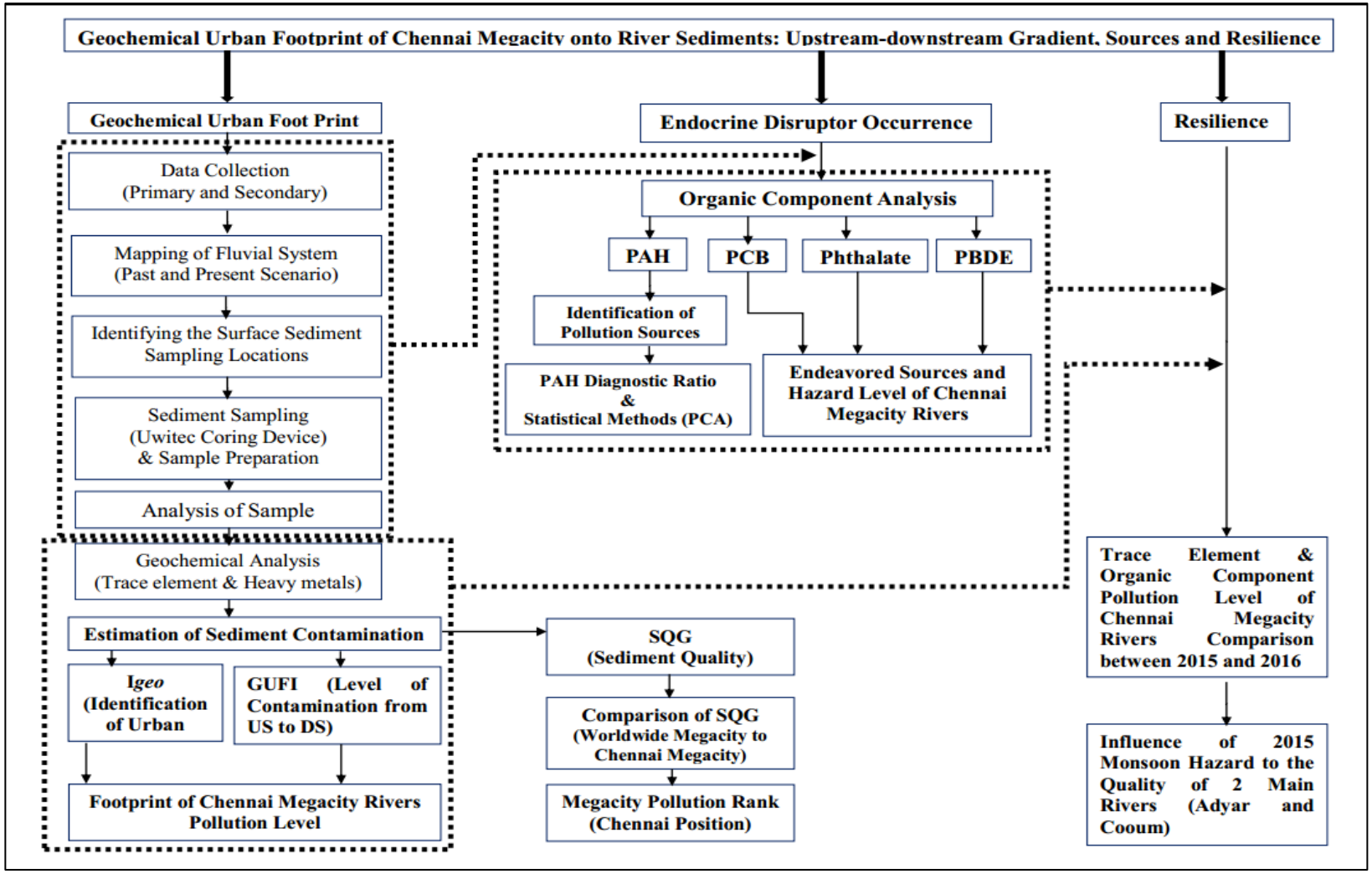


Figure 3.1 Methodology flowchart

3.3 SAMPLING STRATEGY

3.3.1 Sampling

Surface sediment and flood deposit samples were collected from 24 locations (Figure 3.2) from upstream to downstream sites of both rivers (Adyar river stations: A1 - A9; Cooum river stations: C1 - C9) and some major drains (corresponding to stations: A-CSC, A-RP, A-BC, A-YMCA along the Adyar river and C-NMR and C-GR along the Cooum one; Figure. 3.2). Sampling sites were selected according to potential point sources of pollution (industry and urban sewage) and accessibility. The most upstream stations on the Adyar and Cooum rivers were considered to be in Chennai peri-urban area: stations A1 to A4 and C1 to C2 (Figure 3.2). Downstream stations were considered to be in Chennai city (stations A5 to A9 and C3 to C9).

Surface sediments and flood deposits were collected under water at a sediment depth of 0 – 15 cm using an Uwitec coring device in February 2015 and February 2016 (Before and after flood - December 2015) and drainage sediment samples were collected only in February 2015. This upper layer of surface sediment is considered as recent deposits, integrating one hydrological cycle and flood deposits.

3.3.2 Sampling Locations

The locations of collected sediment samples from urban rivers and drains are mentioned with coordinates in the following Table 3.1. Figure 3.2 and Figure 3.3 shows sample collection locations in Adyar and Cooum rivers, Chennai, or the map for easy identification.

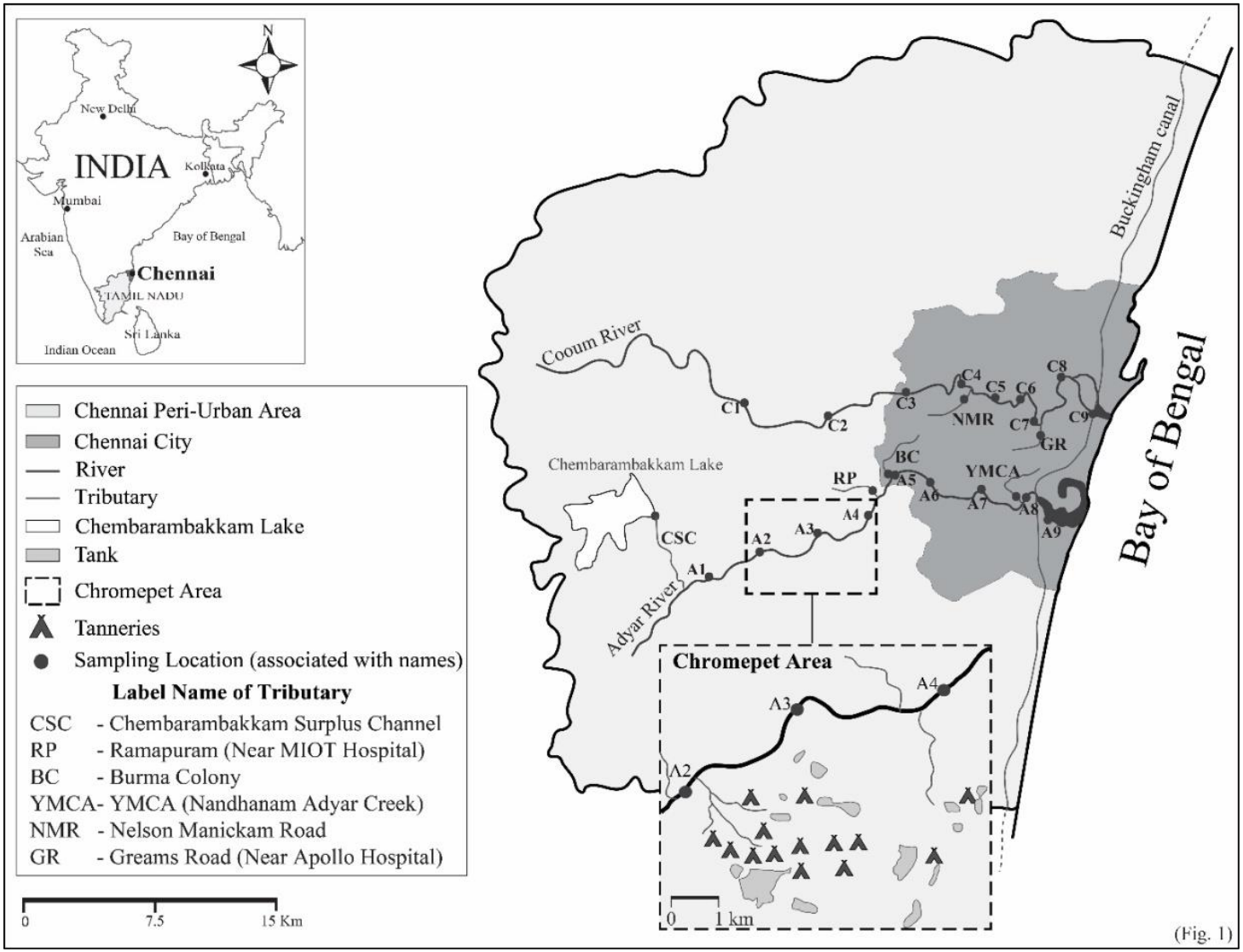


Figure 3.2 Sample locations in urban rivers and drains

Table 3.1 Sample locations in urban rivers and drains

Station	Location	Latitude N	Longitude E
Adyar river			
A1	Thiruneermalai	12°57’55.3”	80°06’35.4”
A2	Anakaputhur	12°59’08.5”	80°07’14.0”
A3	Pozhichalur	12°59’39.2”	80°08’53.8”
A4	Manapakkam	13°00’24.8”	80°10’48.7”
A5	Burma colony	13°01’44.9”	80°11’52.0”
A6	Jafferkhanpet	13°01’34.5”	80°12’30.7”
A7	Maraimalai adigal bridge (saidapet)	13°01’04.3”	80°13’31.3”
A8	Kotturpuram (Near boat club)	13°01’18.0”	80°14’50.1”
A9	Thiru vi ka bridge (Adyar mouth)	13°00’52.3”	80°15’35.1”
Cooum river			
C1	Thiruverkadu	13°04’26.4”	80°06’46.6”
C2	Maduravayal	13°03’44.6”	80°09’30.4”
C3	Thirumangalam	13°04’41.5”	80°11’55.2”
C4	Aminjikarai	13°04’25.2”	80°13’20.4”
C5	Choolaimedu	13°04’06.7”	80°13’54.1”
C6	Moors road, Nungambakkam	13°04’06.9”	80°14’33.6”
C7	College road	13°04’0.17”	80°15’17.6”
C8	Chintadripet	13°04’08.0”	80°16’07.9”
C9	Napier bridge	13°00’52.3”	80°15’35.1”
Drains			
A_CSC	Chembarambakkam Surplus Channel	13°00’54.4”	80°04’43.6”
A_RP	Ramapuram_near MIOT hospital	13°00’21.4”	80°11’19.0”
A_BC	Burma Colony	13°01’45.1”	80°11’50.0”
A_YMCA	YMCA (Nandhanam Adyar Creek)	13°01’22.1”	80°14’10.0”
C_NMR	Nelson Manickam Road	13°41’03.9”	80°13’41.7”
C_GR	Greams Road_near Apollo hospital	13°03’46.2”	80°15’15.9”



Figure 3.3 Sample collection locations in Adyar and Cooum rivers, Chennai

3.3.3 Sample Preparation

Collected sediment samples were immediately transferred to airtight sealed polythene bags and stored at 4ºC in an icebox during sampling campaigns. They were then transferred to the laboratory and after removing coarse shell fragments, lithoclasts and other organic macro-remains, sediments were dried at 60ºC for 72 hours in a well-ventilated oven. Once dried, samples were desegregated in an agate mortar and sieved at <63 µm fraction through disposable Nylon mesh. Then the sediment samples were stored in labelled clean polythene bags. During the drying, grinding, sieving and storage process, care was taken to avoid contamination. Figure 3.4 shows sample preparation of Adyar and Cooum river sediments.



Figure 3.4 Sample preparation of Adyar and Cooum river sediments

3.4 ANALYSIS OF SURFACE SEDIMENT SAMPLE

The surface sediment and flood deposits were analyzed for the following parameters:

- Geochemical Analysis
  - Major elements - Al, Si, Fe, Na, K, Ca, Mg, P., etc
  - Oxides - Al_2O_3, SiO_2, Fe_2O_3, Na_2O, K_2O, CaO, MgO, P_2O_5 computed using conversion factor
  - Heavy metals - Ag, As, Cd, Cu, Cr, Hg, Ni, Pb, Zn etc.,

- Organic component Analysis
    - Endocrine Disruptor- PAHs, PCBs, Phthalates and PBDEs

3.4.1 Geochemical Analysis

Geochemical analyses were performed on the <63 μm fraction to limit grain size effect on trace element concentrations. Samples were completely digested with $LiBO_2$-Li_2B4O_7 on a tunnel oven and placed in an acidic solution. After samples have been dried, the residues were completely re-dissolved with nitric acid (HNO_3). Total contents of major and minor elements were analysed by ICP-AES, trace elements by ICP-MS (Perkin Elmer 5000) except Hg, done by cold vapour AAS (Perkin Elmer 5100). Analyses were conducted at the national CNRS-SARM laboratory, Nancy, France (http://helium.crpg.cnrs-nancy.fr/SARM). All the digestion processes and analyses were quality-checked by the analysis of sample duplicates and internal reference materials (Perkey 2006; Grosbois *et al.* 2012; Dhivert *et al.* 2015a,b & 2016). Accuracy was within 5% of the certified values and analytical errors less than 10% RSD for trace elements concentrations, levels detected were at least 30 times higher than detection limits.

Sediment polished and carbon-coated thin sections of sediments were observed with a Zeiss field emission scanning electron microscope using. an acceleration voltage of 20 kV at a working distance of 9 mm and coupled to an energy dispersive X-ray system for element identification and mapping.

3.4.2 Organic Component Analysis

3.4.2.1 Reagents and chemicals

Standard solution of deuterated surrogates containing anthracene, fluorene, phenanthrene, benzo[a]anthracene, chrysene, fluoranthene, pyrene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, benzo[g,h,i] perylene, indeno[1,2,3–cd]pyrene, benzylbutyl phthalate (BBP), di–n–butyl phthalate

(DBP), di(2–ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP), di–isobutyl phthalate (DiBP), di–isononyl phthalate (DiNP) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The standard D_{10} was purchased from Cambridge Isotope Laboratories. Inc. (Andover, Massachusetts, USA). The purity of the certified standards was above 95%. Individual standard stock solutions (1g/l) were prepared in acetone by accurately weighing 25 mg (±0.1 mg) of standards into 25 ml volumetric flasks and stored at –18°C.

Cyclohexane solution (10 mg/l) of chrysene D_{12}, pyrene D_{10}, galaxolide and tonalide, cyclohexane solution (100 mg/l) of BBP D_4 and cyclohexane mixture (10 mg/l) of 7 PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Nonane solutions (50 mg/l) of BDE 47, BDE 85, BDE 99, BDE 100 and BDE 153, nonane/toluene (3%) mixture (5 mg/l) of $^{13}C_{12}$ – PBDE 47, PBDE 99 and PBDE 153, nonane/toluene (10%) mixture (50 mg/l) of $^{13}C_{12}$ – triclosan and toluene solution (50 mg/l) of tri-n-butylphosphate-d_{27} were purchased from Wellington Laboratories (Guelph, ON, Canada). Acetonitrile solution (100 mg/l) of bisphenol-A $^{13}C_{12}$ and isooctane solution (100 mg/l) of pentachlorobenzene $^{13}C_6$ were purchased from Cambridge Isotope Laboratories, Inc. (Andover, Massachusetts, USA).

Calibration solutions were prepared in acetone by the appropriate dilution of individual standard stock solutions and commercial solutions. Pesticide -grade glass wool was purchased from Supelco (Bellefonte, PA, USA). Glass desorption tubes (17.8 cm length 6 mm O.D. 4 mm I.D.) were purchased from Gerstel GmbH & Co. KG Mulheim an der Ruhr, Germany). Prior to use, glass wool plugs and glass desorption tubes were heated at 350 °C for 5 min to remove trace organic compounds and minimize background peaks.

3.4.2.2 Sample and calibration preparation

Each sample was cut into four quarters using a scalpel on a glass support. The first quarter of the sample was used for the analysis of trace compounds, and the

remaining three quarters were dedicated to the analysis of highly concentrated compounds, such as PAHs or phthalates. Each quarter was then inserted into a glass desorption tube fitted with a glass wool plug to prevent system contamination due to particles pulled by the helium flow.

Each calibration solution in acetone was spiked (1 µl) on a glass wool plug inside a glass desorption tube also fitted with one quarter of an unused PTFE membrane. After the addition of internal standards (ISTDs) by spiking 1 µl of the ISTD solution on the glass wool plug, each glass desorption tube was then immediately transferred to the autosampler for analysis.

3.4.2.3 Sample analysis with GC/MS

GC/MS analysis of sediment extracts were carried out with the thermal desorption device interfaced to a 7890 GC system coupled with a 7000B GC/MS Triple Quad (Agilent Technologies) operated in electron impact ionization (EI) mode (70 eV). The gas chromatographic separation was performed on PCB capillary column (30 m length 0.25 mm I.D., 0.25 µm film thickness) supplied by Restek. Helium was used as the column carrier gas at a constant flow rate of 2.0 ml/min. Chromatographic separation was carried out with the following oven temperature program: 50 °C (hold 2 min), first ramp at 30 °C/min to 140 °C, and second ramp at 10 °C/min to 320 °C (hold 7 min to reach an analysis time of 30 min). The transfer line, ion source and quadrupole temperatures were fixed at 325, 300 and 180 °C, respectively. The mass spectrometer was operated in Multiple Reaction Monitoring (MRM) mode. The two most intense and specific MRM transitions for each compound (quantifier and qualifier transitions) were monitored for identification, confirmation and quantification.

3.4.2.4 Quality assurance and quality control (QA/QC)

This TE-GC/MS/MS method was previously validated in terms of accuracy and precision (Mandin *et al.* 2016) via a replicated analysis of the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). All compounds were

quantified with the appropriate ISTD to compensate for the variability associated with the TE-GC/MS/MS analysis from quadratic calibration curves generated for each compound by analyzing at least five different calibration solutions.

Each batch of 20 samples included: i) several instrumental (a glass wool plug) and procedural (one-quarter of a PTFE membrane and a glass wool plug) blank samples analyzed as regular samples to assess whether the samples may have been contaminated during analysis, ii) several calibration samples analyzed at least at the beginning and end of the batch to check for the stability of the detector response, and iii) one calibration sample prepared from commercial solutions provided by other suppliers to validate the preparation of the calibration solutions. Positive values for each substance were confirmed by comparing retention times and MRM transition ratios between the calibration solutions and the samples.

3.5 ASSESSMENT OF SEDIMENT CONTAMINATION

To assess the sediment contamination, the most common method is to use geochemical indexes such as Enrichment Factors (EF) (Mohiuddin *et al.* 2011) and geoaccumulaion index (I_{geo}) (Franco-Uria *et al.* 2009; Muller 1969; Muller 1981; Mohiuddin *et al.* 2010; Lai *et al.* 2013). In this study a new index was calculated, the Geochemical Urban Footprint Index (GUFI) to establish the pollution status of Chennai megacity rivers. Unlike EF and I_{geo}, this quantitative index is designed to take into account multi-trace element contamination. Finally, to compare the level of Chennai city contamination to that of worldwide megacities, trace element contamination in sediments of various megacities was compared to numerical Sediment Quality Guidelines (SQGs).

Different approaches were adopted to assess the impact of the Chennai megacity on the urban river quality regarding organic pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), Polybrominated Diphenyl Ethers (PBDEs) and phthalates or Alkylphenols.

3.5.1 Geoaccumulation Index (I_{geo})

The intensity of trace element contamination can be evaluated by Geoaccumulaion Index (*I*geo) and it was first proposed by Muller (1969). It is mathematically expressed as,

$$I_{geo} = \log_2 \left\{ \frac{(\mathrm{Me})_{\mathrm{Sample}}}{1.5\ X\ (\mathrm{Me})_{\mathrm{Background\ Sample}}} \right\} \quad (3.1)$$

where,

$(Me)_{sample}$ - measured concentration of an element in the sediment

$(Me)_{Background\ sample}$ - geochemical background concentration of the element. In Tamil Nadu, bedrock charnockites and its trace element composition was already studied by Gassama *et al.* (2012) and Tomson *et al.* (2013). However, trace elements such as Ag, Cd, and Hg are not available in these articles. So, in this study background values used for I_{geo} calculation is standard shale composition described by Wedepohl (1995)

Factor 1.5 - at the denominator is used to minimize the effect of possible variations in the background values due to lithology (Muller 1981)

The geoaccumulation Index (I_{geo}) range consists of seven classes (0-6) for the quantification of trace element accumulation in sediments as mentioned in the Table 3.2.

Table 3.2 Sediment quality based on Geoaccumulation Index (I_{geo})

I_{geo} Class	I_{geo} value	Polluted level
0	<0	Unpolluted sediments
1	0-1	From unpolluted to moderately polluted sediments
2	1-2	Moderately polluted sediments
3	2-3	From moderately polluted to strongly polluted sediments
4	3-4	Strongly polluted sediments
5	4-5	From strongly polluted to extremely polluted sediments
6	>5	Extremely polluted sediments

3.5.2 Geochemical Urban Footprint Index (GUFI)

This study developed the GUFI based on the concentration of silver (Ag), cadmium (Cd), and mercury (Hg), some of the most commonly analysed toxic trace elements in an urban environment (Meybeck *et al.* 2004; Lai *et al.* 2013; Mohiuddin *et al.* 2011). They are influenced by anthropogenic activities such as urban development, industrialization, coal combustion and population density and they are considered to be sensitive urban tracers based on I_{geo} results for this study. Other toxic trace elements including As, Cr, Cu, Ni, Pb and Zn, when available for studies in an urban context, are ubiquitous as they present various anthropogenic sources.

The GUFI was used to determine the level of contamination of sediments, upstream to downstream of the urban area. First, the Metal Urban Index (MUI) is compared to the most upstream sample in the studied river basin where there was no/limited anthropogenic influence. Ratios to aluminium (Al) concentrations were also calculated as Al was conservative along both the rivers studied. The MUI is a similar pollution index to the enrichment factor. The MUI was calculated as follows:

$$\text{Metal Urban Index} = \left\{ \frac{\left(\frac{\text{Me}}{\text{Al}}\right)_{\text{Sample}}}{\left(\frac{\text{Me}}{\text{Al}}\right)_{\text{Most Upstream Sample}}} \right\} \quad (3.2)$$

where,

$(Me/Al)_{Sample}$ – ratio of the concentration of a trace element (Me) to that of aluminium (Al) in the sediment sample

$(Me/Al)_{Most\ Upstream\ Sample}$ – ratio of the concentration of a trace element (Me) to that of aluminium (Al) in the most upstream sample of the studied river basin

Once the MUI had been determined for Ag, Cd and Hg, the GUFI was calculated as follows:

$$\text{Geochemical Urban Footprint Index (GUFI)} = \left\{ \frac{(\text{MUI})_{\text{Ag}} + (\text{MUI})_{\text{Cd}} + (\text{MUI})_{\text{Hg}}}{3} \right\} \quad (3.3)$$

where,

$(MUI)_{Ag}$, $(MUI)_{Cd}$ and $(MUI)_{Hg}$ – metal urban index for Ag, Cd and Hg respectively

The GUFI can be classified as six categories of contamination as shown in Table 3.3. This classification ranges were derived from the result of GUFI. In this result, the upstream station is set to 1.

Table 3.3 Level of contamination based on GUFI

GUFI Range	Level of contamination
1 – 10	Extremely low contamination
10 – 25	Low contamination
25 – 50	Moderate contamination
50 – 75	High contamination
75 – 100	Very High contamination
> 100	Extremely high contamination

3.5.3 Sediment Quality Guidelines (SQG)

Sediment Quality Guidelines (SQGs) are scientific tools that synthesize information regarding the relationships between sediment concentrations of chemicals and any adverse biological effects (Long *et al.* 1995; MacDonald *et al.* 1996; Long & MacDonald 1998). The SQG method defines a lower and upper effect concentration level (Long 1992; MacDonald 1993; Long *et al.* 1995; MacDonald *et al.* 1996) including a Threshold Effect Concentration (TEC) and a Probable Effect Concentration (PEC) (MacDonald *et al.* 2000; Hoda *et al.* 2009; Helen *et al.* 2016). When available in the literature, ubiquitous Cr, Cu, Ni, Pb and Zn are the most frequently analyzed in surface sediments of various megacities. Their concentrations were compared to their respective quality guidelines and a comparative ranking of various megacities was carried out as follows:

$$\text{Mean PEC quotient} = \left\{ \frac{\sum_{i=1}^{n} \frac{(\text{Me})_{i\ \text{Sample}}}{(\text{Me})_{\text{PEC Sample}}}}{n} \right\} \tag{3.4}$$

where,

$(Me)_{sample}$ – measured concentration of of metal in the sediment

$(Me)_{PEC\ Sample}$ – probable effect concentration in the SQGs (MacDonald *et al.* 2000)

n – number of trace elements taken from a megacity

Mean concentration of sediment sample is taken into account for the trace element comparison of megacity. This mean PEC quotient was used to determine the impacted megacity ranking, the higher the most impacted megacity.

3.6 ENDOCRINE DISRUPTORS

The Endocrine disruptor is presented and the results of these different approaches (longitudinal profiles, different stations from up to downstream of Chennai rivers and pollutant loads assessment) are discussed. Thirteen individual Polycyclic Aromatic Hydrocarbons (PAHs) in the list of US Environmental Protection Agency (EPA) priority pollutants, seven PCBs, five PBDEs and six Phthalates were analyzed. Table 3.4 shows the Compounds studied, acronym and the formula considered in this study.

Table 3.4 Compounds studied, acronym and the formula

Compound	Acronym	Molecular Formula
Polycyclic Aromatic Hydrocarbons (PAHs)		
Anthracene	ANT	$C_{14}H_{10}$
Fluorene	FL	$C_{13}H_{10}$
Phenanthrene	PHE	$C_{14}H_{10}$
Benzo[a]anthracene	BaA	$C_{18}H_{12}$
Chrysene	CHR	$C_{18}H_{12}$
Fluoranthene	FLA	$C_{16}H_{10}$
Pyrene	PYR	$C_{16}H_{10}$
Benzo[a]pyrene	BaP	$C_{20}H_{12}$
Benzo[b]fluoranthene	BbF	$C_{20}H_{12}$
Benzo[k]fluoranthene	BkF	$C_{20}H_{12}$
Dibenzo[a,h]anthracene	DahA	$C_{22}H_{12}$
Benzo[g,h,i]perylene	BghiP	$C_{22}H_{12}$
Indeno[1,2,3–cd] pyrene	IcdP	$C_{22}H_{12}$

Table 3.4 (Continued)

Compound	Acronym	Molecular Formula
Polychlorinated Biphenyls (PCBs)		
2,4,4' –Trichlorobiphenyl	PCB 28	$C_{12}H_7CI_{13}$
2,2',5,5' – Tetrachlorobiphenyl	PCB 52	$C_{12}H_6CI_{14}$
2,2',4,5,5' – Pentachlorobiphenyl	PCB 101	$C_{12}H_5CI_{15}$
2,3',4,4',5 – Pentachlorobiphenyl	PCB 118	$C_{12}H_5CI_{15}$
2,2',3,4,4',5 – Hexachlorobiphenyl	PCB 138	$C_{12}H_4CI_{16}$
2,2',4,4',5,5' – Hexachlorobiphenyl	PCB 153	$C_{12}H_4CI_{16}$
2,2',3,4,4',5,5' – Heptachlorobiphenyl	PCB 180	$C_{12}H_3CI_{17}$
Phthalates		
Benzylbutyl Phthalate	BBP	$C_{19}H_{20}O_4$
Di–n–butyl Phthalate	DBP	$C_{16}H_{22}O_4$
Di(2–ethylhexyl) Phthalate	DEHP	$C_{24}H_{38}O_4$
Diethyl Phthalate	DEP	$C_{12}H_{14}O_4$
Di–isobutyl Phthalate	DiBP	$C_{16}H_{22}O_4$
Di–isononyl Phthalate	DiNP	$C_{26}H_{43}O_4$
Polybrominated Diphenyl Ethers (PBDEs)		
2,2',4,4' – TetraBDE	BDE 47	$C_{12}H_6Br_4O$
2,2',3,4,4' – PentaBDE	BDE 85	$C_{12}H_5Br_5O$
2,2',4,4',5 – PentaBDE	BDE 99	$C_{12}H_5Br_5O$
2,2',4,4',6 – PentaBDE	BDE 100	$C_{12}H_5Br_5O$
2,2',4,4',5,5' – HexaBDE	BDE 153	$C_{12}H_4Br_6O$

3.7 IDENTIFICATION OF POLLUTION SOURCES

3.7.1 PAH Diagnostic Ratios

PAH diagnostic ratios are one of the most common tools in identifying and assessing the appropriate pollution emission sources (Boll *et al.* 2008; Tobiszewski & Namiesnik 2012; Islam *et al.* 2017). The ratio applicable to PAHs is determined in different environmental media. Among the different diagnostic ratio (Table 3.5), several commonly used ratios like Fluoranthene to the sum of Fluoranthene and Pyrene (FLA/(FLA+PYR)), Anthracene to the sum of Anthracene and Phenanthrene (ANT/(ANT+PHE)), Benzo[a]anthracene to the sum of Benzo[a]anthracene and Chrysene (BaA/(BaA+CHR)), and Indeno[1,2,3–cd] pyrene to the sum of Indeno[1,2,3–cd] pyrene and Benzo[g,h,i]perylene (IcdP/(IcdP+ BghiP)) of 1.0 suggested to distinguish emissions from petrogenic or pyrogenic sources (Page *et al.* 1999).

Table 3.5 Diagnostic ratios used with their typically reported values

PAH Ratio	Value Range	Source	References
FLA / (FLA + PYR)	< 0.4	Petrogenic	De La Torre–Roche *et al.* 2009
	0.4 – 0.5	Fossil Fuel	
	> 0.5	Grass, Wood, Coal combustion	
ANT / (ANT + PHE)	< 0.1	Petrogenic	Pies *et al.* 2008
	> 0.1	Pyrogenic	
BaA / (BaA + CHR)	< 0.2	Petrogenic	Akyuz & Cabuk, 2010
	0.2–0.35	Coal combustion	
	> 0.35	Vehicular Emission	
IcdP / (IcdP + BghiP)	< 0.2	Petrogenic	Oliveria *et al.* 2011
	0.2 – 0.5	Petroleum combustion	
	> 0.5	Grass, wood and coal combustion	

- A ratio FLA / (FLA + PYR), <0.40 indicates petrogenic sources, while ratios >0.50 are indication of pyrogenic sources (Grass, Wood, Coal combustion) and the ratio between 0.40 and 0.50 is an indicator of petroleum combustion sources like vehicle emissions (De La Torre–Roche *et al.* 2009; Islam *et al.* 2017; Zhuo *et al.* 2017).

- For ANT / (ANT + PHE), a value <0.10 is usually taken as an indication of petrogenic origin, while ratios >0.10 indicate pyrogenic origin (Boll *et al.* 2008; Pies *et al.* 2008).

- For ratio BaA / (BaA+CHR), a value <0.2 is indicates petrogenic sources, while ratio >0.35 is an indication of vehicular emission and the ratio between 0.20 and 0.35 is an indicator of coal combustion (Akyuz & Cabuk 2010).

- Similar profiles for the ratio are IcdP / (IcdP + BghiP) values <0.2 indicates petrogenic sources, while ratio >0.5 is an indication of Grass, wood and coal combustion and the ratio between 0.20 and 0.50 is an indicator of petroleum combustion (Oliveria *et al.* 2011).

A cross plots of diagnostic source ratios are applied to the sediment source samples in both rivers of Chennai megacity.

3.7.2 Statistical Analysis

3.7.2.1 Principal component analysis (PCA)

PCA, as a multivariate analytical tool, is applied for further investigations of possible sources of PAHs contamination in the sediment. PCA were grouped into two factors; Principal Components (PCs) that defined as PC1 and PC2 based on high percentage of variance and their eigen values (>1). The results of PCA showed that primary portion of data variance through these factors; therefore, the PAHs representative of each PCs were selected as source tracers.

3.7.2.2 Correlation matrix analysis

Correlation matrix analysis was adopted in the extraction of main components for analysing relationships among the variables. These statistical methods identify the main pollutant sources along with elucidation of the pollution trends in order to study the inter-elemental associations.

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CHAPTER 4

TRACE ELEMENT URBAN FOOTPRINT OF MEGACITY ONTO RIVER SEDIMENTS

CHAPTER 4

TRACE ELEMENT URBAN FOOTPRINT OF MEGACITY ONTO RIVER SEDIMENTS

4.1 GENERAL

In India, industrialization and urbanization have significantly influenced the quality of surface water resources (Singh & Singh 2007; Singare *et al.* 2012). For a long time, urban rivers have been associated with pollution as they were carriers of untreated domestic and industrial wastes (Walker *et al.* 1999; Khadse *et al.* 2008; Venugopal *et al.* 2009; Veerasingam *et al.* 2012). An attempt is made to study upstream-downstream sediment to assess the gradient and sources of contamination and relate it pollution of megacity rivers.

This study was conducted to ascertain the present pollution status of Chennai megacity, along the two urban rivers, Adyar and Cooum, and also to identify the sources of trace elements and their transport to the Bay of Bengal. The main aims were to (i) establish an upstream-downstream characterization of the fluvial system (ii) develop a new urban trace design to study impact of anthropogenic inputs as pollutants in urban river and apply it to Chennai city to study the impact (iii) identify polluting hotspots for various urban and industrial sources of incoming pollution and (iv) compare the level of Chennai contamination with worldwide megacity pollution.

4.2 UPSTREAM-DOWNSTREAM CONTAMINATIONS OF TRACE ELEMENTS IN SEDIMENTS

The main aim of this study was to estimate the spatial variations of upstream-downstream concentrations of trace elements in surface sediments and to quantify the present pollution level of the two studied urban rivers and the major drains which connect with these rivers. Sediment concentrations of trace elements and Aluminium concentration (mg/kg) in Adyar river basin (A stations), Cooum river basin (C station) from upstream-downstream sampled station and its associated drains are presented in Table 4.1 according to kilometric points (KP, in km; KP 0.0 being the most upstream station sampled) – see Figure 3.2 for locations.

Table 4.1 Trace Element and Aluminium Concentration (mg/kg) in Chennai megacity rivers and drains

Station		Kilometric point (km)	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Al
Adyar River	A1	00.0	0.1	3.1	0.2	141	68	> 0.0	66	22	115	93121
	A2	03.0	0.8	3.1	0.8	1517	237	0.1	67	55	1392	76064
	A3	06.6	0.6	2.4	0.4	925	82	0.1	62	28	155	86361
	A4	12.0	0.2	1.8	0.4	700	83	0.1	76	24	145	77097
	A5	14.7	1.8	1.8	0.8	74	74	0.3	18	26	122	54581
	A6	15.9	18.8	3.7	4.8	348	325	1.4	55	54	722	61267
	A7	18.4	7.1	2.9	1.5	164	182	0.5	44	60	308	67530
	A8	21.9	12.1	4.1	2.3	359	192	1.8	56	65	321	76408
	A9	23.7	4.4	3.1	1.1	167	85	0.5	28	33	155	62459
	Min.		**0.1**	**1.8**	**0.2**	**74**	**68**	**0.0**	**18**	**22**	**115**	**54581**
	Max.		**18.8**	**4.1**	**4.8**	**1517**	**325**	**1.8**	**76**	**65**	**1392**	**93121**

Table 4.1 (Continued)

Station		Kilometric point (km)	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Al
Coum River	C1	00.0	1.2	4.9	0.4	109	61	0.1	46	38	148	82920
	C2	04.1	9.3	3.8	1.1	185	188	0.1	46	340	381	80458
	C3	09.2	2.6	4.5	0.9	123	86	5.7	44	52	203	81342
	C4	12.8	17.7	3.9	9.9	113	179	3.7	42	79	517	73788
	C5	14.6	22.4	4.3	16.2	119	254	1.7	47	71	586	70431
	C6	15.8	31.0	3.7	17.4	105	223	6.6	39	84	595	71871
	C7	17.4	16.1	3.5	7.3	95	155	4.3	36	58	382	73512
	C8	19.8	15.4	4.0	10.1	104	173	1.5	36	71	471	71787
	C9	23.5	9.0	10.8	7.8	226	302	1.8	49	145	402	77282
	Min.		**1.2**	**3.5**	**0.4**	**95**	**61**	**0.1**	**36**	**38**	**148**	**70431**
	Max.		**31.0**	**10.8**	**17.4**	**226**	**302**	**6.6**	**49**	**340**	**595**	**82920**
Drains	A_CSC	-	0.1	2.6	0.4	96	45	0.0	37	17	65	82391
	A_RP	-	7.2	3.9	0.7	267	159	1.7	61	59	776	74264
	A_BC	-	9.7	3.0	0.9	226	336	1.8	56	75	457	63803
	A_YMCA	-	14.3	3.9	10.0	131	239	1.4	44	65	415	70220
	C_NMR	-	14.5	4.3	37.6	95	346	1.5	40	54	442	64544
	C_GR	-	5.9	4.4	0.5	93	104	1.0	36	59	358	70749
	Min.		**0.1**	**2.6**	**0.4**	**93**	**45**	**0.0**	**36**	**17**	**65**	**63803**
	Max.		**14.5**	**4.4**	**37.6**	**267**	**346**	**1.8**	**61**	**75**	**776**	**82391**

4.2.1 Adyar River

In Adyar river, on analysis of sediments, it was found that trace elements such as Ag, Cd, Cu, Hg, Pb and Zn (0.1, 0.2, 68, > 0.0, 22 and 115 mg/kg respectively) were found in the minimum concentrations at most upstream station (A1) of the river. The source of Zn in sediment as could be from automobile industries and untreated waste water (Mohiuddin *et al.* 2010). At station A4, As and Ni are found to have least concentration. At station A5, Cr and Ni are found to be a least concentration. The highest sediment concentrations were found at station A6 for the trace element of Ag, Cd, Cu and at station A8 (6 km downstream from A6), for As, Hg and Pb.

Figure 4.1 shows the visible pollution status at sampling location in Adyar river, Chennai. These results indicate that most of the trace elements (Ag, As, Cd, Cu, Hg and Pb) increase from upstream to downstream of the Adyar river, which may be related to an increase of human activities with industrial or urban influences in the downstream (Lai *et al.* 2013). Other trace elements such as Cr, Zn (1517, 1392 mg/kg) are the highest at station A2 and Ni (76 mg/kg) at station A4 in the upstream part of the basin. The source of these trace elements may be from industrial and commercial uses. These are sensitive indicator of urban water pollution (Singare *et al.* 2012). The chromium (Cr) concentration is very high in the upstream stations like A2, A3 and A4 (1517, 925 and 700 mg/kg respectively). It decreases from downstream station A4 towards the river mouth.

Stations A2, A3 and A4 are located in Chromepet area (Figure 3.2) where many industries are present including metallurgical, electroplating, production of paints and pigments, tanneries, pulp and paper production. Especially, tanning industry is a large contributor of chromium pollution in water resources (Chandra *et al.* 1997; Islam *et al.* 2015).

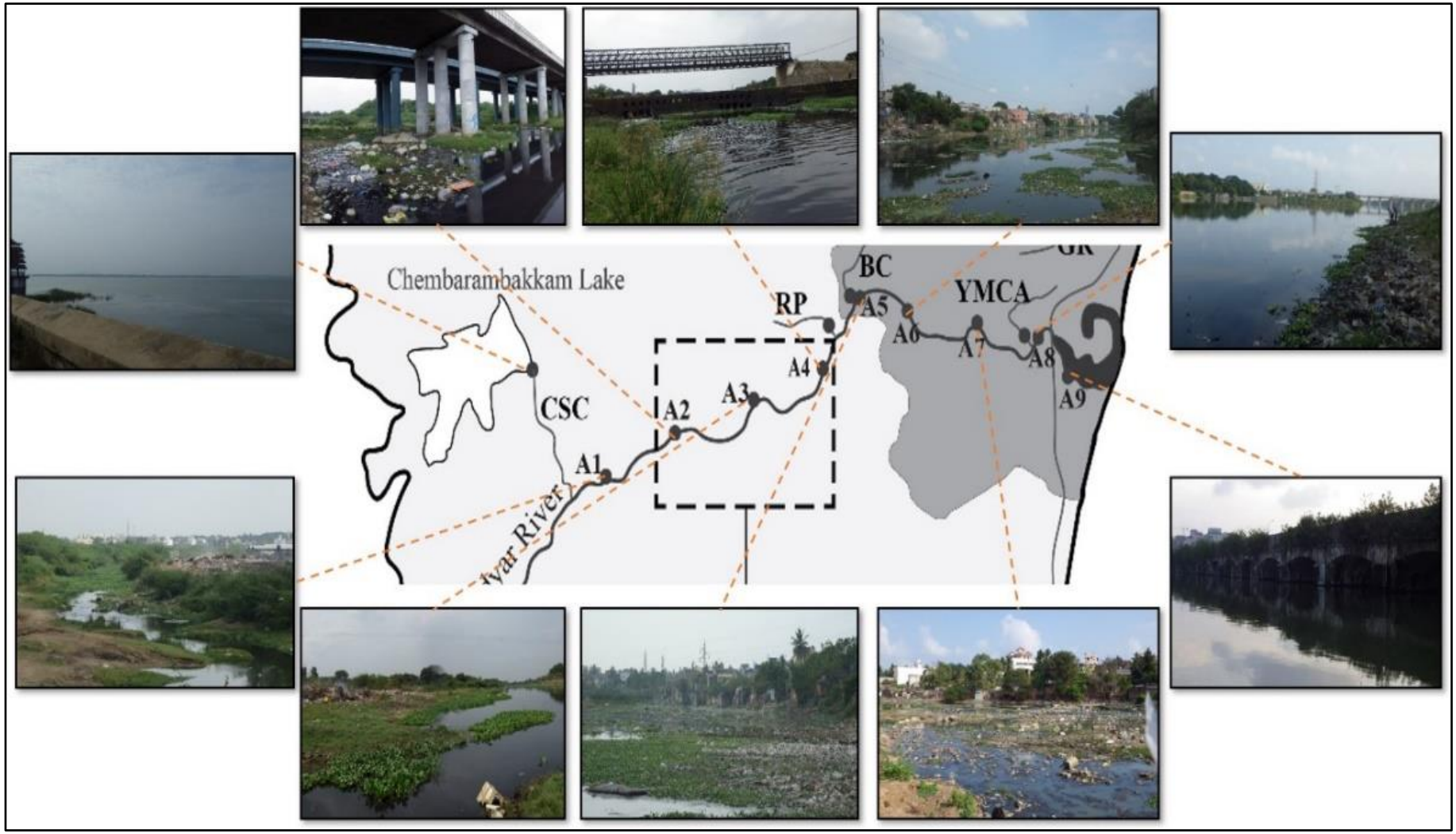


Figure 4.1 Visible pollution status in Adyar river sampling locations, Chennai

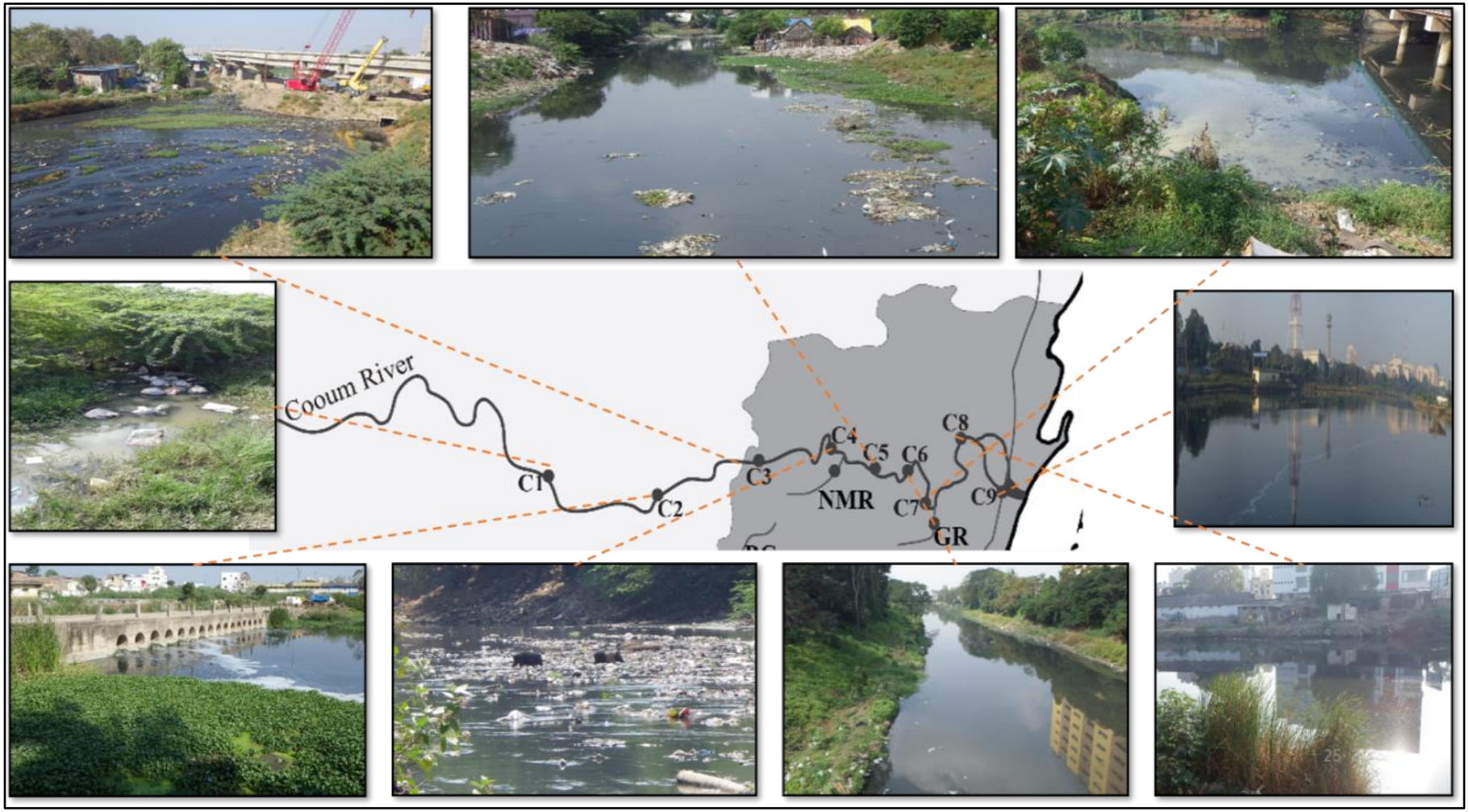


Figure 4.2 Visible pollution status in Cooum river sampling locations, Chennai

A cluster of around 152 tanneries are in the Chromepet area. Before establishment of treatment plant in 1995, effluents were discharged untreated into Adyar river (Ramesh kumar and Riyazuddin 2010). According to this augmentation of chromium content in sediments for this region, some leaching or malfunctioning of treatment plant can still occur in Chromepet area.

4.2.2 Cooum River

In Cooum river at station C6, highest concentrations of trace elements Ag, Cd, Hg, Zn and As, Cr, Cu, Ni was found at station C9. These results indicate that the downstream part of the river is influenced by anthropogenic activities. The highest concentration of Pb (340 mg/kg) is found in the upstream station C2. In this station, many numbers of automobile repair and service outlets, Small scale industries which are called auto garages are present, and they are discharge their effluents directly in the vicinity of station C3.

Normally Lead in urban dusts is a good indicator of traffic related sources and battery recycling plants (Singare *et al.* 2012) and is considered as an indicator of pollution by urban runoff water (Mohiuddin *et al.* 2011). The minimum concentration of trace elements Ag, Cd, Cu, Hg, Pb and Zn were found at the most upstream station C1 and also As, Cr and Ni the minimum concentrations are located at the downstream station C7. Figure 4.2 shows the visible pollution status at sampling locations in Cooum river, Chennai

4.2.3 Drains

Several types of drain were sampled in order to identify some potential trace element sources and to get a level of contaminant inputs. The drains collect untreated waste water from household, commercial establishments and hospital discharge in to the drain at station A_RP and C_GR. A_BC, A_YMCA and C_NMR are stations located at the drains which flow through the core Chennai city, hence collect waste water from urban activities. An additional station A_CSC (Chembarambakkam Surplus Channel), was taken into account to access the local and natural input levels as

surplus water is discharged into the Adyar river. Among the drains from Chennai Metropolitan Area (CMA), the minimum concentration of trace elements Ag, As, Cd, Cu, Hg, Pb and Zn were found in upstream station (Chembarambakkam Surplus Channel-CSC) which lies in Chennai peri-urban area. It reveals that the upstream stations are not influenced by urban activity.

The highest concentration measured at station A_RP (Ramapuram_near MIOT hospital) showed the trace elements Cr, Ni and Zn. Station A_BC (Burma Colony) for Hg and Pb are higher in Adyar river basin. Similarly, Cooum river basin at station C_NMR (Nelson Manickam Road) for the result of trace element Ag, Cd, Cu, and As at station C_GR (Greams Road_near Apollo hospital). This highest concentration results (station A_BC, A_YMCA, C_NMR, C_GR) are located, inside the boundary of Chennai city. In downstream, most of the stations show higher concentration in both rivers. Especially in Adyar river station A8 and A6 have highest concentration. This may be due to overflow of combined sewers from the drain (A_BC and A_YMCA) into the Adyar river.

The specific city of Chennai is related to the presence of drains, collecting dumped solid waste, unchecked discharge of untreated industrial effluents (mechanical, steel, plastics, fibre, textile, and surgical instruments factories, petrochemical industries and car workshops), effluent from a large number of educational institutions, hospitals and hotels, and domestic sewage from slums spreading extensively along the river banks. A total of 58 drain outlets discharge 0.775 million litres per day (MLD) of industrial effluent and 8.1 MLD of domestic sewage into the Adyar river between stations A6 and A9 (Veerasingam *et al.* 2012). Similarly, in Cooum river, 158 sewage/storm water outlets bring raw sewage and untreated water within the city limits. The Cooum river receives 0.4 MLD of industrial effluent and ten times more domestic sewage (80 MLD) from the drains than the Adyar river (Gowri & Ramachandran 2008). Therefore, several drains were sampled in order to quantify trace element levels from some potential source of pollution as they are considered as representative of specific urban inputs.

4.3 ASSESSMENT OF URBAN TRACER IDENTIFICATION

The most widely adopted pollution index, Geoaccumulation Index (I_{geo}), was calculated in this study and its spatial variations (Table 4.2 & 4.3) were used to identify specific urban tracers in river sediments of Chennai megacity. Mean I_{geo} were calculated for the upstream peri-urban area, considered in the Adyar river between KP 0 to 14 (4 stations, A1 to A4) and in the Cooum river, from KP 0 to 9 (stations C1 and C2) and for the urban area, downstream these stations up to the estuary. The I_{geo} value of the trace element (Ag, Cd, Cr and Hg) are illustrated in Figure 4.3 & 4.4 according to the kilometric points (KP).

In the upstream basins of both rivers, all the mean I_{geo} are lower than 3 for all the trace elements except Cr in the Adyar river (I_{geo} up to 4.8) and Ag in the Cooum river (I_{geo} up to 6.8; Figure 4.3 & 4.4). For chromium, the upstream part of Adyar river is located in the Chromepet area (Figure 3.2) where there are many industries including metallurgy, electroplating, paint and pigment production, tanneries, pulp and paper production. Tanning industry is a well-known contributor to chromium pollution of water resources (Chandra *et al.* 1997; Islam *et al.* 2015). Around 152 tanneries are clustered in the Chromepet area.

Table 4.2 Geoaccumulation Index (I_{geo}) of the trace elements in surface sediments of Adyar and Cooum rivers

Station		Kilometric point (km)	Geoaccumulation Index (I_{geo})								
			Ag	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Background shale value (Wedepohl 1995)			**0.055**	**2**	**0.102**	**35**	**14.3**	**0.056**	**18.6**	**17**	**52**
Adyar River	A1	00.0	0.28	0.03	0.56	1.42	1.66	-1.44	1.23	-0.22	0.56
	A2	03.0	3.18	0.04	2.29	4.85	3.46	0.32	1.27	1.12	4.16
	A3	06.6	2.96	-0.32	1.35	4.14	1.93	0.24	1.15	0.11	0.99
	A4	12.0	1.54	-0.75	1.45	3.74	1.94	0.08	1.45	-0.11	0.89
	A5	14.7	4.48	-0.71	2.41	0.50	1.78	1.91	-0.64	0.02	0.64
	A6	15.9	7.83	0.29	4.96	2.73	3.92	4.09	0.98	1.08	3.21
	A7	18.4	6.42	-0.04	3.31	1.64	3.08	2.57	0.65	1.23	1.98
	A8	21.9	7.20	0.46	3.89	2.77	3.16	4.44	1.01	1.36	2.04
	A9	23.7	5.75	0.06	2.89	1.67	1.98	2.54	0.00	0.39	0.99
	Min.	-	**0.28**	**-0.75**	**0.56**	**0.50**	**1.66**	**-1.44**	**-0.64**	**-0.22**	**0.56**
	Max.	-	**7.83**	**0.46**	**4.96**	**4.85**	**3.92**	**4.44**	**1.45**	**1.36**	**4.16**
Cooum River	C1	00.0	3.90	0.72	1.47	1.06	1.50	-0.35	0.71	0.58	0.92
	C2	04.1	6.81	0.33	2.80	1.82	3.13	0.18	0.73	3.74	2.29
	C3	09.2	4.99	0.59	2.56	1.22	2.00	6.08	0.67	1.03	1.38
	C4	12.8	7.75	0.38	6.02	1.11	3.06	5.46	0.60	1.62	2.73
	C5	14.6	8.08	0.52	6.73	1.18	3.57	4.35	0.75	1.47	2.91
	C6	15.8	8.55	0.32	6.83	1.00	3.37	6.29	0.50	1.71	2.93
	C7	17.4	7.61	0.24	5.58	0.86	2.85	5.69	0.38	1.19	2.29
	C8	19.8	7.54	0.40	6.04	0.98	3.01	4.18	0.38	1.47	2.59
	C9	23.5	6.77	1.85	5.68	2.11	3.82	4.45	0.82	2.51	2.37
	Min.	-	**3.90**	**0.24**	**1.47**	**0.86**	**1.50**	**-0.35**	**0.38**	**0.58**	**0.92**
	Max.	-	**8.55**	**1.85**	**6.83**	**2.11**	**3.82**	**6.29**	**0.82**	**3.74**	**2.93**

Table 4.3 Pollution classification of surface sediments

I_{geo} Class	I_{geo} Value	Polluted Level	Mean Value of Chennai Peri-urban Area		Mean Value of Chennai City	
			Adyar River (A1 to A4)	Cooum River (C1 & C2)	Adyar River (A5 to A9)	Cooum River (C3 to C9)
0	<0	Unpolluted	As, Hg	Hg	-	-
1	0-1	From Unpolluted to Moderately polluted	Pb	As, Ni	As, Ni, Pb	As, Ni
2	1-2	Moderately polluted	Ag, Cd, Ni, Zn	Cr, Zn	Cr, Zn	Cr, Pb
3	2-3	From Moderately polluted to Strongly polluted	Cu	Cd, Cu, Pb	Cu	Zn
4	3-4	Strongly polluted	Cr	-	Cd, Hg	Cu
5	4-5	From Strongly polluted to Extremely polluted	-	-	-	-
6	>5	Extremely polluted	-	**Ag**	**Ag**	**Ag, Cd, Hg**

Before the building of a waste/ water treatment plant in 1995, untreated effluent was discharged into Adyar river (Ramesh kumar & Riyazuddin 2010). The increase in the chromium content of sediments but also for Ag, Cd, Cu and Ni in this area would suggest that leaking and/or malfunctioning of the treatment plant is still occurring in the Chromepet area. For silver, its elevated I_{geo} in the upstream part of Cooum river (station C2) is associated with elevated I_{geo} for Cd, Cu, Pb and Zn. All these I_{geo} probably corresponds to specific inputs but not identified yet and to atmospheric deposition of finer particles from smelting operations, electrical products and coal combustion.

The mean I_{geo} value in Chennai city sediments were below the class 2 for As, Cr, Ni and Pb for both rivers and for Zn level in Adyar river sediment only (Table 4.3). Adyar river sediments are moderate to highly polluted in Cd, Cu and Hg and Cooum river sediments in Cu and Zn. The most elevated I_{geo} mean value was for Ag in Adyar river and for Ag, Cd and Hg in Cooum river sediments (Figure 4.4), corresponding to class >5 which indicate a highly to extremely polluted state. Specifically, sources of Ag can be related to metallurgy activities, electronic products, medical equipment and/or practices, health care product use, jewellery, antimicrobial agents used in fibres and water purification systems (Chambers *et al.* 2016).

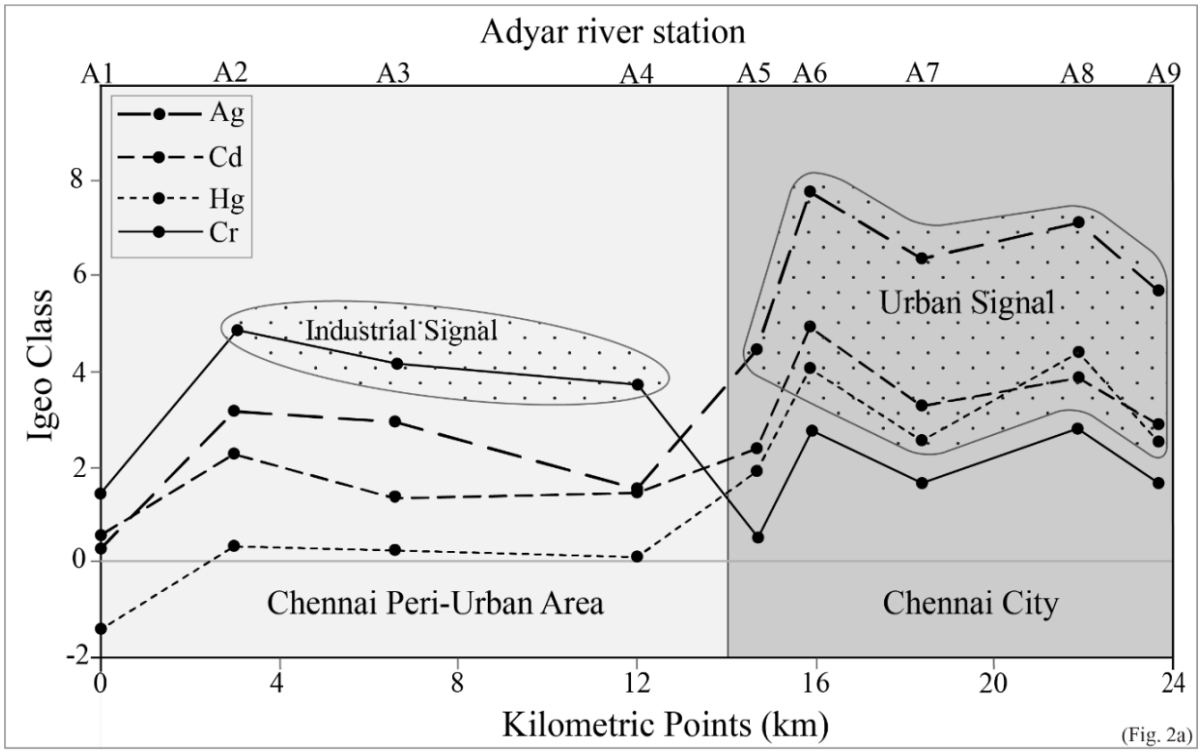


Figure 4.3 Geoaccumulation Index (I_{geo}) value of trace element (Ag, Cd, Cr and Hg) in Adyar river sediments

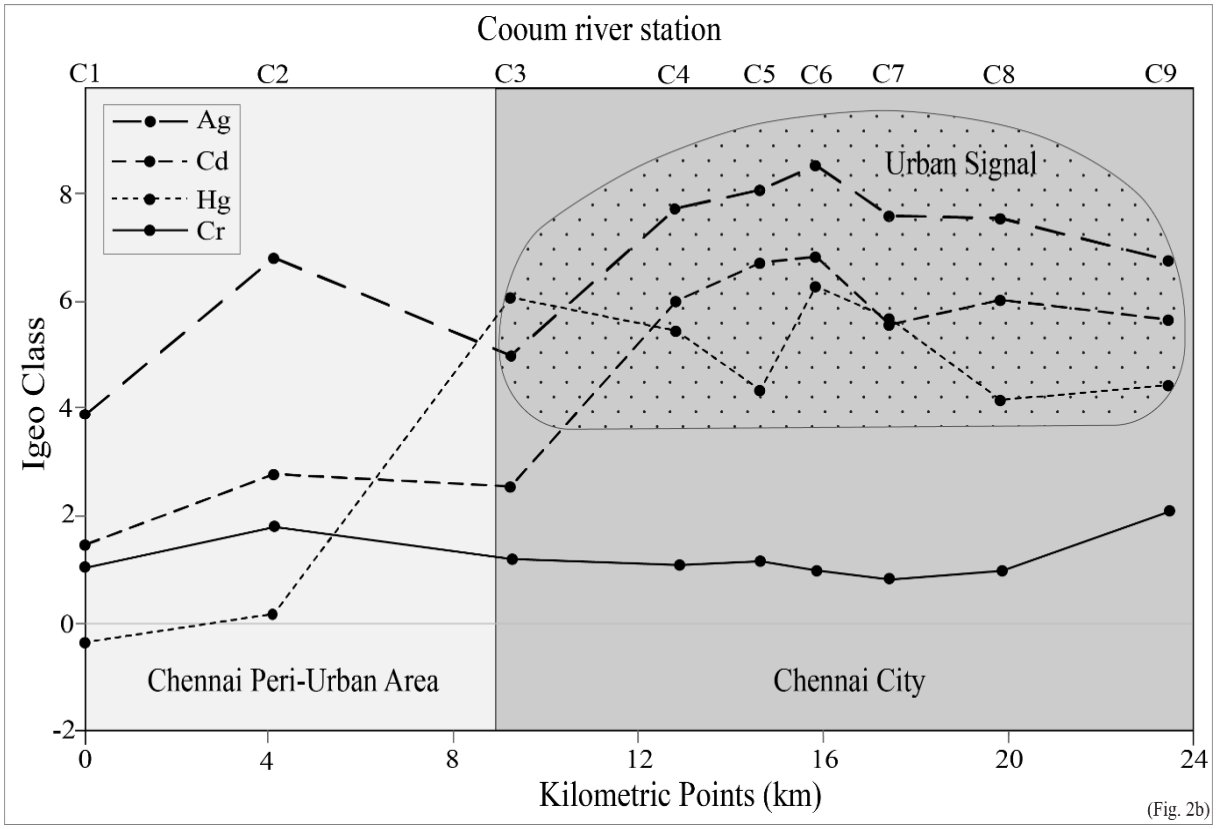


Figure 4.4 Geoaccumulation Index (I_{geo}) value of trace element (Ag, Cd, Cr and Hg) in Cooum river sediments

Some very small particles of pure Ag have been detected in Adyar sediments at station A6 using SEM-EDX observations (Figure 4.5). Their angular shape, small size (<8-10 µm) linked with their mono-elemental composition can be associated with very low sedimentary transport and an anthropogenic origin.

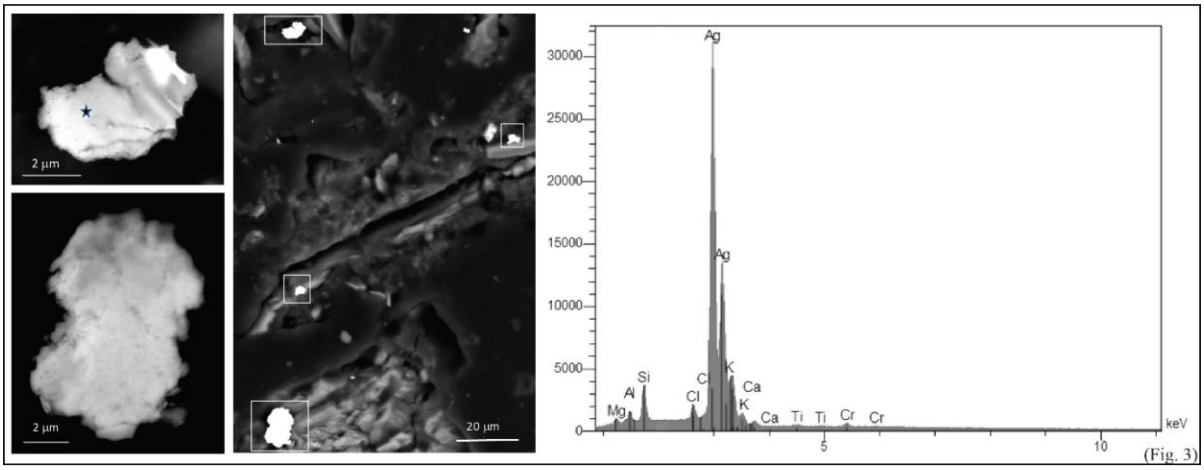


Figure 4.5 Particles of metallic Ag in Adyar river sediments

Hence, the increase of mean I_{geo} values of Ag, Cd and Hg is clearly significant in Chennai urban area of both rivers when compared with the upstream reaches (Figure 4.3 and 4.4). These 3 trace elements can thus be used as urban pollution tracers in Chennai.

4.4 ASSESSMENT OF A GLOBAL URBAN FOOTPRINT INDEX

The Geochemical Urban Footprint Index (GUFI) was specifically developed for this study. This new index combines a spatial reference (here the most upstream station the least impacted) and the three main urban pollution tracers, Ag, Cd and Hg, selected on the basis of the results of I_{geo} analyses. The GUFI analysis was designed to represent a global urban geochemical footprint and independent of specific human activities or local effluents. The MUI and GUFI levels of contamination of each river station are then calculated at each river station (Table 4.4 & 4.5) and associated to population density and to identified polluting hotspots at the ward scale.

In the entire Chennai peri-urban area (station A1 to A4 in Adyar river and C1 and C2 in Cooum river), the GUFI results show that contamination of the sediment is low in both rivers. In the city of Chennai, the spatial trend of GUFI results indicate moderate to extreme contamination, particularly for downstream stations (station A6 to A9 in Adyar river and C3 to C7 in Cooum river). However, this type of contamination is most complex for multiple sources of pollution. For this reason, sediment samples taken from major drains in Chennai city were useful to identify sources of pollution and their respective levels of contamination.

Table 4.4 MUI and GUFI of the trace elements from surface sediments of Adyar and Cooum rivers

Station		Kilometric point (km)	MUI			GUFI
			Ag	Cd	Hg	
Adyar River	A1	00.0	1.00	1.00	1.00	1.00
	A2	03.0	9.18	4.08	4.15	5.80
	A3	06.6	6.90	1.87	3.44	4.07
	A4	12.0	2.90	2.24	3.47	2.87
	A5	14.7	31.39	6.15	17.34	18.29
	A6	15.9	285.74	32.27	70.11	129.38
	A7	18.4	97.35	9.33	22.24	42.97
	A8	21.9	147.47	12.29	71.75	77.17
	A9	23.7	66.20	7.52	23.57	32.43
	Min.	-	**1.00**	**1.00**	**0.51**	**1.00**
	Max.	-	**285.74**	**32.27**	**71.75**	**129.38**
Coum River	C1	00.0	1.00	1.00	1.00	1.00
	C2	04.1	7.75	2.58	1.48	3.94
	C3	09.2	2.18	2.16	88.04	30.79
	C4	12.8	16.17	26.17	62.83	35.06
	C5	14.6	21.44	44.85	30.59	32.29
	C6	15.8	29.08	47.26	114.85	63.73
	C7	17.4	14.76	19.42	74.00	36.06
	C8	19.8	14.46	27.45	26.60	22.84
	C9	23.5	7.83	19.74	29.83	19.13
	Min.	-	**1.00**	**1.00**	**1.00**	**1.00**
	Max.	-	**29.08**	**47.26**	**114.85**	**63.73**
Drains	A_CSC	-	1.13	1.88	0.51	1.17
	A_RP	-	13.53	77.57	7.70	32.93
	A_BC	-	21.28	94.94	12.00	42.74
	A_YMCA	-	28.50	63.70	121.43	71.21
	C_NMR	-	83.21	102.40	317.27	167.63
	C_GR	-	30.68	60.94	4.00	31.87
	Min.	-	**1.13**	**1.88**	**0.51**	**1.17**
	Max.	-	**83.21**	**102.40**	**317.27**	**167.63**

Table 4.5 GUFI classification based on the level of contamination from surface sediments of Adyar and Cooum rivers

GUFI Range	Level of Contamination	Adyar River	Cooum River	Drains
1 – 10	Extremely Low Contamination	A1, A2, A3, A4	C1, C2	CSC
10 – 25	Low Contamination	A5	C8, C9	-
25 – 50	Moderate Contamination	A7, A9	C3, C4, C5, C7	RP, BC, GR
50 – 75	High Contamination		C6	YMCA
75 – 100	Very High Contamination	A8	-	-
> 100	Extremely High Contamination	A6	-	NMR

Inside the city, all the sampled drains were contaminated from moderate to extreme levels. The results clearly show that pollution sources came directly from the urban area and related to different urban activities, such as untreated sewage water outputs, dumping areas, hospital effluent outlets and unplanned urban growth. The GUFI results of the drains studied in the city reveal that contamination levels originated from various sources, in line with the overall trend of population density, the city development and punctual industrial hotspots.

Socioeconomic data was collected to identify the causes of these pollution hotspots. For administrative purposes, Chennai is divided into 155 wards, the limits of which are fixed by the Chennai Metropolitan Development Authority (CMDA) (Figure 4.6).

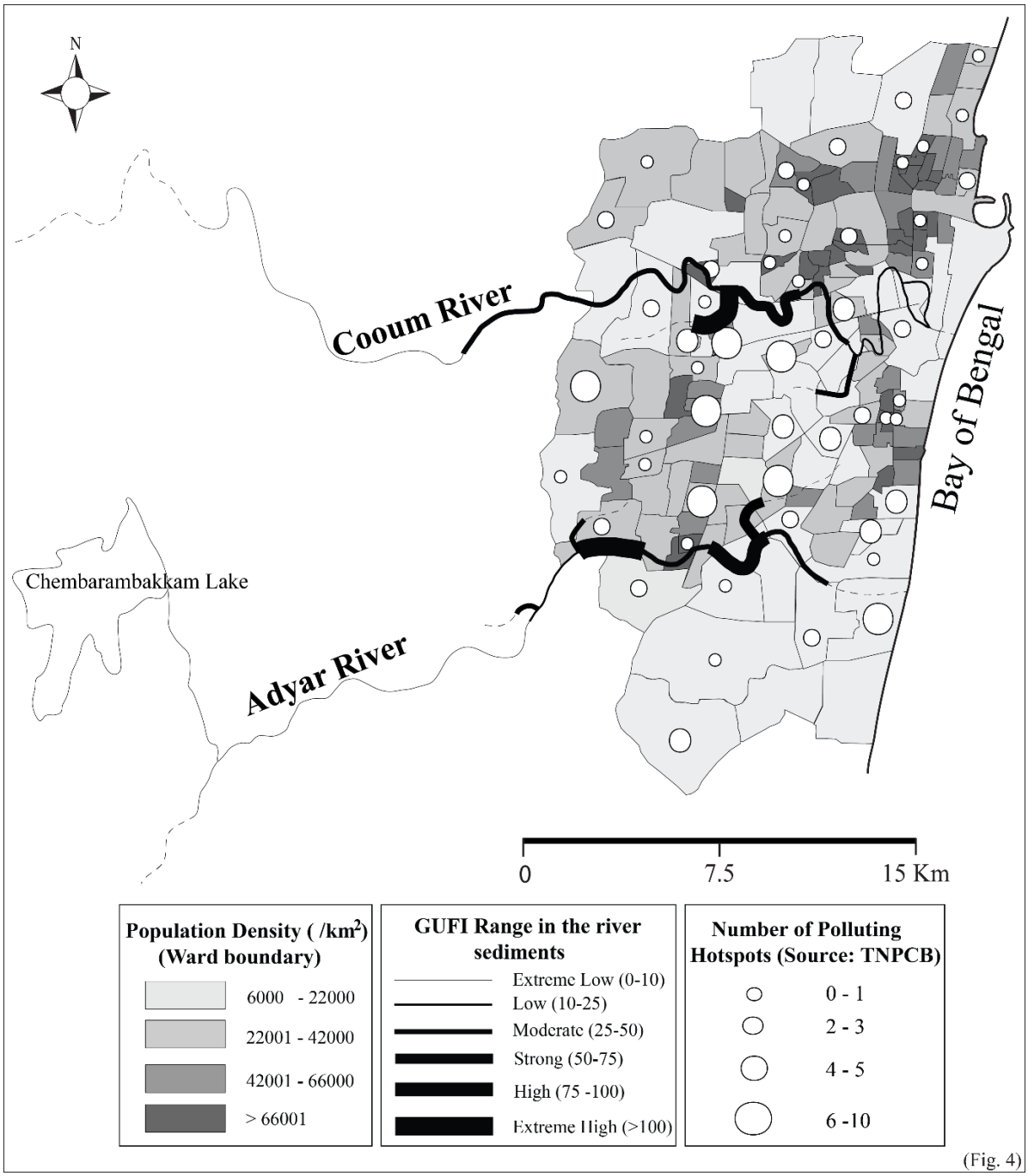


Figure 4.6 Longitudinal variation of the GUFI in Chennai megacity

These polluting hotspots originate from industries, institutions, commercial buildings, sewage treatment plants, effluent treatment plants, etc. and information about them was obtained from the Tamil Nadu Pollution Control Board (TNPCB), which classifies hotspots into three categories: red, orange and green, based on sewage/effluent discharge levels from various activities. Each category is subdivided into three classifications: large, medium and small.

For this study, only large and medium red hotspots were taken into account, corresponding to the most polluting hotspots which discharge huge amounts of effluent. All the data on population and polluting hotspot are trying to frame deprivation index and to identify the cause of Chennai Pollution. However, Baud *et al.* (2009) mentioned that Chennai is a complex city and a straight comparison is less valid than in other Indian megacities due to population density and industrial hotspots.

4.5 COMPARATIVE ANALYSIS OF MEGACITY POLLUTION LEVEL USING SQGS

This comparative analysis was conducted on worldwide megacities and their respective geochemical state in order to assess trace element concentrations in the megacity of Chennai. The following megacities were statistically selected, according to different criteria such as:

- Population range greater than 10 million
- The presence of river flowing inside the megacity limits
- Availability of data on trace element levels in the corresponding sediments

In the literature dedicated to urban sediments, concentrations of such trace elements Cr, Cu, Ni, Pb and Zn are the most surveyed in megacity rivers and canals as they are ubiquitous. Information about population density and world population rank were also collected for all these megacities from Demographia, (April 2017), a robust and exhaustive database (Table 4.6).

Concentrations below the Threshold Effect Concentration (TEC) indicate no harmful effects and those above the Probable Effect Concentration (PEC) indicate that harmful effects can be expected (Helen *et al.* 2016). In the selected megacity rivers, mean concentrations of Cu, Pb and Zn are lower than the proposed TECs level (Table 4.6), indicating no harmful effects in Jakarta (Ciliwung river, Indonesia) and Kinshasa (Congo river, DR Congo). Whereas, the mean concentrations of Cr, Cu, Pb, Ni and Zn in surface sediments for Tokyo-Yokohama (Tsurumi river, Japan), Jakarta (Ciliwung river, Indonesia) and Seoul (Han river, Korea) are higher than the PEC level.

Other megacity rivers present concentrations lower than the PEC except for a few trace elements, including: (i) the Pearl river in Guangzhou (China) with Cu concentration exceeding the PEC level due to local sources from the urban area (Wang *et al.* 2011); (ii) the Congo river in Kinshasa, (DR Congo) with Ni concentrations exceeding due to human activities and the presence of uncontrolled landfills (Mwanamoki *et al.* 2014); (iii) the Seine river in Paris (France) with Pb concentrations exceeding due to smelting and metallurgical industries (Grosbois *et al.* 2006); (iv) the discharge canal in Lagos (Nigeria) with Cr and Pb concentrations as a result of industrial and anthropogenic sources in the city (Ajibola & Ladipo 2011); (v) the Tham Luong canal in Ho Chi Minh City (Vietnam) with Zn and Cr concentrations coming from chemical plant wastes released directly into the canal and indirectly from a dry land (Huy *et al.* 2003).

Similarly, in South Asian countries rivers such as Yamuna river in Delhi, Mithi river in Mumbai and Buriganga river in Dhaka, concentrations are higher than the proposed PEC levels for Zn, Cr, Cu, Pb and Ni (except Pb in Delhi). These results show that, factors such as population growth, industrial aggravation (automobile, tanneries etc.), untreated industrial discharges and domestic waste waters of households may have influenced trace element concentrations. All these controlled and uncontrolled discharges impact biological life of the river (Sing 2001; Singare *et al.* 2012; Mohiuddin *et al.* 2011).

Table 4.6 Mean concentration of trace elements in surface sediments of various megacity rivers and canals and their associated megacity pollution rank based on SQG

Name of the megacity	World population rank (Apr 2017)	Population (million)	Population density (/km^2)	Name of the river	Trace Element (mg/kg)					References	Megacity Pollution Rank *
					Zn	Cr	Cu	Pb	Ni		
SQGs for TEC level					**121**	**43**	**32**	**36**	**23**	MacDonald *et al.* 2000	
SQGs for PEC level					**459**	**111**	**149**	**128**	**49**	MacDonald *et al.* 2000	
Tokyo-Yokohama, Japan	1	37.900	4400	Tsurumi river	381	103	133	41	37	Mohiuddin *et al.* 2010	**9**
Jakarta, Indonesia	2	31.760	9600	ciliwung river	10	-	2.8	0.8	-	Yasuda *et al.* 2011	**12**
Delhi, India	3	26.495	12000	yamuna river	561	394	275	76	159	Sing. 2001	**3**
Seoul, Korea	5	24.105	8800	Han river	225	84	55	45	34	Lai *et al.* 2013	**10**
Mumbai, India	8	22.885	26000	Mithi river	-	477	-	849	860	Singare *et al.* 2012	**1**
Guangzhou, China	13	19.075	5000	Pearl river	388	97	352	103	-	Wang *et al.* 2011	**6**
Dhaka, Bangladesh	15	16.820	45700	Buriganga river	836	610	232	476	125	Mohiuddin *et al.* 2011	**2**
Lagos, Nigeria	24	13.360	9400	Discharge canal	319	157	68	130	48	Ajibola and Ladipo 2011	**8**
Kinshasa, DR Congo	28	11.855	20300	Congo river	50	59	24	9.3	58	Mwanamoki *et al.* 2014	**11**
Paris, France	31	10.950	3700	Seine river	231	-	56	169	-	Grosbois *et al.* 2006	**7**
Ho Chi Minh City, Vietnam	35	10.380	6600	Tham Luong canal	719	256	-	55	-	Huy *et al.* 2003	**4**
Chennai, India	36	10.265	9900	Adyar river	381	488	147	41	52	Present Study	**5**
Chennai, India	36	10.265	9900	Cooum river	409	131	180	104	43	Present Study	**5**

*** The rank is based on trace element concentration using PEC levels**

The megacities selected can be ranked according to (i) a population rank and Tokyo-Yokohama (Japan) present the largest population in the world (37.9 million) but also to (ii)- a megacity pollution rank. For this latter ranking, a comparative analysis of the megacities selected was carried out with the mean PEC quotient defined about (Table 4) and the order is from the most to the least impacted megacity: Jakarta > Kinshasa > Seoul > Tokyo-Yokohama > Lagos > Paris > Guangzhou > Chennai > Ho Chi Minh City > Delhi > Dhaka > Mumbai. This ranking of megacity pollution enables the cities to be divided into two groups:

- The first group refers to cities in Asia, the top six ranked cities are: Mumbai (India); Dhaka (Bangladesh); Delhi (India); Ho Chi Minh City (Vietnam); Chennai (India) and Guangzhou (China). Similar levels of pollution can be observed in all of them due to rapid urban population and industrial growth. In terms of geochemical footprint, emerging cities which combine massive population growth and industrial activities have changed from traditional practises to modern economical activities. Chennai is the fifth most polluting megacity worldwide. It is on a par with the level of pollution of Ho Chi Minh City (Vietnam) and Guangzhou (China).

- The second group of megacities is composed of Paris (France), Lagos (Nigeria), Tokyo-Yokohama (Japan), Seoul (Korea) and Kinshasa (DR Congo). These five cities have similar pollution levels. However, Nigeria and DR Congo are in developing countries, whereas France, Japan and Korea are developed. In upcoming decades, if such development in Nigeria and DR Congo continued, Lagos and Kinshasa may result in pollution levels of the first group. On the other hand, the Seine in Paris (France) showed greater pollution during the 1980s but with the introduction of strict regulations on water bodies pollution, its status has greatly improved. Similarly, in Tokyo-Yokohama (Japan)

and Seoul (Korea) pollution levels must now comply with strict regulations.

- For Jakarta (Indonesia), concentration is probably out of range with concentrations at least 10 times lower than other megacity sediments. This megacity presents the second highest population in the world and water quality of the river is very poor due to discharging municipal waste (Palupi *et al.* 1995). So, this study Yasuda *et al.* (2011) will not be taken into account for Ciliwung river sediments

The comparison of ubiquitous trace element pollution of megacities is presented in Figure 4.7. The Chennai sediment quality (9 samples each from the Adyar and Cooum, rivers) was compared to worldwide megacity river sediments (11 megacity) using PEC values.

The three plots represent the Adyar river, Cooum river and the mean value for worldwide megacity rivers, and median concentrations are compared with the PEC threshold. The median concentration of Zn and Pb are below the PEC threshold in the three cases and other trace elements (Cr and Ni) are also below the PEC level only in Cooum river and remaining rivers (Adyar and other megacity) are above the PEC levels. The higher PEC level concentrations are increased by the influence of industrial activities. Example: In Adyar river Cr concentration level is 1517 mg/kg at station A2 (Table 4.1) showing an influence of tanneries from Chromepet area (Figure 4.2).

Similarly, worldwide megacity concentration of the element Cr is higher in the megacity of Delhi, Mumbai, Dhaka, Lagos, Ho Chi Minh city, with an impact of multi-source of industrial activities. The same impact has affected in worldwide megacities, for the element of Ni concentration. The median concentration of Cu is above the PEC level in Cooum river and below the PEC level in Adyar and worldwide megacities rivers. These megacity comparison, Cr and Ni concentrations are observed in many megacities and Cu, Pb and Zn concentrations are observed in very few megacities and commonly associated with urban pollution.

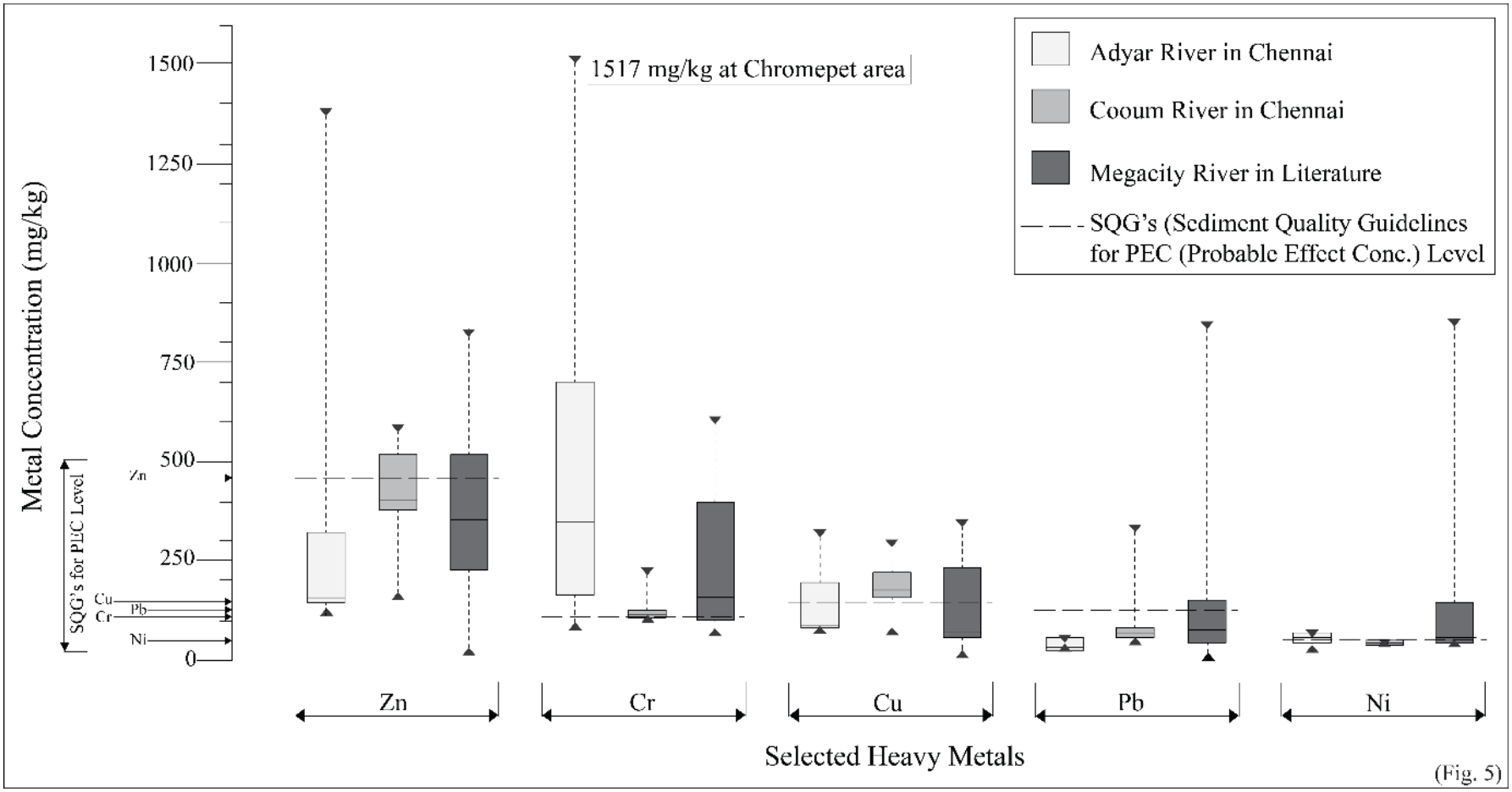


Figure 4.7 Box plots of selected ubiquitous trace element comparison of Chennai sediment quality to worldwide megacity sediments using SQGs

The megacity has a trend pattern in the following order of ubiquitous trace element as Zn < Cr < Cu < Pb < Ni. Most of these element concentrations are dissociate by various industrial effluents and subsequently changed geochemical character of the urban environment. This kind of worldwide megacities river sediment comparison is new from the previous research report, because this study has newly developed pollution ranking based on the ubiquitous trace element from the river sediments and compare to the different megacities pollution levels.

4.6 CONCLUSION

This study was conducted to determine and understand sediment quality of the two main rivers in Chennai megacity. The overall results of sediment concentrations indicate an extremely polluted urban fluvial system. The geoaccumulation Index (I_{geo}) revealed that concentration of Ag, Cd and Hg were present at levels indicating a highly to extremely polluted level for sediments in the urban area. Concentration of Cr, however, did indicate an extremely polluted state in the most upstream part of the Adyar river due to the influence of the tanning region. In general, this extremely polluted state can be linked to various pollutants discharged via diffuse urban and point industrial sources operating in and around the river bed. Thus Ag, Cd and Hg concentrations can be used as urban tracers and Cr concentration can be considered as an industrial marker in Chennai megacity.

The Geochemical Urban Footprint Index (GUFI), specifically developed in this study, was calculated by combining the concentrations of these three key trace elements (Ag, Cd and Hg), compared to the most upstream and non-impacted station. The GUFI was designed to represent a global urban geochemical footprint, regardless of specific human activities and local effluents and it appears to be an indicator of anthropogenic impact in Chennai rivers. The GUFI results show that Chennai peri-urban area sediment has an extremely low level of contamination, indicating that these stations are not influenced by urban activity. Downstream in Chennai city, GUFI trends for both rivers and drains are moderately to extremely high contamination, particularly for sediment concentrations at stations A6 and A8 on the Adyar river

where levels were very high to extremely high. This increase in GUFI levels in the urban area is directly related to overflow of combined sewers as shown with the analysis of highly impacted sediments in sampled urban drains. It can also be linked to an overall trend of population and industrial increases. However, this correlation could not be direct as no upstream to downstream gradient could be evidenced with population density nor the number of identified point pollution hotspots. Therefore, the new GUFI developed here can provide an alternative to the I_{geo} to assess and quantify the pollution severity status of any megacity river which is influenced by contamination due to urbanisation.

Surface sediment concentration of ubiquitous trace element (Cr, Cu, Ni, Pb, Zn) in various rivers and drains of megacities worldwide were compared using the mean PEC quotient for pollution. According to this megacity pollution ranking, Chennai is ranked fifth. It can be noted, here that the first six rankings all being megacities in Asian countries. This ranking puts Chennai on a par in terms of pollution with other highly populated megacities in the world, such as Ho Chi Minh City (Vietnam) and Guangzhou (China). Their pollution levels are similar in terms of the geochemical footprint of emerging cities combining massive population growth and industrial activity.

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CHAPTER 5

ENDOCRINE DISRUPTOR OCCURRENCE

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5.1 GENERAL

The organic pollutants, which cause adverse effects on the environment and human health. These are ubiquitous and highly persistent in the environment, in soils, sediments, air or biota (Boll *et al.* 2008; Radice *et al.* 2008). Large amount of organic pollutant is transported to receiving waters and accumulated into the sediments. Sediments constitute one of the main constituent of the aquatic environment where organic contaminants can be accumulated. Some pollutants may be associated with fine sediment particles causing gradual or instant deterioration of the aquatic system (Boll *et al.* 2008; Dos santos *et al.* 2018). Hence, a better understanding of the fate of endocrine disruptors is required and is ultimately essential for managing organic contaminant levels in the urban environments. The present study is designed to: (i) identify spatial distribution of organic contaminants (PAHs, PCBs, Phthalates and PBDEs); (ii) identify and assess the pollution emission sources using PAHs diagnostic ratios; (iii) endeavored sources, concentrations and hazard levels of PCBs, PBDEs and Phthalates in the surface sediments.

5.2 SPATIAL DISTRIBUTION OF ORGANIC COMPONENTS

The prime aim of this study is to describe the spatial distribution of organic contaminants (PAHs) in surface sediments of the two studied urban rivers. Sampling locations of urban rivers are shown in Figure 5.1. The concentration of PAHs obtained from sediment samples of the Chennai megacity rivers are reported in Table 5.1. The total of 13 PAHs in sediments sample were identified and quantified to the concentrations.

In Adyar river, total concentration of PAH (Σ_{13} PAHs) ranged from 0.136 to 2.032 mg/kg. Similarly, Cooum river ranged from 0.471 to 3.753 mg/kg. The total

concentrations of Σ_{13} PAHs in sediment samples are greater in Cooum river than in the Adyar river.

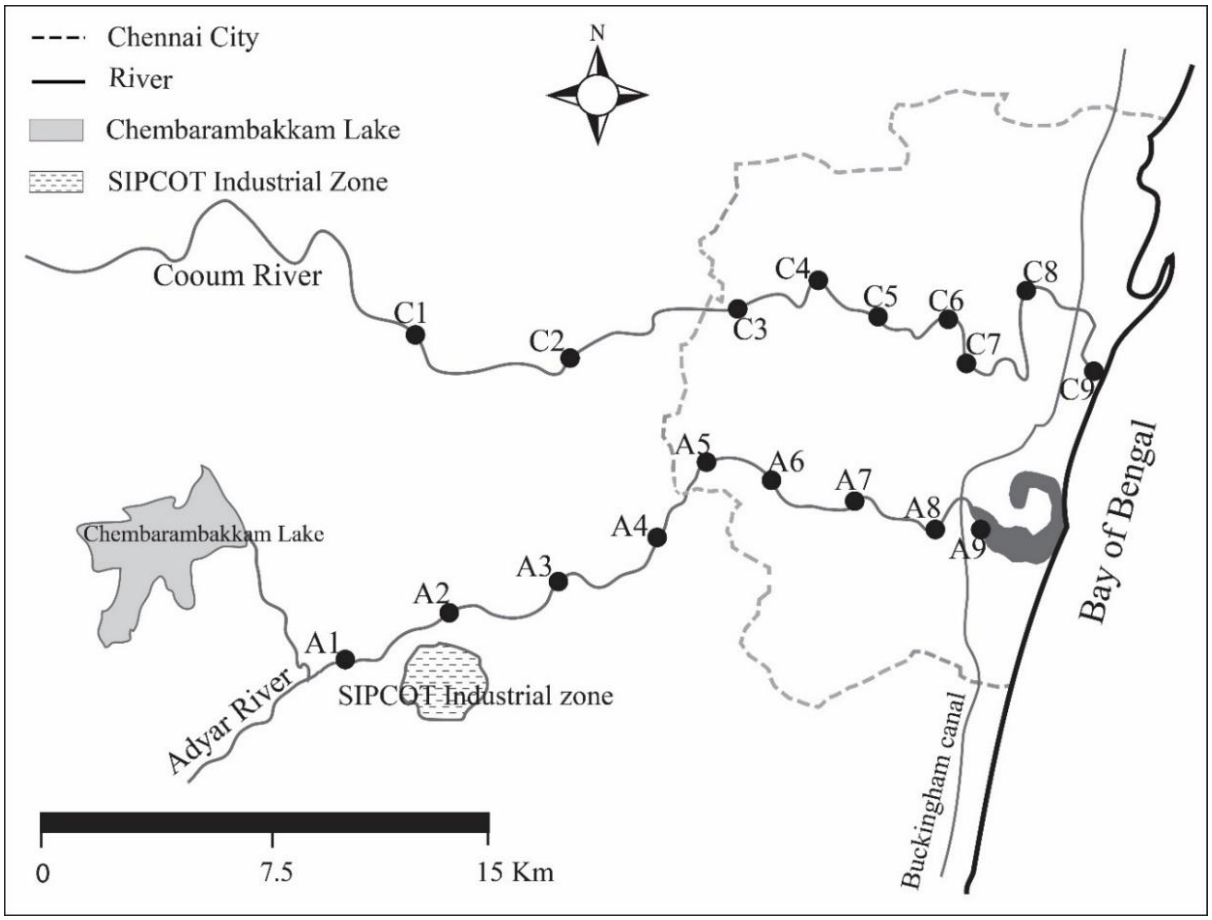


Figure 5.1 Sampling locations in urban rivers

Table 5.1 Sediment concentrations of thirteen individual PAHs (mg/kg) of Chennai megacity rivers – see Figure 6.1 for locations

Station		ANT	FL	PHE	BaA	CHR	FLA	PYR	BaP	BbF	BkF	DahA	BghiP	IcdP	Σ_{13} PAH
Adyar River	**A1**	-	0.043	0.059	-	-	-	0.034	-	-	-	-	-	-	**0.136**
	A2	0.085	0.135	0.187	0.087	0.112	0.15	0.347	0.044	0.072	-	-	0.038	-	**1.256**
	A3	0.036	0.103	0.096	0.031	0.039	0.027	0.069	-	-	-	-	-	-	**0.401**
	A4	0.033	0.07	0.075	0.035	0.043	-	0.099	-	-	-	-	-	-	**0.355**
	A5	0.026	0.041	0.083	-	0.044	0.061	0.045	-	0.044	-	-	0.056	0.023	**0.423**
	A6	0.17	0.124	0.356	0.065	0.171	0.387	0.264	0.057	0.251	0.045	-	0.202	0.069	**2.161**
	A7	0.129	0.089	0.306	0.141	0.111	0.254	0.255	0.089	0.243	0.055	-	0.125	0.072	**1.869**
	A8	0.215	0.133	0.184	0.138	0.198	0.202	0.201	0.126	0.323	0.066	-	0.144	0.103	**2.032**
	A9	0.025	0.028	0.048	-	0.023	0.027	0.041	-	0.031	-	-	0.027	-	**0.250**
Cooum River	**C1**	0.075	0.139	0.089	0.043	0.066	-	0.021	0.057	0.02	-	-	0.03	-	**0.539**
	C2	0.08	0.091	0.154	0.022	0.033	0.045	0.047	-	-	-	-	-	-	**0.471**
	C3	0.119	0.128	0.147	0.082	0.164	0.1	0.094	-	0.031	-	-	0.093	-	**0.959**
	C4	0.231	0.135	0.252	0.139	0.148	0.267	0.228	0.117	0.307	0.06	-	0.159	0.105	**2.148**
	C5	0.333	0.137	0.352	0.238	0.148	0.453	0.366	0.141	0.469	0.096	0.021	0.251	0.147	**3.152**
	C6	0.281	0.171	0.268	0.094	0.117	0.19	0.17	0.06	0.221	0.038	-	0.142	0.081	**1.833**
	C7	0.15	0.136	0.281	0.14	0.201	0.269	0.238	0.094	0.247	0.046	-	0.118	0.086	**2.005**
	C8	0.139	0.113	0.243	0.287	0.283	0.27	0.269	0.103	0.298	0.06	0.035	0.169	0.113	**2.381**
	C9	0.355	0.147	0.373	0.298	0.254	0.377	0.449	0.195	0.643	0.138	0.037	0.292	0.196	**3.753**

The minimum concentration Σ_{13} PAHs are in the upstream side of both the rivers, except station A2 of Adyar river due to the effluents of industrial zone in SIPCOT. Inside the SIPCOT many industries, such as chemical plants, tanneries, automobile, mechanical, steel and plastic industries located close to the station A2 (Chandra *et al.* 1997; Ramesh kumar & Riyazuddin 2010; Veerasingam *et al.* 2012; Saravanan *et al.* 2019). These Industries are emitting the pollution and accumulating large volumes of organic sludges. Similarly, the higher concentration Σ_{13}PAHs are sited in downstream side (station A6 to A8 in Adyar river and station C4 to C9 in Cooum river) of the river, except station A9 in Adyar river, this is due to the influence of backwater of sea and saline intrusion. These sites were all within the main urban area of Chennai megacity, with a higher population density (Saravanan *et al.* 2019). The organic pollutions were directly associated with dense population and proximity to waste water (Wang *et al.* 2018). Therefore, domestic wastewater and sewage might be the main source of these stations.

5.2.1 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) has been applied to evaluate the samples in Adyar and Cooum river (Figure 5.2 & 5.3). The PC 1 contributes with 81.98% of the variance in Adyar river and 80.25% in Cooum river. It is observed that the dominant variables in PC 1 are ANT, FL, PHE, BaA, CHR, FLA, PYR, BaP, BaF and BghiP. The higher molecular weight compounds (4, 5 and 6 rings) presented higher absolute loadings (> 0.1). These compounds presented more contribution to discrimination of sediment samples. Normally these compounds are caused by pyrolytic processes and anthropogenic origin (Santos *et al.* 2018).

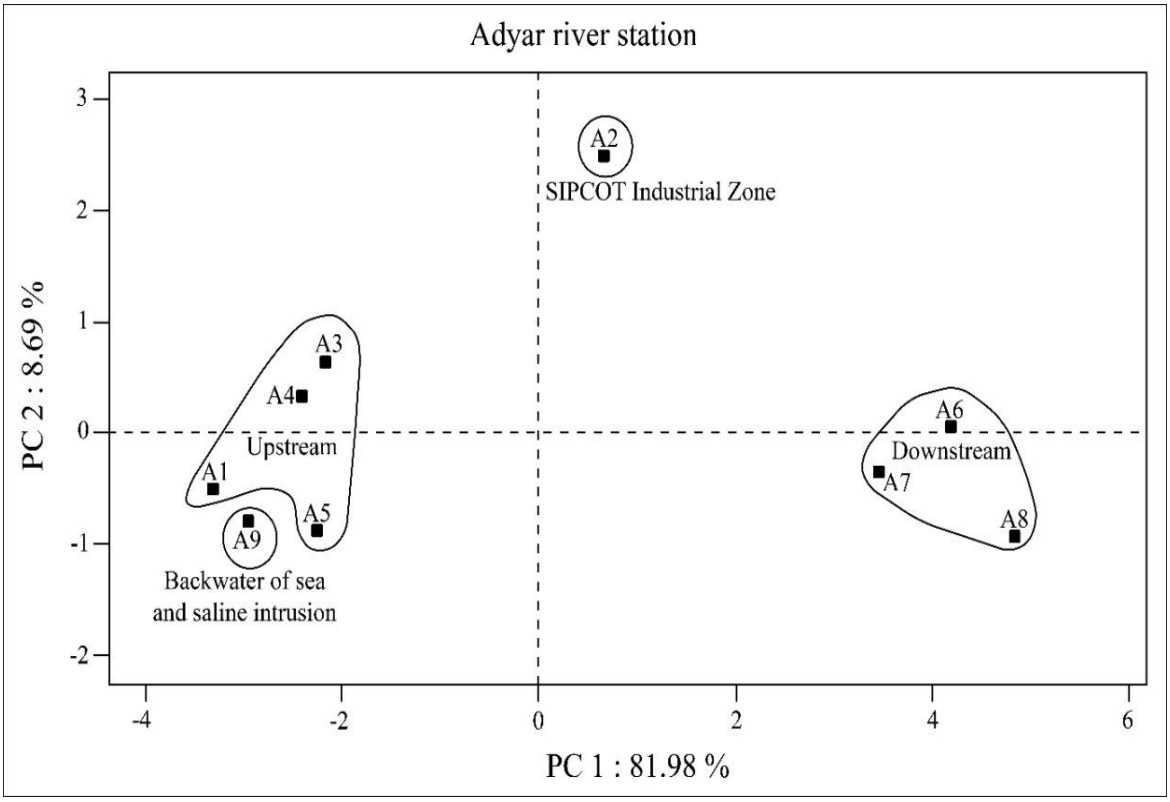


Figure 5.2 Principal component analysis of sediment samples in Adyar river stations

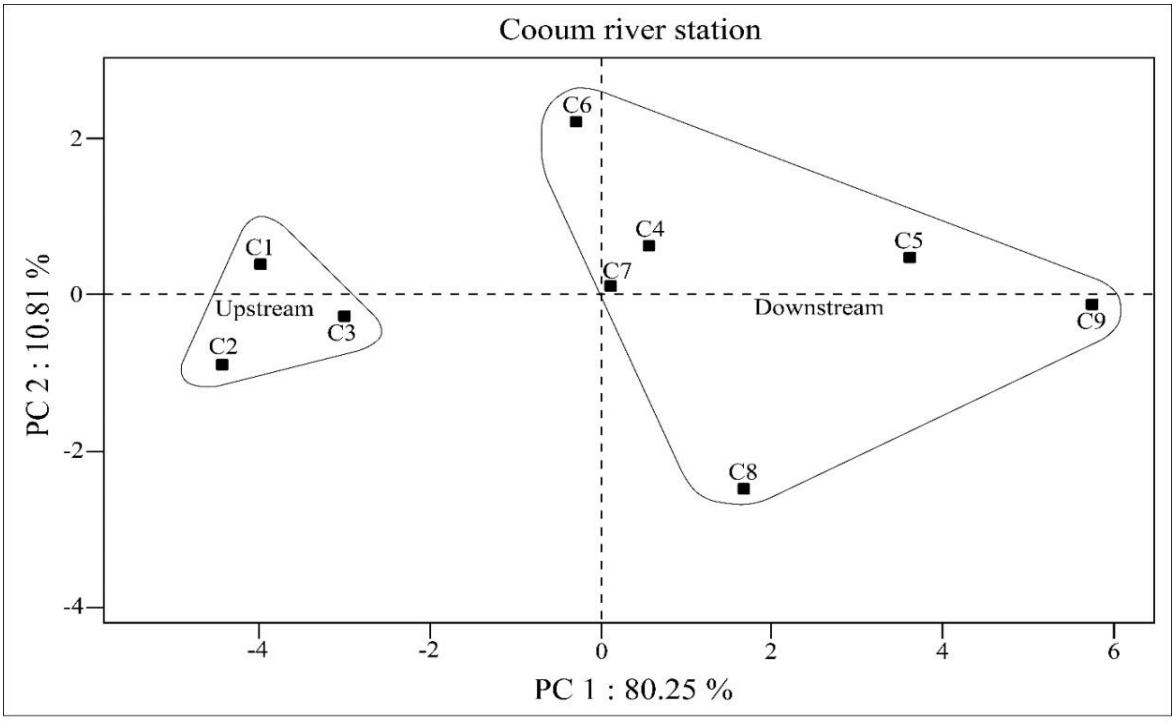


Figure 5.3 Principal component analysis of sediment sample in Cooum river stations

From the Figure 5.2 & 5.3, on PC1 it is possible to observe the formation of two clusters. The clusters with negative scores can be characterized of petrogenic origin (Adyar river station A1, A2, A3, A4, A5 and A9; Cooum river station C1, C2, C3, C6 and C7) due to smaller presence of low molecular weight compounds. The clusters with positive scores can be characterized by pyrogenic origin (Adyar river stations A6, A7 and A8; Cooum river stations C4, C5, C8 and C9) due to greater contribution of high molecular weight compounds. Samples were grouped according to the source of contamination from petrogenic and pyrogenic. The higher percentage of petrogenic sources in sediments are likely to originate from wastewater discharged from households and Industries. Similarly, multiple pyrogenic sources of PAHs such as, gasoline combustion from the rapidly increasing number of motor vehicles and motorbikes, diesel oil, coal-fired cooking (Katsoyiannis *et al.* 2007; De La Torre–Roche *et al.* 2009; Islam *et al.* 2017) are contributing to contamination of both rivers in Chennai megacity.

Table 5.2 Percentage of mean concentration of 3, 4, 5 and 6-ring PAHs in sediment sample of Chennai megacity rivers

Rings compounds	Adyar river (percentage)	Cooum river (percentage)
3-rings	32	30
4-rings	42	38
5-rings	16	20
6-rings	10	12

The PAHs identified can be classified according to its molecular structure. The three fused rings or low molecular weight PAHs (LPAHs) are most abundant in sediments of both rivers in Chennai megacity. The abundance of three rings compounds was 32% in Adyar river and 30% in Cooum rivers. Similarly, more than

four rings (4-6 rings) compounds or Higher molecular weight PAHs (HPAHs) originate from combustion and was observed in 68% (4 rings 42%, 5 rings 16% and 6 rings 10%) in Adyar river and 70% (4 rings 38%, 5 rings 20% and 6 rings 12%) in Cooum rivers (Table 5.2). Hence, it can be inferred that sediments of both rivers are highly polluted by by HPAHs.

5.2.2 Correlation Matrix Analysis

Correlation analysis provides useful information on sources between different PAHs. Most of the different pairs of PAHs have significant correlation, which are shown in Table 5.3. The good correlation among all the different PAHs showed that these different PAHs in Chennai megacity rivers shared identical sources and similar evolution. However, DahA (Dibenzo[a,h]anthracene) was less correlated with FL (Fluorene) and PHE (Phenanthrene). This might come from degradation of LPAHs or petrogenic sources.

Table 5.3 Correlation matrix for different PAHs in Chennai megacity river sediments

Variables	ANT	BaA	BaP	BbF	BkF	BghiP	CHR	DahA	FLA	FL	IcdP	PHE	PYR
ANT	**1**												
BaA	0.780	**1**											
BaP	0.863	0.891	**1**										
BbF	0.909	0.889	0.957	**1**									
BkF	0.890	0.888	0.952	0.994	**1**								
BghiP	0.910	0.842	0.876	0.955	0.935	**1**							
CHR	0.700	0.875	0.786	0.784	0.759	0.814	**1**						
DahA	0.543	0.848	0.653	0.708	0.719	0.661	0.655	**1**					
FLA	0.840	0.799	0.826	0.898	0.872	0.941	0.773	0.555	**1**				
FL	0.749	0.570	0.624	0.552	0.515	0.584	0.651	0.254	0.569	**1**			
IcdP	0.896	0.894	0.944	0.987	0.985	0.940	0.789	0.719	0.877	0.532	**1**		
PHE	0.847	0.766	0.796	0.860	0.842	0.896	0.743	0.496	0.958	0.]	0.836	**1**	
PYR	0.767	0.839	0.828	0.859	0.830	0.824	0.756	0.625	0.882	0.581	0.807	0.867	**1**

5.3 SOURCE IDENTIFICATION BASED ON THE COMPOSITION OF PAHs

The present study provides a total of 13 PAHs in sediment samples observed among the different sampling stations in Chennai megacity rivers (Table 5.1), which indicate that PAHs are likely to originate from specific point sources at some locations in both rivers. To identify point sources, diagnostic ratios have been used to discriminate the resulting profiles in Table 5.4.

5.3.1 Diagnostic Ratios

The FLA/(FLA+PYR) ratio derived from sediment samples in Adyar river at station A5 to A8 show the values from 0.50 to 0.57. For Cooum river stations C3 to C8 the ratio is 0.50 to 0.55. So, it can be seen that FLA/(FLA+PYR) ratio is the same for both rivers. ANT/(ANT+PHE) ratio between the ranges 0.24 to 0.54 in Adyar river stations A2 to A9 and Cooum river stations C1 to C9 are 0.34 to 0.51; which suggest that mixed pyrogenic sources are the main contributor. Similarly, the ratio of BaA/(BaA+CHR) for 5 sampling stations A2, A3, A4, A7 and A8 of Adyar river and all stations (except C3) of Cooum river is greater than 0.35. This may be due to vehicular emissions are coming from motor vehicles occurring near the sampling stations. Also, the ratio of IcdP/(IcdP+ BghiP) and its equivalent values fall within the 0.20 and 0.50 in the downstream stations of both rivers. In particular, those with two stroke engines with low fuel efficiency contribute (Boll *et al.* 2008) PAH emissions (Chen *et al.* 2015).

The Cross plot of diagnostic sources ratio for sediment samples (Figure 5.4) between FLA/(FLA+PYR) and ANT/(ANT+PHE) represent the mixed pyrogenic sources (from stations A5 to A8 of Adyar river and C2 to C9 of Cooum river) of PAHs in both rivers except Adyar river stations A2, A3 (sources from SIPCOT industry) and A9 (backwater of saline intrusion).

Table 5.4 Diagnostic ratios of PAHs of surface sediment samples of Chennai megacity rivers

Station		FLA / (FLA + PYR)	ANT / (ANT + PHE)	BaA / (BaA + CHR)	IcdP / (IcdP+BghiP)
		<0.4 Petrogenic	<0.1 Petrogenic	<0.2 Petrogenic	<0.2 Petrogenic
		0.4 - 0.5 Fossil Fuel	**>0.1 Pyrogenic**	0.2-0.35 Coal Combustion	**0.2 – 0.5 Petroleum combustion**
		>0.5 Grass, Wood, Coal combustion	-	**>0.35 Vehicular Emission**	>0.5 Grass, wood and coal combustion
Adyar River	A1	-	-	-	-
	A2	0.30	**0.31**	**0.44**	-
	A3	0.28	**0.27**	**0.44**	-
	A4	-	**0.31**	**0.45**	-
	A5	**0.57**	**0.24**	-	**0.29**
	A6	**0.59**	**0.32**	0.28	**0.25**
	A7	**0.50**	**0.30**	**0.56**	**0.37**
	A8	**0.50**	**0.54**	**0.41**	**0.42**
	A9	0.39	**0.35**	-	-
Coum River	C1	-	**0.46**	**0.39**	-
	C2	0.49	**0.34**	**0.40**	-
	C3	**0.51**	**0.45**	0.33	-
	C4	**0.54**	**0.48**	**0.49**	**0.40**
	C5	**0.55**	**0.49**	**0.62**	**0.37**
	C6	**0.53**	**0.51**	**0.44**	**0.36**
	C7	**0.53**	**0.35**	**0.41**	**0.42**
	C8	**0.50**	**0.36**	**0.50**	**0.40**
	C9	0.46	**0.49**	**0.54**	**0.40**

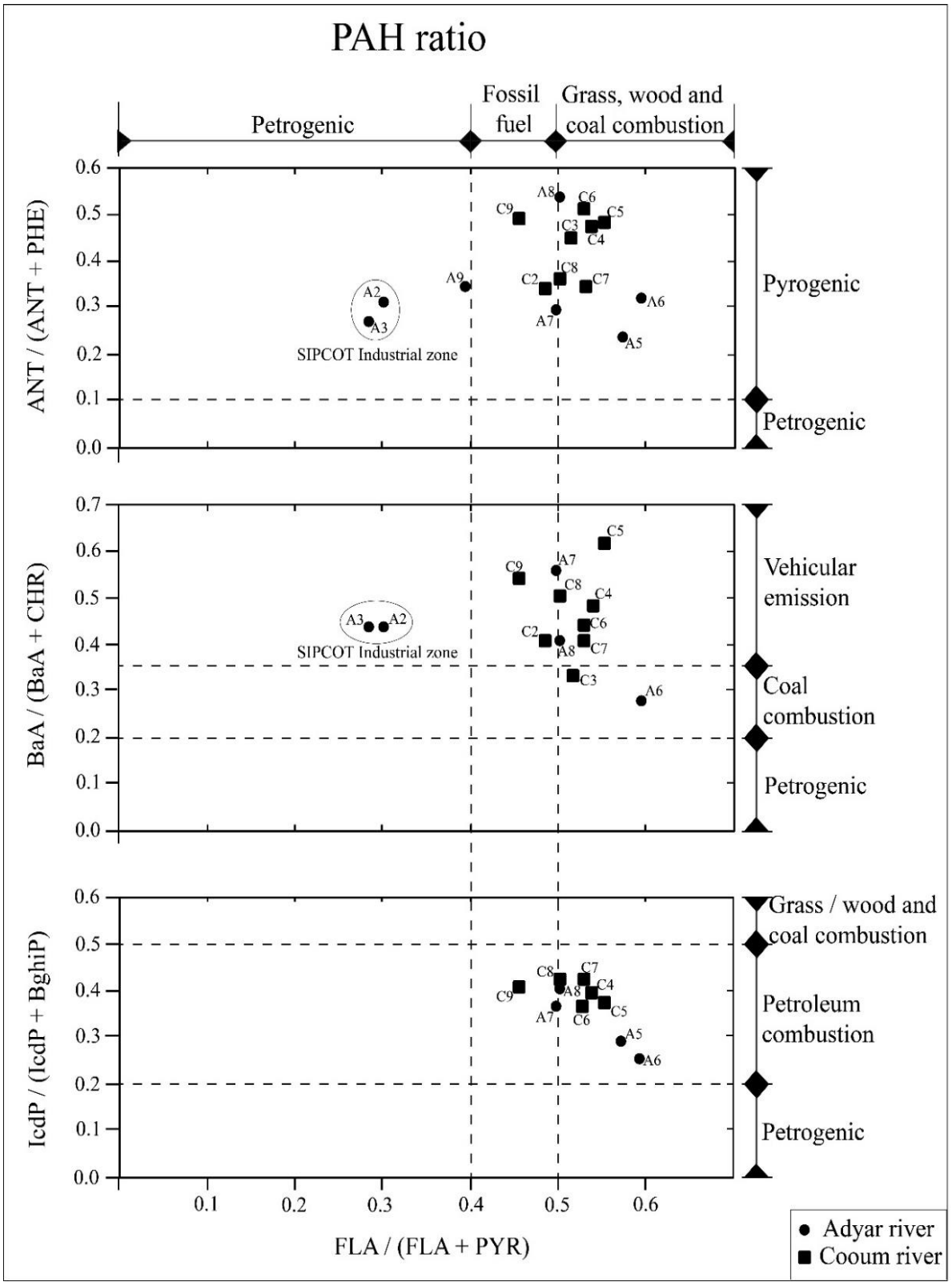


Figure 5.4 Cross plots for multiple characteristic ratio of the sources of PAHs in surface sediment samples of Chennai megacity rivers

The ratio between FLA/(FLA+PYR) and BaA/(BaA+CHR) represents the vehicular emissions of PAHs (from the station A7 and A8 in Adyar river and C2, C4 to C9 in Cooum river) except stations A2 and A3 (Adyar river - sources from SIPCOT industry), and A6 in Adyar river and C3 in Cooum river as derived from coal or biomass combustion; For similar ratio between FLA/(FLA+PYR) and IcdP/(IcdP+ BghiP), it is found that the pollution sources of PAHs in the sediments are derived from petroleum and fossil fuel combustion along downstream side (stations A5 to A8 in Adyar river and C4 to C9 in Cooum river) of both rivers in Chennai megacity.

However, the total concentration of PAHs in this study showed that hotspots of PAHs were observed at downstream stations close to relatively high density of population and industrial sectors that would give great chances to sediment to absorb PAHs of higher concentration (Lu *et al.* 2015). The higher concentrations are likely to originate from wastewater discharged from households and industries in Chennai megacity.

5.4 LEVELS AND DISTRIBUTION OF PCBs, PHTHALATEs AND PBDEs IN SURFACE SEDIMENTS

In this study, the presence of following PCBs, Phthalates and PBDEs were estimated in sediment samples. The seven most commonly found PCBs are PCB28, –52, –101, –118, –138, –153 and –180. The common six phthalates (BBP, DBP, DEHP, DEP, DiBP and DiNP) and five PBDEs (BDE 47, –85, –99, –100 and –153) from the sediment samples of Chennai megacity are summarised in Table 5.5.

Table 5.5 Sediment concentrations (mg/kg) of PCBs, Phthalates and PBDEs of Chennai megacity rivers – see Figure 6.1 for locations

	Adyar River						Cooum River						
	A1 to A4	**A5**	**A6**	**A7**	**A8**	**A9**	**C1 to C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**
PCB 28	-	-	-	-	-	-	-	-	-	0.0059	-	-	-
PCB 52	-	-	0.0054	-	-	-	-	-	-	-	-	-	-
PCB 101	-	-	0.0054	-	-	-	-	0.0062	0.0058	0.0062	-	-	-
PCB 118	-	-	-	-	-	-	-	-	-	-	-	-	-
PCB 138	-	-	-	-	-	-	-	-	-	-	-	-	-
PCB 153	-	-	-	-	-	-	-	-	-	-	-	-	-
PCB 180	-	-	-	-	-	-	-	-	-	-	-	-	-
Σ PCB	**-**	**-**	**0.0108**	**-**	**-**	**-**	**-**	**0.0062**	**0.0058**	**0.0121**	**-**	**-**	**-**
BBP	-	-	-	-	-	-	-	-	-	-	-	-	-
DBP	-	-	-	-	1.23	-	-	3.20	5.97	2.06	1.64	8.27	-
DEHP	-	-	2.51	-	-	-	-	-	3.59	-	-	-	-
DEP	-	-	-	-	-	-	-	-	-	-	-	-	-
DiBP	-	-	-	-	-	-	-	-	0.41	-	1.16	-	-
DiNP	-	2.33	2.47	2.90	1.40	2.02	-	-	4.48	-	-	-	-
Σ Phthalate	**-**	**2.33**	**4.98**	**2.90**	**2.63**	**2.02**	**-**	**3.20**	**14.46**	**2.06**	**2.80**	**8.27**	**-**
BDE 47	-	-	-	-	-	-	-	-	-	-	-	-	-
BDE 85	-	-	-	-	-	-	-	-	-	-	-	-	-
BDE 99	-	-	-	-	-	-	-	-	-	-	-	-	-
BDE 100	-	-	-	-	-	-	-	-	-	-	-	-	-
BDE 153	-	-	-	-	-	-	-	-	-	-	-	-	-
Σ PBDE	**-**	-	-	-	-	-	-	-	-	-	-	-	-

5.4.1 PCBs

The 2 PCBs (PCB52 and PCB101) congeners were detected among 7 PCBs in Adyar river and 2 PCBs (PCB28 and PCB101) in Cooum river sediments, indicating that PCBs are widespread pollutants in Chennai megacity. The total concentration of Σ PCBs is detected from only one station of Adyar river (station A6 = 0.0108 mg/kg) and three stations (C4, C5 and C6 are 0.0062, 0.0058 and 0.0121 mg/kg respectively) of Cooum river. These stations are most common hotspot locations as per the result of PAHs (Table 5.5). Here, PCB101 is common congener in both river sediments from the detected stations. This PCB101 sources may be the contribution from the commercial mixtures that have been widely used in electrical products or equipments, transformers and different industries (Barakat *et al.* 2002; Ragab *et al.* 2016). So, this PCB101 is chosen as the detection target which served as one of the indicators for PCBs pollution.

5.4.2 Phthalates and PBDEs

The sediment concentration of phthalates, among 6 phthalates congeners two phthalates (Di–isononyl Phthalate (DiNP) in Adyar river and Di–n–butyl Phthalate (DBP) in Cooum river) detected from sediments of downstream stations in both the rivers. The total sediment concentrations of Σ phthalate are 2.33, 4.98, 2.90, 2.63 and 2.02 with respect to the stations of A5, A6, A7, A8 and A9 of Adyar river, and 3.20, 14.46, 2.06, 2.80 and 8.27 with respect to the stations of C4, C5, C6, C7 and C8 of Cooum river. This DiNP and DBP sources come from the plasticizers (example toys, erasers etc.) of both commercial and industrial products (Sanchez-Avila *et al.* 2009) with dominant compounds present in Chennai megacity. The sediment concentration of PBDEs congeners are not detected anywhere in the Chennai megacity river samples.

5.5 CONCLUSION

The study shows information on the priority hazard (PAHs, PCBs, Phthalates and PBDEs) occurrence of surface sediments in the 2 main rivers of Chennai megacity. The sediment concentration results showed that the occurrence and

behavior of PAHs varied spatially and temporally. The higher concentration Σ_{13}PAHs are sited in downstream stations (A6 to A8 in Adyar river and C4 to C9 in Cooum river) of the river. Also, the total concentrations of Σ_{13} PAHs in sediment samples are greater in Cooum river than Adyar river. These sites were all within the core urban area of Chennai megacity, with a higher population density and industrial area. Therefore, domestic wastewater and sewage might be the main sources for the presence of organic pollutants in these stations. The sediment concentrations are heavily polluted by HPAHs (4-6 rings) than the LPAHs (3 rings), which indicate that urban and industrial sources contribute to the increased concentrations. Based on the use of diagnostic ratios it is presumed that, PAHs are originated from specific point sources of mixed pyrogenic sources (vehicular emission and grass, wood and coal combustion) of both rivers.

Similarly, the PCBs concentration in sediments are very low or below the detection limits as per international standards except PCB 101. The source of PCB 101 may be contribution from commercial mixtures that have been widely used in electrical products of different commercial and industrial formulations. Also, the phthalates (DiNP, DBP) are dominant compounds present in Chennai megacity river sediments due to plasticizers from both commercial and industrial products and PBDEs concentrations are not detected in both river sediments.

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CHAPTER 6

INFLUENCE OF 2015 FLOOD HAZARD

CHAPTER 6

INFLUENCE OF 2015 FLOOD HAZARD

6.1 GENERAL

The 2015 south Indian devastating floods that hit Chennai city (Figure 6.1) and other parts of Tamil Nadu during northeast monsoon in November-December 2015 have claimed more than 400 lives and affected 4 million people with caused enormous economic damages that cost around US $3 billion (The National, 2015). There was very heavy rainfall on November 8, 9, 12, 13, 15, 23 and December 1. During the 24 hours ending 8:30 am on December 2, 2015, “extremely heavy rainfall” was reported in Chennai: 470 mm at Chembarambakkam in Kancheepuram district and an average rainfall of 400 mm in Chennai district (Narasimhan *et al.* 2016). According to the United States’ National Aeronautics and Space Administration’s (NASA’s) Integrated Multi-Satellite Retrievals for Global Precipitation Measurement or GPM (IMERG), from November 29 to December 2 over 400 mm of rainfall fell over areas south of Chennai (Narasimhan *et al.* 2016). This flood was the costliest to have occurred in 2015, and among the costliest natural disasters of the year. So, the objective of research is designed for an influence of 2015 flood hazard onto trace elements and organic compound pollution regards to the quality of the two main rivers. These include: (i) Changes in geochemical and organic composition of river sediments after the 2015 flood in Chennai; (ii) investigate the sediment quality and flood influence on the urban tracer level; (iii) compare the state of sediment contamination of special index (GUFI); (iv) evaluation of pollution and toxicity levels of organic contaminants (PAHs, PCBs, Phthalate and PBDEs) after 2015 floods.



Figure 6.1 Devastating floods in Chennai megacity



Figure 6.2 The 2015 post flood at our studied sediment stations in Adyar river



***(a) Burma Colony – Bridge damage, *(b) NMR (Nelson Manickam Road drain) – Urban effluents, *(c) Thiru vi ka bridge (Adyar river mouth) – Sand bar and back water of sea, *(d) Jafferkhanpet – Floating plastic**

Figure 6.3 2015 Post flood effects in Chennai megacity rivers

6.2 INFLUENCE OF 2015 FLOOD FLUVIAL DEPOSIT

The city of Chennai and its suburb areas recorded multiple torrential rainfall events during November – December 2015 that inundated the coastal districts of Chennai, Kancheepuram and Tiruvallur. The surface sediment and flood deposit samples were collected during February 2016 from both rivers, on the same locations of sediment survey carried out in February 2015 (Figure 3.2). The sediment survey of February 2016, sampling locations (Figure 3.2) seemed to be affected by the flood waters especially in Adyar river compared to Cooum river. Figure 6.2 shows the 2015 flood influence at our studied sediment stations in Adyar river and Flood effects are shown in Figure 6.3. During field visit, the local residents informed that during the earlier floods of 2005 the waters had come only up to ankle height (a few inches above ground) in that area. However, during the floods of 2015, the area was almost 6ft (150cm) under water. The flood water levels were noted based on the feedback of the local people.

6.3 UNDER THE INFLUENCE OF 2015 FLOOD

The geochemical results estimated the spatial variations of upstream – downstream concentrations of the trace elements in surface sediments to quantify the pollution level due to are the influence of 2015 flood in the two studied urban rivers (Adyar and Cooum). Sediment concentrations of trace elements are presented in Table 6.1 according to kilometric points (KP, in km; KP 0.0 being the most upstream sample station) to compare the concentrations as shown in Table 4.1.

Table 6.1 Trace Element and Aluminium Concentration (mg/kg) in 2015 flood post deposited sediments

Station		Kilometric point (km)	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Al
Adyar River	A1	00.0	-	4.0	0.1	138	64	> 0.0	67	23	107	92433
	A2	03.0	0.6	3.8	1.1	3346	139	0.1	111	21	473	78378
	A3	06.6	-	2.3	0.4	944	109	0.1	65	27	177	84799
	A4	12.0	0.8	2.4	0.2	4332	60	0.0	70	22	148	63120
	A5	14.7	6.7	2.8	1.2	407	143	0.7	50	27	334	56529
	A6	15.9	6.2	2.5	1.2	246	158	0.6	35	28	366	29376
	A7	18.4	1.8	3.4	0.4	198	107	0.3	67	48	205	88119
	A8	21.9	14.4	4.1	1.4	412	202	0.8	67	76	479	78208
	A9	23.7	10.8	2.4	3.1	278	178	1.0	49	54	359	77134
	Min.		**0.6**	**2.3**	**0.1**	**138**	**60**	**0.0**	**35**	**21**	**107**	**29376**
	Max.		**14.4**	**4.1**	**3.1**	**4332**	**202**	**1.0**	**111**	**76**	**479**	**92433**
Cooum River	C1	00.0	0.3	3.8	0.2	115	54	> 0.0	54	30	102	96298
	C2	04.1	-	2.6	0.5	103	62	0.1	35	228	145	85223
	C3	09.2	14.2	4.4	1.2	172	226	2.6	55	93	704	71342
	C4	12.8	8.4	4.0	9.2	126	186	1.0	42	86	440	71321
	C5	14.6	8.3	4.1	10.4	125	178	2.0	44	102	397	78499
	C6	15.8	24.2	4.2	15.5	122	249	1.5	46	71	584	77388
	C7	17.4	38.2	5.5	15.9	124	310	3.4	51	93	669	72200
	C8	19.8	8.8	4.5	11.2	132	198	0.9	49	91	425	77239
	C9	23.5	12.0	8.8	9.0	204	354	2.3	52	131	435	77531
	Min.		**0.3**	**2.6**	**0.2**	**103**	**54**	**0.0**	**35**	**30**	**102**	**71321**
	Max.		**38.2**	**8.8**	**15.9**	**204**	**354**	**3.4**	**55**	**228**	**704**	**96298**

6.3.1 Trace Element Concentration of before and after 2015 Floods

6.3.1.1 Adyar river

In Adyar river, the minimum concentrations of trace element Cd, Cr, Hg and Zn (0.1, 138, > 0.0 and 107 mg/kg respectively) were found in sediment sample at most upstream station (A1) of the river. For other trace elements, their minimum concentrations are at station A2 for Ag and Pb (0.5 and 21 mg/kg), station A3 (As = 2.3 mg/kg), station A4 (Cu = 60 mg/kg) and station A6 for Ni concentration is 34 mg/kg respectively. The highest sediment concentrations were found along the downstream of the basin at station A8 for the trace elements Ag, As, Cu, Pb and Zn (14.4, 4.1, 202, 76 and 479 mg/kg respectively) and at station A9 for Cd and Hg (3.1 and 1.0 mg/kg respectively). These sediment concentrations were compared as shown in the Table 4.1 (before 2015 flood hazard sediment concentrations). The results of the trace elements Ag, As, Cd, Cu, Hg, Pb and Zn concentrations of sediment level is reduced except Cr and Ni. The Cr and Ni (4331 mg/kg at station A4 and 110 mg/kg at station A2) concentrations are higher in after the flood of 2015. Especially, the Cr concentration in station A2, A3 and A4 (3345, 944 and 4331 mg/kg respectively).

In particularly, station A2 is 2 times and station A4 is 6 times higher in the sediment concentration when compare to pre-flood levels at 2015. Ni concentration is higher in the station A2. These higher concentrations of trace element Cr and Ni may be related for industrial and commercial products (electronic, plastic etc) are washed out and deposited during the flood of 2015 (Figure 6.3 (d)). The station A2 to A4 concentrations are high because of upcoming station bridges are heavily damaged and flow is distracted due to this commercial product are deposited in the stretch of A2 to A4 (Figure 6.2, Anakapudhar and Manapakkam bridge). Other trace element concentrations are high at station A8 and A9 in the flood of 2015. Before flood (Table 4.1), the higher concentrations are in the station A6 and A8. These higher concentrations of sediment variations occur either due to the pollution washed from upstream to downstream stations or influenced by sea tide (backwater).

6.3.1.2 Cooum river

In Cooum river, the trace elements of Ag, Cd, Cu, Hg, Pb, Zn (0.3, 0.2, 54, >0.0, 30, 102 mg/kg respectively) at most upstream station (C1) and at station (C2) As, Cr and Ni (2.6, 103, 35 mg/kg respectively) were found is minimum concentrations are located in the upstream stations of the river. The highest sediment concentrations were found in the downstream part of the basin stations C7 (Ag = 38.2; Cd = 15.9; Hg = 3.4 mg/kg) and C9 (As = 8.8; Cr = 204; Cu = 354 mg/kg) respectively. These results indicate, that the downstream part of the river is influenced by anthropogenic activities and saline water intrusion. Other trace element concentrations are Pb = 228 mg/kg in station C2 and at station (C3) Ni and Zn (55 and 704 mg/kg respectively). These higher sediment concentrations were compared and tabulated in the Table 4.1 (before 2015 flood hazard sediment concentrations). The results of the trace elements As, Cd, Cr, Hg and Pb show that the concentrations of sediment level are reduced and also Ag, Cu, Ni and Zn sediment concentrations are at same level as 2015 flood. From the results it can be inferred that trace element concentration in sediments of Cooum river is, either reduced or not changed.

6.4 SEDIMENT QUALITY SURVEY

In this study, Geoaccumulation Index (I_{geo}) is used to identify the quality of sediments of Chennai megacity rivers. The calculated I_{geo} of all the studied trace elements in surface sediments of 2015 flood of Adyar and Cooum rivers as shown in Table (6.2 & 6.3).

Table 6.2 Geoaccumulation Index (I_{geo}) in 2015 post flood deposited sediments of Chennai megacity rivers

Station		Kilometric point (km)	Geoaccumulation Index (I_{geo})								
			Ag	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Background Shale value (Wedepohl 1995)			**0.055**	**2**	**0.102**	**35**	**14.3**	**0.056**	**18.6**	**17**	**52**
Adyar River	A1	00.0	-	0.43	-0.49	1.40	1.59	-1.58	1.27	-0.15	0.46
	A2	03.0	2.76	0.32	2.82	5.99	2.69	-0.51	1.99	-0.26	2.60
	A3	06.6	-	-0.38	1.22	4.17	2.35	-0.24	1.22	0.09	1.18
	A4	12.0	3.30	-0.30	0.50	6.37	1.49	-0.84	1.32	-0.23	0.93
	A5	14.7	6.34	-0.11	2.92	2.95	2.74	3.13	0.83	0.07	2.10
	A6	15.9	6.24	-0.25	2.94	2.23	2.89	2.76	0.32	0.15	2.23
	A7	18.4	4.44	0.16	1.52	1.92	2.32	1.71	1.26	0.90	1.39
	A8	21.9	7.45	0.46	3.14	2.97	3.24	3.21	1.27	1.58	2.62
	A9	23.7	7.03	-0.30	4.35	2.41	3.05	3.61	0.81	1.09	2.20
	Min.	-	**2.76**	**-0.38**	**-0.49**	**1.40**	**1.49**	**-1.58**	**0.32**	**-0.26**	**0.46**
	Max.	-	**7.45**	**0.46**	**4.35**	**6.37**	**3.24**	**3.61**	**1.99**	**1.58**	**2.62**
Coum River	C1	00.0	1.66	0.33	0.21	1.13	1.32	-1.93	0.96	0.24	0.38
	C2	04.1	-	-0.20	1.66	0.98	1.54	-0.69	0.34	3.16	0.90
	C3	09.2	7.43	0.57	2.92	1.71	3.40	4.94	0.97	1.86	3.18
	C4	12.8	6.66	0.40	5.91	1.26	3.12	3.54	0.58	1.75	2.49
	C5	14.6	6.65	0.46	6.09	1.25	3.06	4.60	0.67	2.00	2.35
	C6	15.8	8.20	0.48	6.67	1.22	3.54	4.11	0.71	1.48	2.90
	C7	17.4	8.85	0.86	6.70	1.24	3.85	5.34	0.86	1.86	3.10
	C8	19.8	6.74	0.58	6.20	1.32	3.21	3.34	0.81	1.84	2.44
	C9	23.5	7.18	1.55	5.88	1.96	4.04	4.79	0.90	2.36	2.48
	Min.	-	**1.66**	**-0.20**	**0.21**	**0.98**	**1.32**	**-1.93**	**0.34**	**0.24**	**0.38**
	Max.	-	**8.85**	**1.55**	**6.70**	**1.96**	**4.04**	**5.34**	**0.97**	**3.16**	**3.18**

Table 6.3 Pollution classification of surface sediments in 2015 post flood

I_{geo} Class	I_{geo} Value	Polluted Level	Mean Value of Chennai Peri-urban Area		Mean Value of Chennai City	
			Adyar River (A1 to A4)	Cooum River (C1 & C2)	Adyar River (A5 to A9)	Cooum River (C3 to C9)
0	<0	Unpolluted	Hg, Pb	Hg	As	-
1	0-1	From Unpolluted to Moderately polluted	As	As, Cd, Ni, Zn	Ni, Pb	As, Ni
2	1-2	Moderately polluted	Cd, Ni, Zn	Ag, Cr, Cu, Pb	-	Cr, Pb
3	2-3	From Moderately polluted to Strongly polluted	Ag, Cu	-	Cd, Cr, Cu, Hg, Zn	Zn
4	3-4	Strongly polluted	Cr	-	-	Cu
5	4-5	From Strongly polluted to Extremely polluted	-	-	-	**Hg**
6	>5	Extremely polluted	-	-	**Ag**	**Ag, Cd**

In the upstream basin corresponding to Chennai peri-urban area, the I_{geo} mean value for the trace elements Ag, As, Cd, Cu, Hg, Ni, Pb and Zn range between I_{geo} class 0 and 3 (Table 6.3), except Cr in Adyar river sediment concentration. These sediment concentrations are unpolluted to moderately polluted and the trace element Cr concentration is strongly polluted from the upstream station of Adyar river sediments. Similarly, the I_{geo} mean value of Chennai city for trace elements As, Cd, Cr, Cu, Hg, Ni, Pb and Zn sediment concentrations are unpolluted to moderately polluted and Ag concentration is extremely polluted in Adyar river and Cooum river As, Cr, Ni, Pb and Zn sediment concentrations are unpolluted to moderately polluted and Ag, Cd, Cu and Hg concentrations are strongly polluted to extremely polluted. The higher inputs in the downstream station, might have been originated from urban and industrial wastes.

6.5 EFFECT OF 2015 POST FLOOD INFLUENCE FOR I_{geo} OF RIVER SEDIMENTS IN CHENNAI MEGACITY

The effect of 2015 flood influence of Chennai megacity rivers in the sediment concentration of Geoaccumulation Index (I_{geo}), were compared to the quality of sediment or pollution level as tabulated in Table 4.3 and Table 6.3 and shown in the Figures 6.4 and 6.5.

In comparison of 2015 flood influence of sediment concentrations in Adyar river (Figure 6.4), Chennai peri-urban area pollution level or quality of the sediments of the trace elements (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) with same concentration as before and after the flood event of December 2015. But, in Chennai city sediment concentration level varied for the trace elements of Cd and Hg. Before 2015 flood, Cd and Hg concentrations of sediments were in the I_{geo} class (3-6) strongly polluted to extremely polluted but after 2015 flood, Cd and Hg concentrations are reduced in the I_{geo} class from (3-6) to (0-3) as unpolluted to strongly polluted.

Similarly, in Cooum river (Figure 6.5), Before 2015 flood, Ag concentration was in the I_{geo} class (3-6) strongly polluted to extremely polluted but after 2015 flood, Ag concentration is reduced in the I_{geo} class (0-3) as unpolluted to strongly polluted in Chennai peri-urban area. In Chennai city pollution level or quality of the sediments of the trace elements (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) are same as before and after the flood event of December 2015.

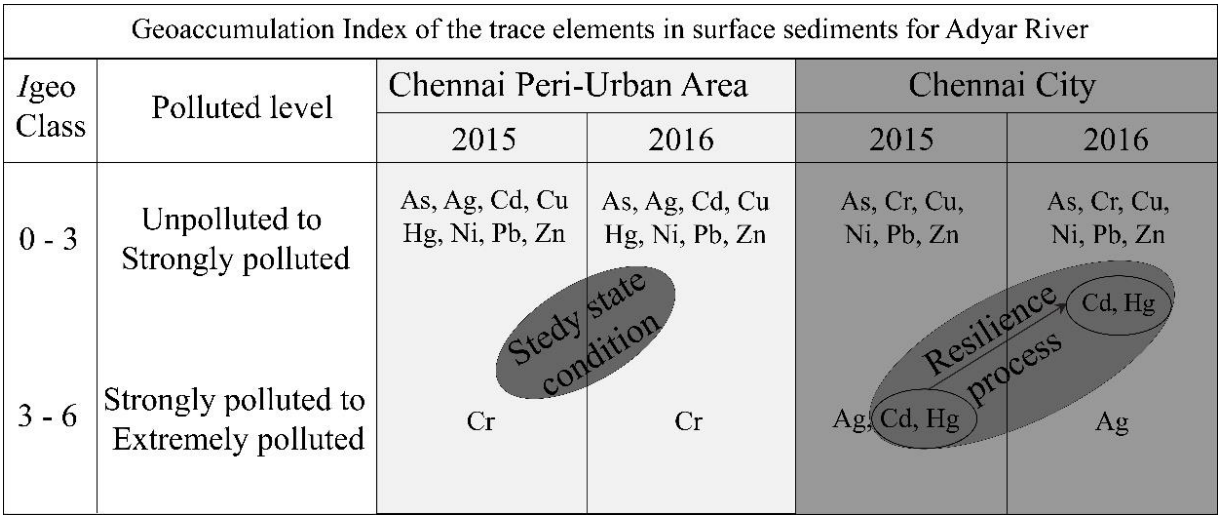


Figure 6.4 Effect of 2015 post flood influence on I_{geo} of Adyar River sediments

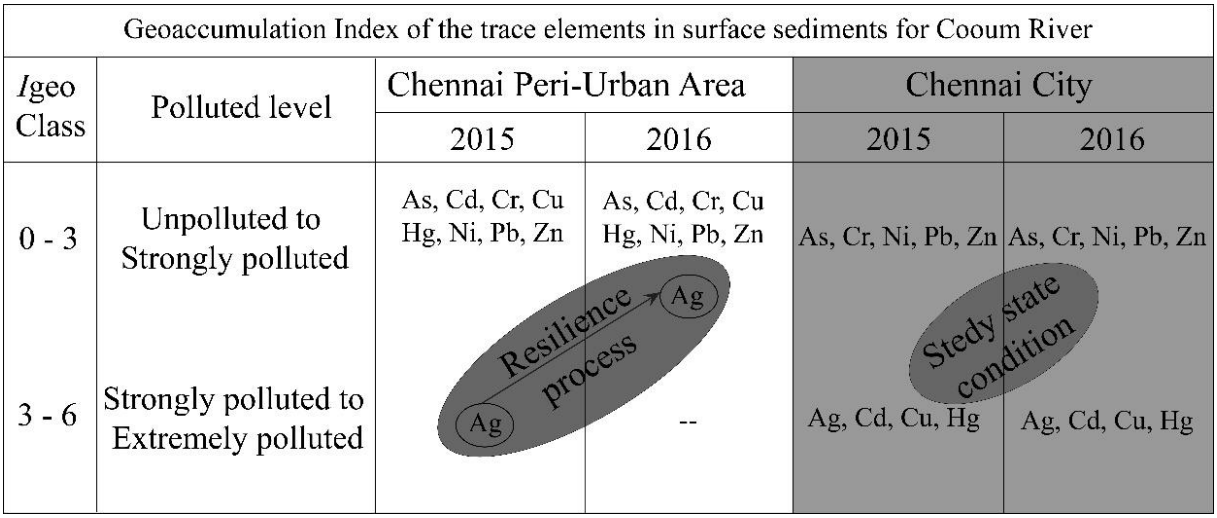


Figure 6.5 Effect of 2015 post flood influence on I_{geo} of Cooum river sediments

6.5.1 Post Flood Influence of Urban Tracer Level

The Geoaccumulation Index (I_{geo}) revealed that, the concentration of trace element (Ag, Cd and Hg) concentrations are used as urban tracers and Cr concentration is considered as an industrial signal in Chennai megacity. The 2015 flood influence of urban tracer levels in Adyar and Cooum rivers are illustrated in the following Figures 6.6 to 6.13. These illustrations are compare the concentration of sediment samples before and after the flood 2015 in Chennai megacity rivers.

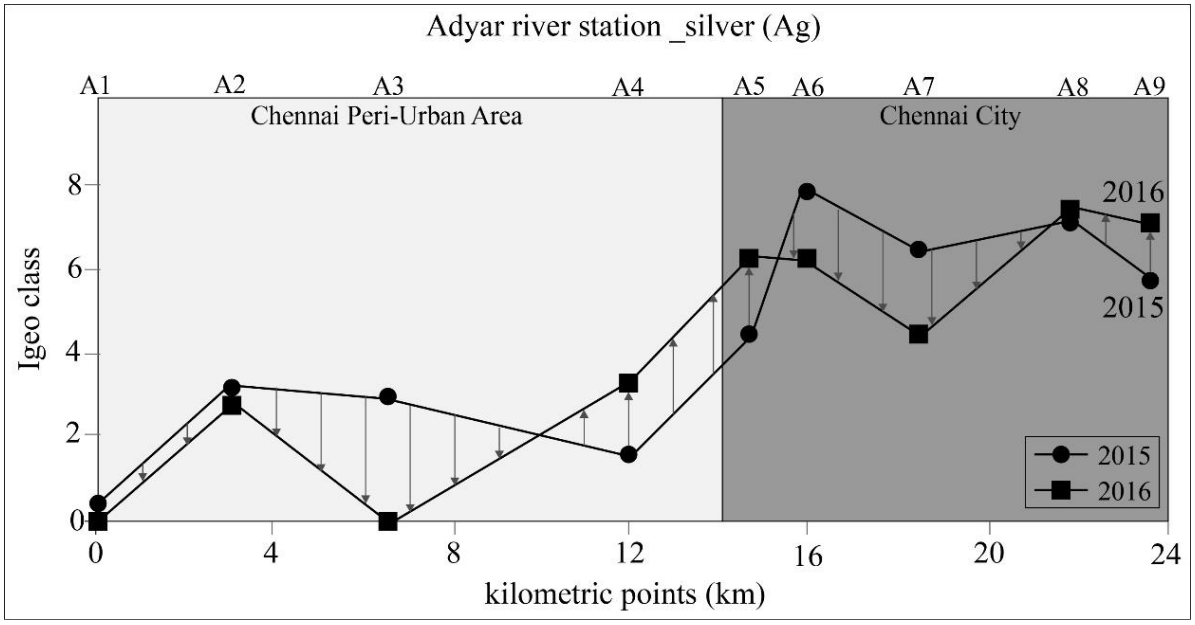


Figure 6.6 Effect of 2015 post flood influence on (I_{geo}) of silver (Ag) in Adyar river sediments

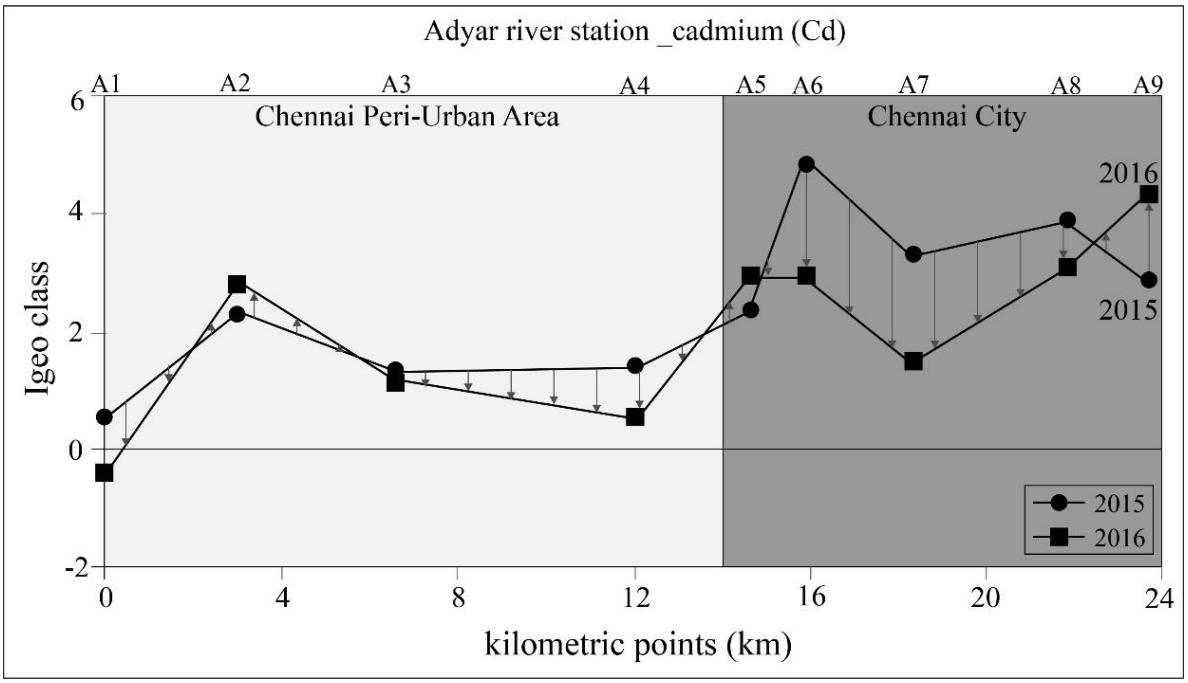


Figure 6.7 Effect of 2015 post flood influence on (I_{geo}) of cadmium (Cd) in Adyar river sediments

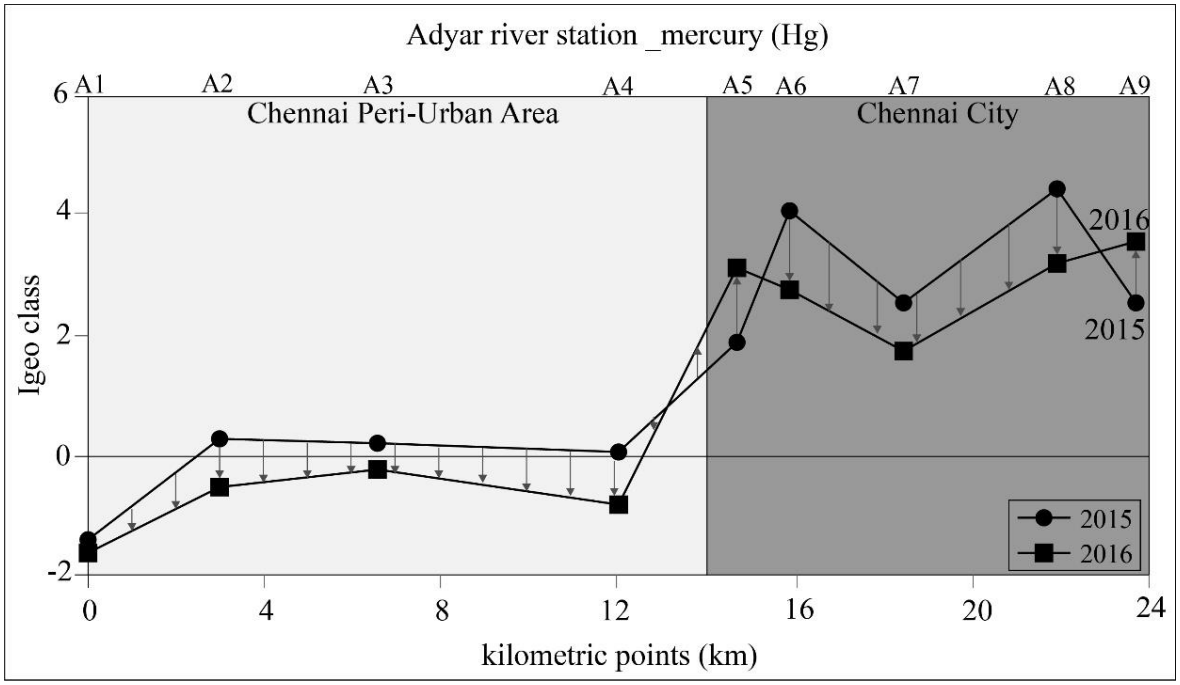


Figure 6.8 Effect of 2015 post flood influence on (I_{geo}) of mercury (Hg) in Adyar river sediments

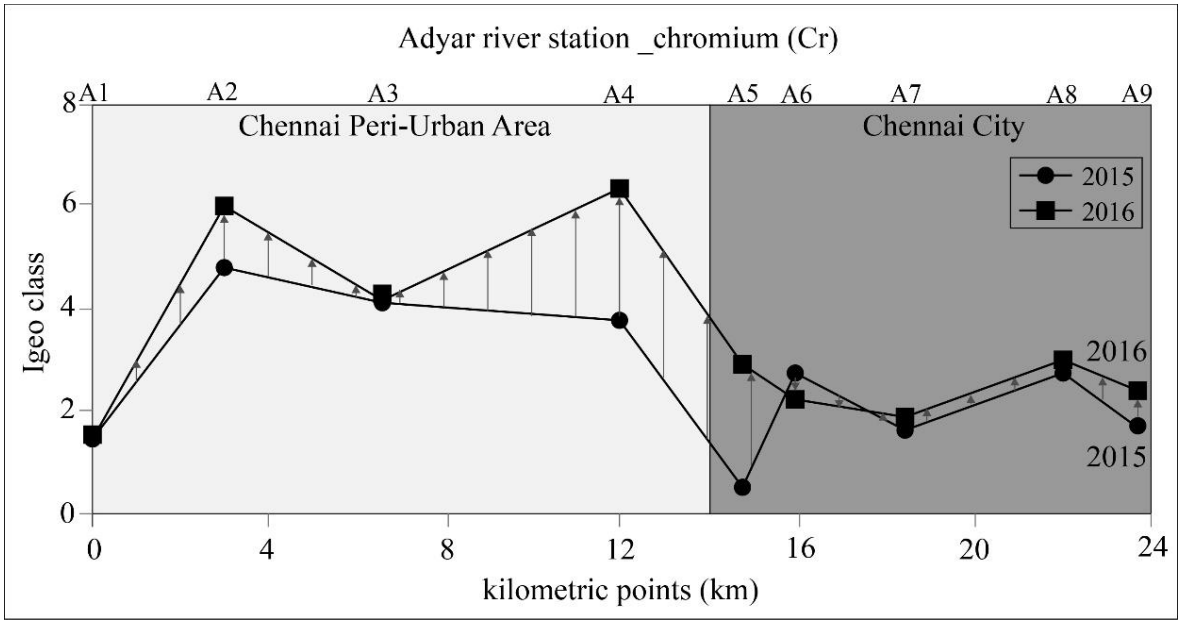


Figure 6.9 Effect of 2015 post flood influence on (I_{geo}) of chromium (Cr) in Adyar river sediments

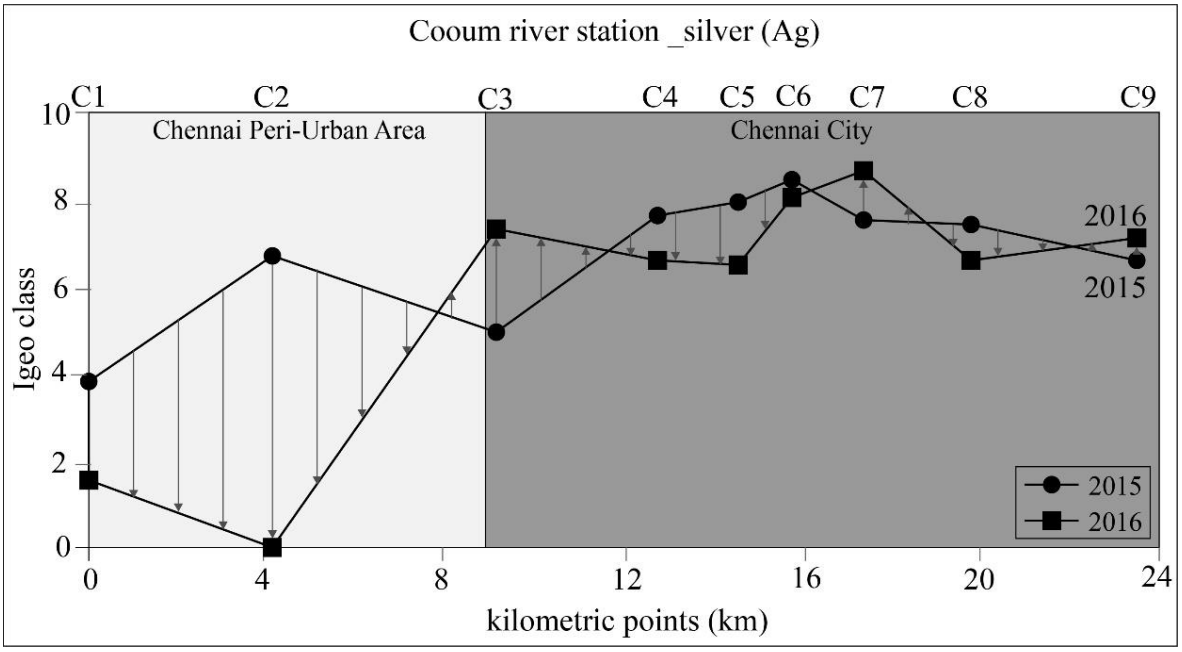


Figure 6.10 Effect of 2015 post flood influence on (I_{geo}) of silver (Ag) in Cooum river sediments

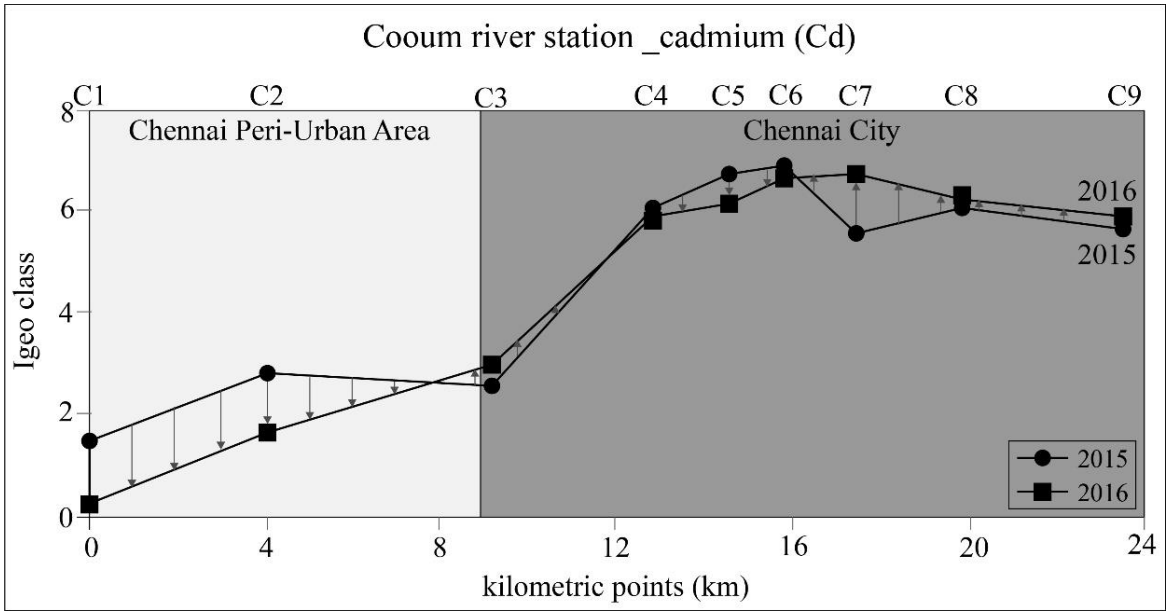


Figure 6.11 Effect of 2015 post flood influence on (I_{geo}) of cadmium (Cd) in Cooum river sediments

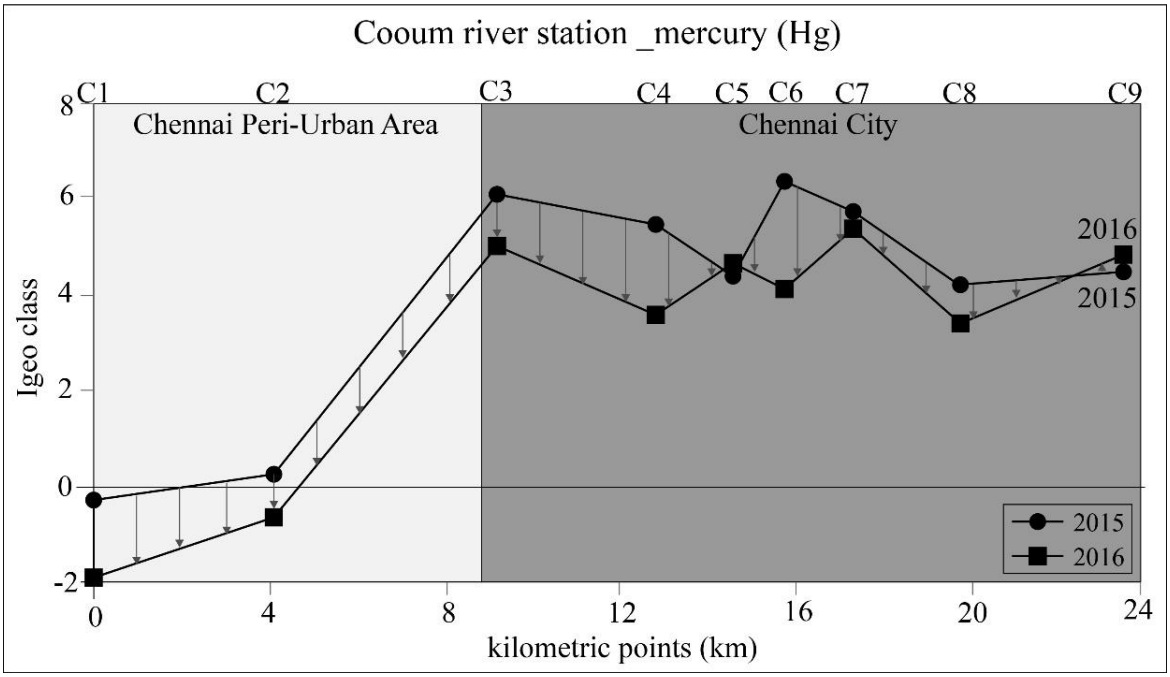


Figure 6.12 Effect of 2015 post flood influence on (I_{geo}) of mercury (Hg) in Cooum river sediments

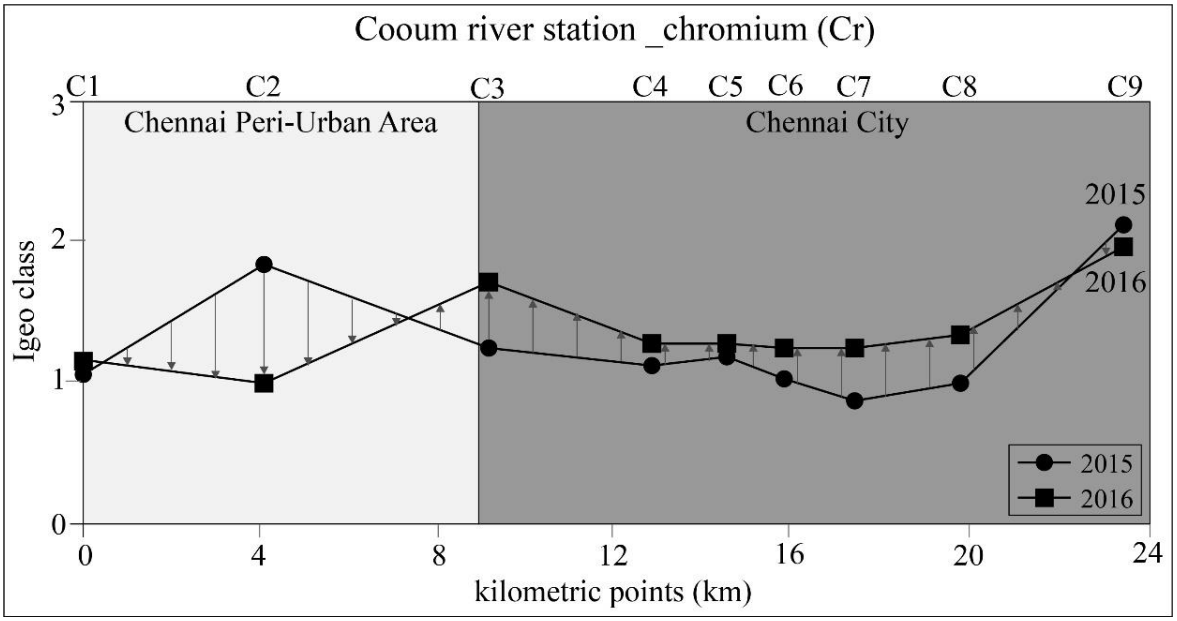


Figure 6.13 Effect of 2015 post flood influence on (I_{geo}) of chromium (Cr) in Cooum river sediments

The effect of 2015 flood influence in Adyar river sediment concentrations are, silver (Ag) in stations A4, A5, A8 and A9 (Figure 6.5), cadmium (Cd) in stations A2, A5 and A9 (Figure 6.6) and mercury (Hg) in stations A5 and A9 (Figure 6.7). The level of concentration is high compared to the sediment concentration before the flood of 2015. The trace elements Ag, Cd, Hg sources are from different anthropogenic sources. Especially the higher concentration levels occurred as the flow is disturbed due to damage of the bridges in Anakapudhar, Manapakkam, Burma colony and Jafferkhanpet. In this distraction of flow the rate of sedimentation was high from the multiple sources of contamination.

Similarly, in Cooum river sediment concentrations silver (Ag) was in stations C3, C7 and C9 (Figure 7.9), cadmium (Cd) in stations C3, C7, C8 and C9 (Figure 6.10) and mercury (Hg) in stations C5 and C9 (Figure 6.11). The level of concentration is high compared to the sediment concentrations before the flood event of 2015. This higher concentration levels occurred from the multiple sources of pollution in urban area. Especially, in river mouth A8 and A9 of Adyar river and C7 to C9 of Cooum river concentrations increase are influenced by sea tides (backwater) because, most of the downstream stations do not allow free flow from river to sea and the water bodies are in stagnant condition (Figure 6.2 (c)).

The trace element Cr concentration in sediment of Adyar river (Figure 6.8) stations A2 to A5 and A7 to A9 and in Cooum river (Figure 6.12) stations C3 to C8 the level of concentrations are high compared to the sediment concentrations before the flood of 2015. Chromium (Cr) is an industrial signal. So, these higher concentrations of trace element Cr might have been related to the industrial and commercial products (electronic, plastic products) which were washed out and deposited in both rivers. Especially along the downstream side of the Cooum river, lot of automobile industries exist. Due to the flood, these automobile products join the river and deposit with sediments.

The overall result on influence of floods on concentrating trace element on rivers, revels that the urban tracer levels are moderately reduced in after 2015 flood.

6.6 SEDIMENT CONTAMINATION FEATURES FOR THE SPECIFIC GUFI

Geochemical Urban Footprint Index (GUFI), is a special index to identify the sediment contamination in Chennai megacity rivers. The calculated MUI and GUFI for the studied trace elements in surface sediments of 2015 flood of Adyar and Cooum rivers are shown in Table 6.4 and the level of contaminations are shown in Table 6.5. The level of contamination of GUFI in the upstream stations are extremely low contamination in both rivers (Table 6.5). However, downstream stations have moderate contamination in Adyar river stations A5, A6, A8 and A9. Similarly, in Cooum river (stations C3 to C9) are strong to high contamination. This type of contamination is most complex due to the multiple sources of pollution in urban and industrial activities.

Table 6.4 MUI and GUFI of the trace elements in surface sediments of 2015 post flood in Adyar and Cooum rivers

Station		Kilometric point (km)	MUI			GUFI
			Ag	Cd	Hg	
Adyar River	A1	00.0	-	1.00	1.00	1.00
	A2	03.0	1.18	11.75	2.49	5.14
	A3	06.6	-	3.56	2.76	2.11
	A4	12.0	2.12	2.92	2.46	2.50
	A5	14.7	19.53	17.45	42.92	26.63
	A6	15.9	34.95	34.02	64.05	44.34
	A7	18.4	3.35	4.24	10.30	5.96
	A8	21.9	30.39	14.69	32.71	25.93
	A9	23.7	23.11	34.30	43.87	33.76
	Min.	-	**1.18**	**1.00**	**1.00**	**1.00**
	Max.	-	**34.95**	**34.30**	**64.05**	**44.34**
Coum River	C1	00.0	1.00	1.00	1.00	1.00
	C2	04.1	-	3.10	2.67	1.92
	C3	09.2	73.72	8.83	158.30	80.28
	C4	12.8	43.36	70.13	59.84	57.78
	C5	14.6	39.02	72.13	113.47	74.87
	C6	15.8	115.82	109.18	82.01	102.34
	C7	17.4	195.96	119.95	206.43	174.12
	C8	19.8	42.20	79.13	48.17	56.50
	C9	23.5	57.33	63.09	131.26	83.89
	Min.	-	**1.00**	**1.00**	**1.00**	**1.00**
	Max.	-	**195.96**	**119.95**	**206.43**	**174.12**

Table 6.5 GUFI classification based on the level of contamination in surface sediments of Adyar and Cooum rivers

GUFI Range	Level of Contamination	Adyar River	Cooum River
1 – 10	Extremely Low Contamination	A1, A2, A3, A4, A7	C1, C2
10 – 25	Low Contamination	-	-
25 – 50	Moderate Contamination	A5, A6, A8, A9	-
50 – 75	High Contamination	-	C4, C5, C8
75 – 100	Very High Contamination	-	C3, C6, C7, C9
> 100	Extremely High Contamination	-	-

6.7 SEDIMENT CONTAMINATION COMPARISION IN CHENNAI MEGACITY RIVERS BEFORE AND AFTER THE FLOOD OF 2015

Geochemical Urban Footprint Index (GUFI), compare the sediment contamination levels in Chennai megacity rivers before and after the flood of 2015. The 2015 floods influence of Metal Urban Index (MUI) for Adyar and Cooum rivers are illustrated in the Figures 6.14 to 6.19. and GUFI in 6.20 to 6.21.

6.7.1 2015 Vs 2016 of MUI

The effect of 2015 flood in Adyar river sediment on the trace element of silver (Ag) is that its concentration level got decreased, cadmium (Cd) is increased at all the stations at station A7 and mercury at stations A5 and A9 got increased, when compared to the sediment concentrations before the flood of 2015. Similarly, in Cooum river all the 3-urban tracer (Ag, Cd, Hg) concentrations increased at all the stations (Figures 6.17 to 6.19) (except Ag at station C2 and Hg at C6) when compared to the sediment concentrations before the flood of 2015. These increased concentration levels occurred due to the multiple sources of pollution at the sampling stations.

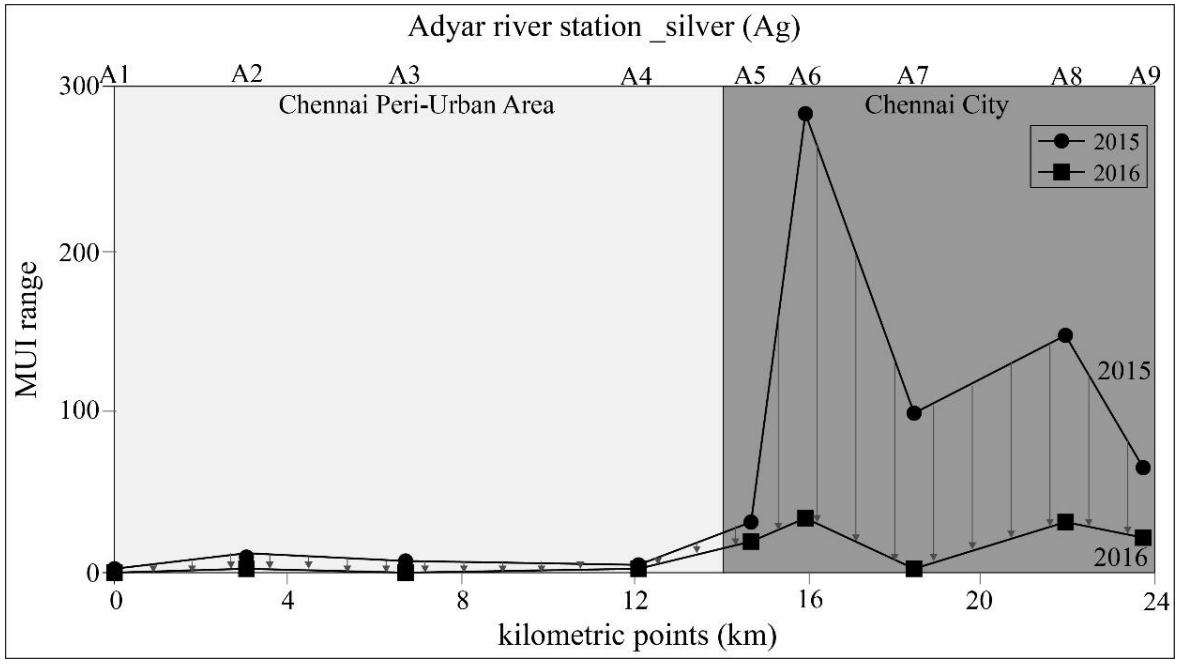


Figure 6.14 Effect of 2015 post flood influence on MUI of silver (Ag) in Adyar river sediments

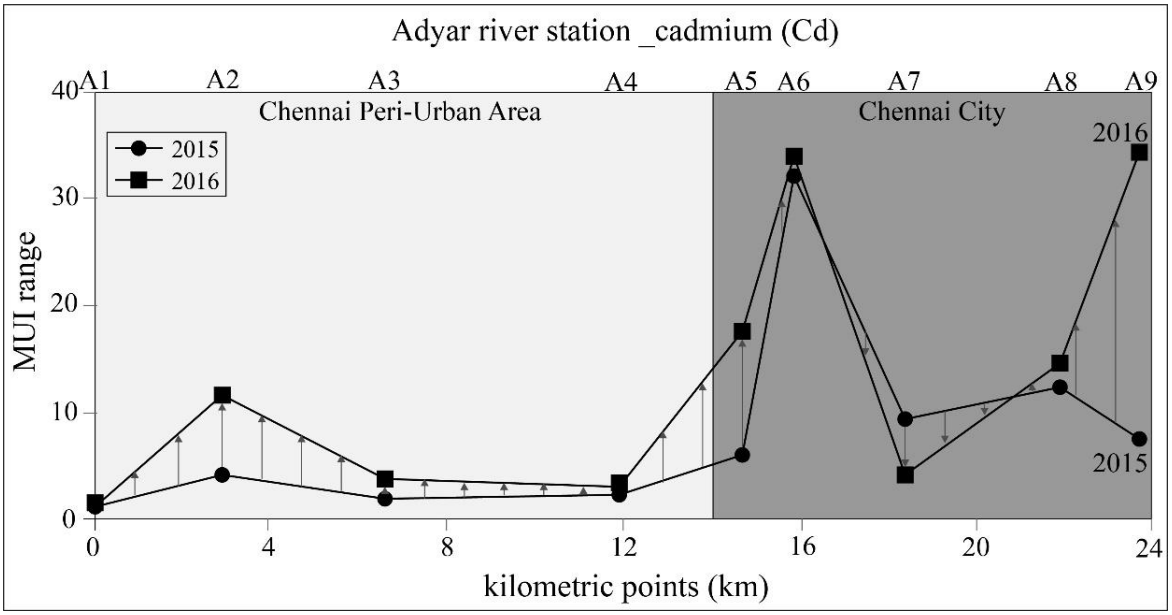


Figure 6.15 Effect of 2015 post flood influence on MUI of cadmium (Cd) in Adyar river sediments

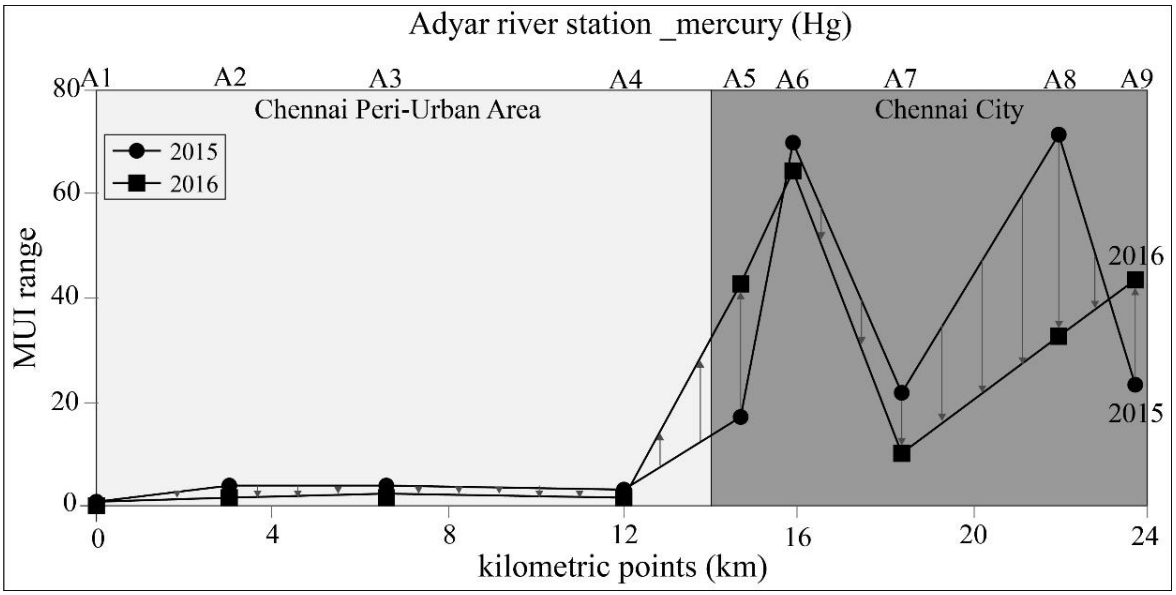


Figure 6.16 Effect of 2015 post flood influence on MUI of mercury (Hg) in Adyar river sediments

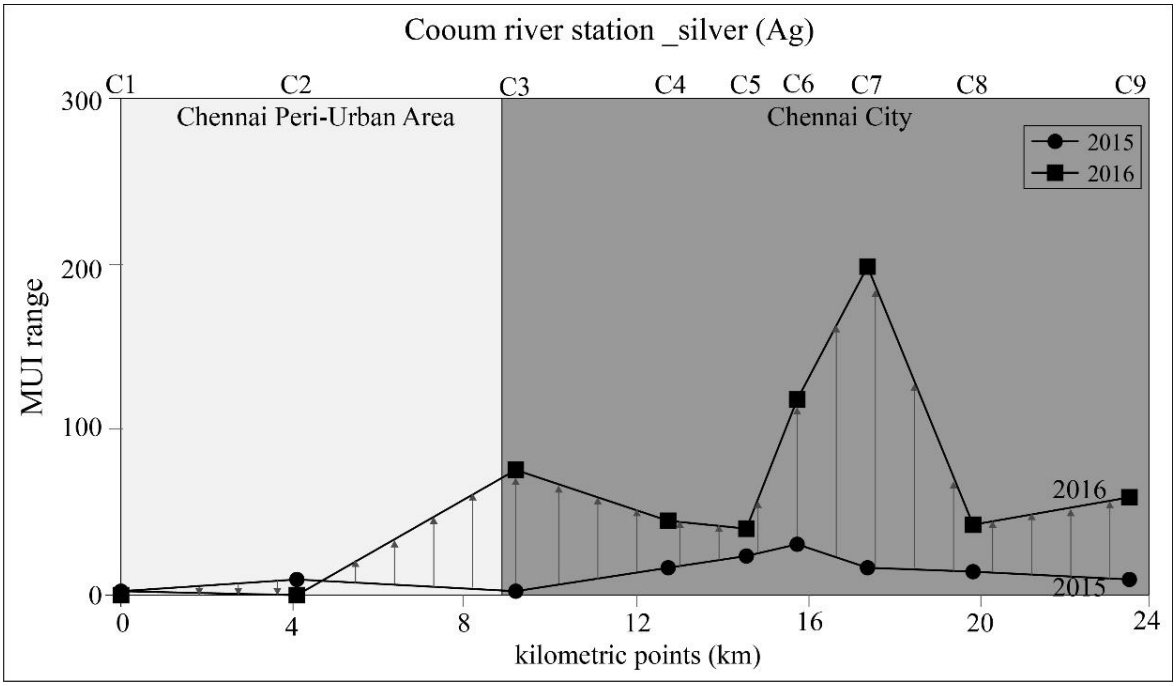


Figure 6.17 Effect of 2015 post flood influence on MUI of silver (Ag) in Cooum river sediments

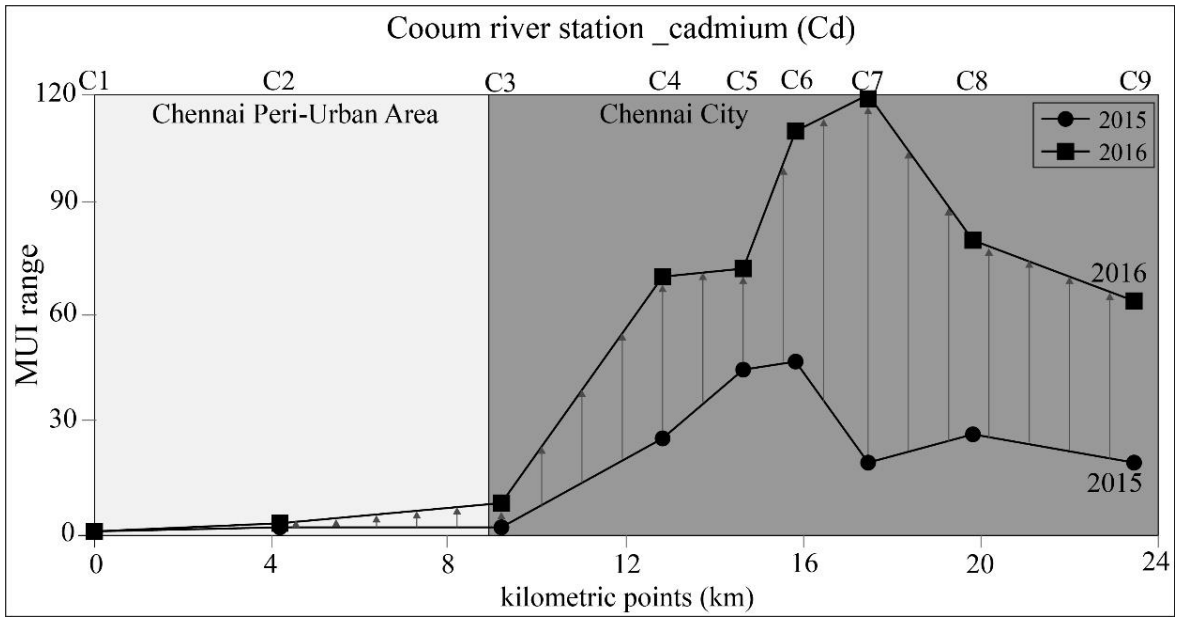


Figure 6.18 Effect of 2015 post flood influence on MUI of cadmium (Cd) in Cooum river sediments

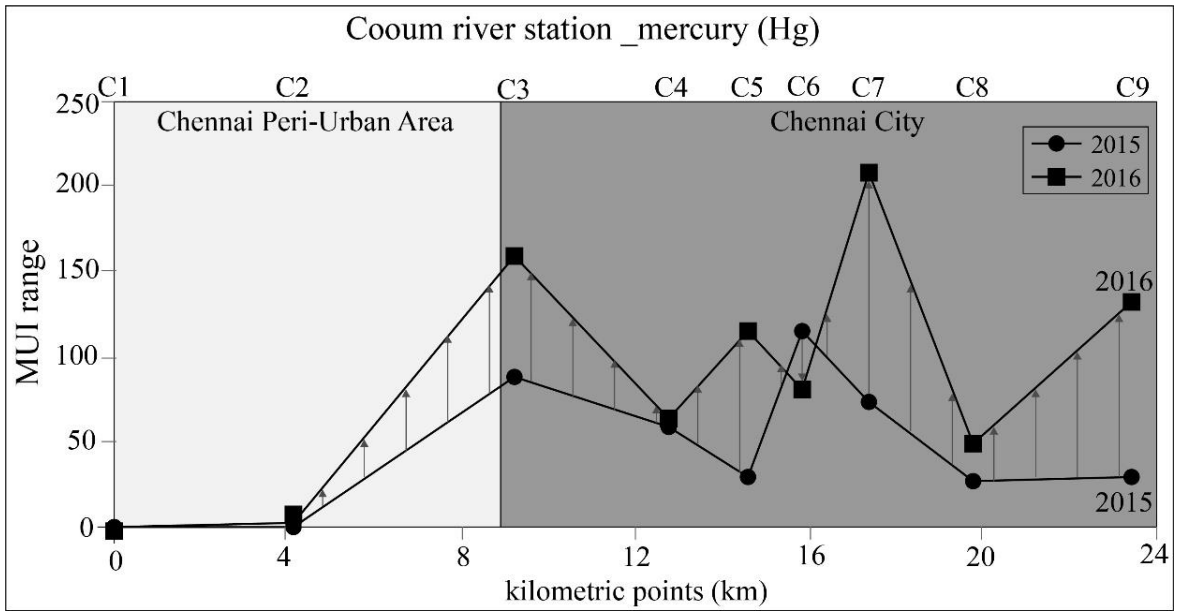


Figure 6.19 Effect of 2015 post flood influence on MUI of mercury (Hg) in Cooum river sediments

6.7.2 2015 Vs 2016 of GUFI Contamination Level

A decrease in the contamination level of GUFI due to the influence of 2015 flood in Adyar river sediments are between high to moderate contamination at the downstream stations A6 to A8 (Figure 6.19) but, in Cooum river sediments the contamination level increased from moderate to high contamination between the stations C3 to C9 (Figure 6.20).

In Cooum river, high contamination occurred due to stagnation (Figure 6.2 (c)). Due to this stagnation, downstream stations did not have free flow from river to sea. Also, the river receives higher sediment rate and deposition.

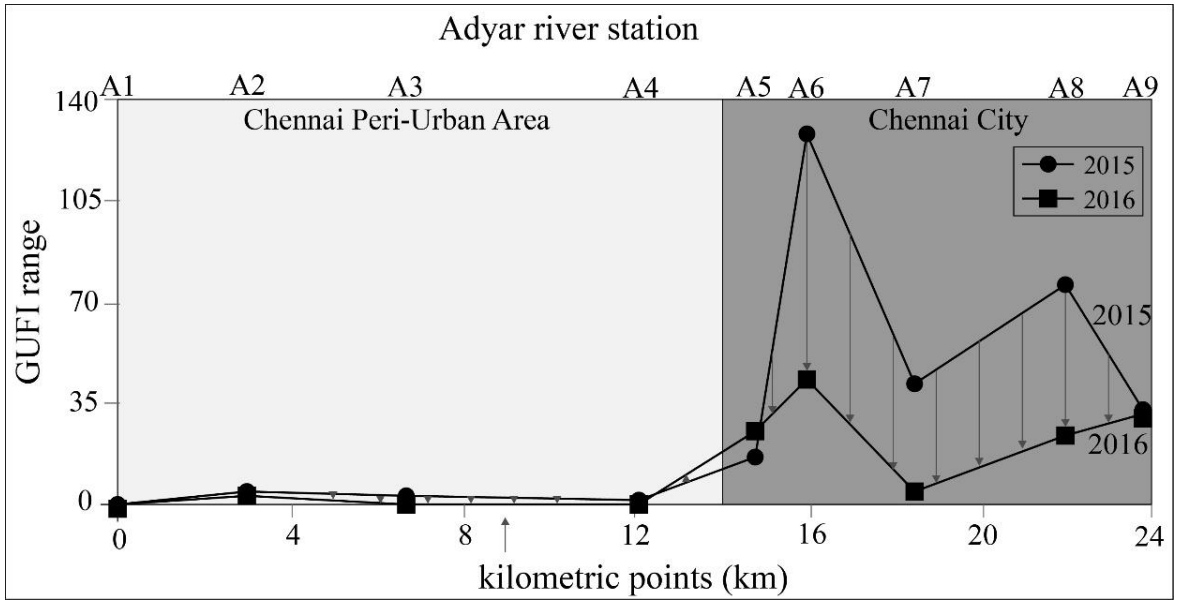


Figure 6.20 Effect of 2015 post flood influence on GUFI range in Adyar river sediments

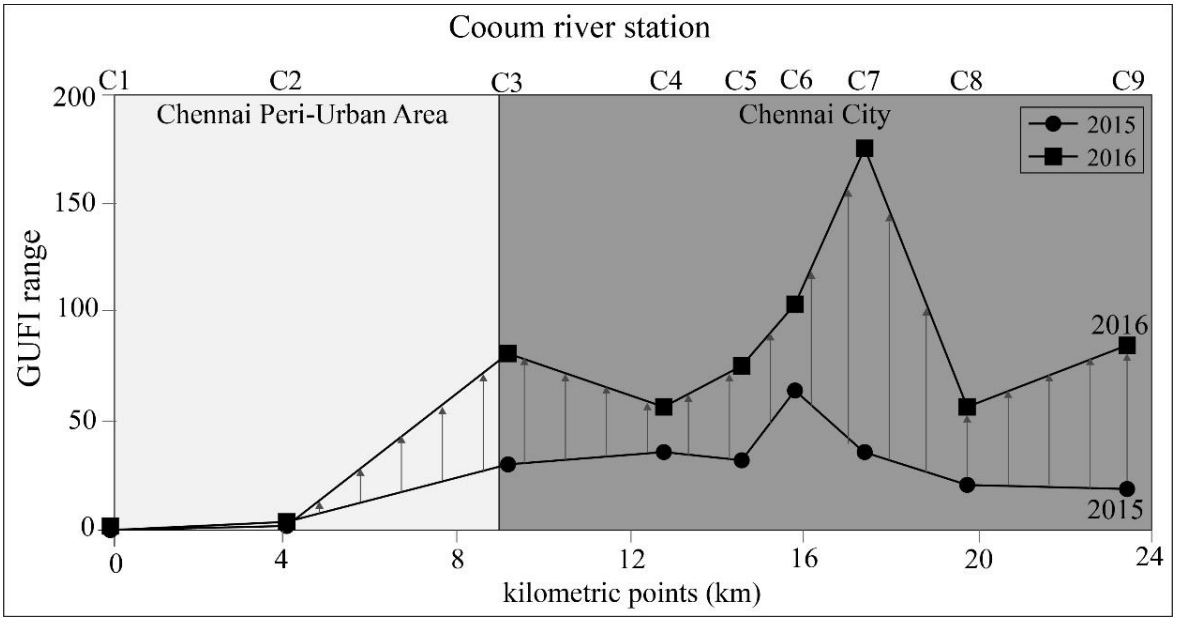


Figure 6.21 Effect of 2015 post flood influence on GUFI range in Cooum river sediments

6.8 INFLUENCE OF 2015 POST FLOOD ONTO TOXICITY LEVELS OF ORGANIC CONTAMINANTS

6.8.1 PAHs Concentration of Post Deposited Sediments of 2015 Flood

The endocrine disruptor of Chennai megacity river sediments outcome of PAHs concentration is described in Table 6.6 and compared the concentration as shown in Table 5.1. In Adyar river, total concentration of PAH (Σ_{13} PAH) ranged from 0.127 to 1.800 mg/kg. Similarly, in Cooum river ranged from 0.205 to 10.089 mg/kg. The total concentrations of Σ_{13} PAH of sediment samples in Chennai megacity rivers are much reduced due to the 2015 flood, except at river mouth (A9 in Adyar river and C9 in Cooum river) This higher concentrations show that the rivers are under the influence of saline intrusion due to back water. Cooum river station C9 has 3 times higher concentration of Σ_{13} PAH after the floods.

Table 6.6 Post deposited sediments concentrations of 2015 flood – see Figure 6.1 for locations

Station		ANT	FL	PHE	BaA	CHR	FLA	PYR	BaP	BbF	BkF	DahA	BghiP	IcdP	Σ PAH
Adyar river	**A1**	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
	A2	0.047	0.126	0.066	-	0.047	0.022	-	-	-	-	-	-	-	**0.308**
	A3	0.020	0.057	0.029	-	0.021	-	-	-	-	-	-	-	-	**0.127**
	A4	0.034	0.097	0.079	-	0.024	-	-	-	-	-	-	-	-	**0.235**
	A5	0.061	0.041	0.078	0.025	0.038	0.064	0.110	0.020	0.046	-	-	-	-	**0.483**
	A6	0.140	0.211	0.349	0.104	0.088	0.284	0.167	0.096	0.144	0.099	0.022	-	0.097	**1.800**
	A7	0.075	0.140	0.120	-	0.039	0.054	0.044	-	-	-	-	-	-	**0.472**
	A8	0.100	0.069	0.073	-	0.123	0.092	0.107	0.030	0.090	0.037	-	-	0.020	**0.741**
	A9	0.094	0.081	0.085	0.064	0.052	0.152	0.133	0.036	0.082	0.045	-	-	0.025	**0.849**
Coum River	**C1**	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
	C2	0.026	0.056	0.049	-	0.033	0.020	0.021	-	-	-	-	-	-	**0.205**
	C3	0.189	0.132	0.314	0.092	0.145	0.320	0.291	0.056	0.176	0.071	-	0.033	0.028	**1.848**
	C4	0.076	0.077	0.095	-	0.132	0.093	0.101	0.027	0.083	0.035	-	-	-	**0.718**
	C5	0.155	0.118	0.219	0.058	0.146	0.196	0.228	0.041	0.156	0.060	-	0.023	0.031	**1.433**
	C6	0.121	0.101	0.101	-	0.130	0.051	0.074	0.030	0.096	0.051	-	-	0.027	**0.781**
	C7	0.476	0.301	0.261	0.147	0.213	0.514	0.662	0.121	0.297	0.151	-	0.050	0.088	**3.281**
	C8	0.097	0.120	0.152	0.023	0.138	0.125	0.127	0.038	0.085	0.043	-	0.042	0.024	**1.015**
	C9	1.483	0.371	0.738	0.680	0.472	1.144	2.760	0.614	1.147	0.271	0.024	0.226	0.159	**10.089**

The PAHs identified can be classified according to their molecular structure. The three fused ring (LPAHs) compounds are 45% in Adyar river and 30% in Cooum rivers. Similarly, more than four ring (4-6 rings) compounds (HPAHs) observed are 55% (4 rings 37%, 5 rings 15% and 6 rings 3%) in Adyar river and 70% (4 rings 47%, 5 rings 19% and 6 rings 4%) in Cooum river are shown in Table 6.7.

Table 6.7 Percentage of mean concentration of 3, 4, 5 and 6-ring PAHs in sediment sample of Chennai megacity rivers

Rings compounds	Adyar river (percentage)	Cooum river (percentage)
3-rings	45	30
4-rings	37	47
5-rings	15	19
6-rings	03	04

The molecular structure compounds comparison (Table 5.2 and 6.7) before and after 2015 flood, showed that the percentage of LPAHs increased from 32% to 45% and HPAHs decreased from 68% to 55% in Adyar river sediment. Similarly, in Cooum river sediments of LPAHs and HPAHs remain with the same percentage (30%) but, 4 ring compounds increased from 38% to 47% compared to before and after 2015 flood. These 4 ring compounds are pyrolytic sources due to combustion. Due to the influence of 2015 flood, the molecular compounds clearly identified in Adyar river sediments with reduced organic pollution level and in Cooum river there is an increase of some specific compounds. This is due to the effect of stagnation in Cooum river.

6.8.2 Diagnostic Ratios of PAHs in Post Flood Deposited Sediments Samples of Chennai Megacity Rivers

PAHs diagnostic ratio is to identify point sources, in the surface sediment samples after the 2015 flood. The resulting profiles are shown in Table 6.8. The

sediment samples from the Adyar river station (A5 to A9) values are ranging between 0.37 to 0.63 and Cooum river stations (C2 to C8) are 0.41 to 0.52. For FLA/(FLA+PYR) and ANT/(ANT+PHE) they are between the ranges 0.29 to 0.58 in Adyar river and stations (A2 to A9) and in Cooum river stations (C2 to C9) from 0.35 to 0.67; which suggests mixed pyrogenic sources are the main contributors. Similarly, the ratio of BaA/(BaA+CHR) for sampling stations A5, A6 and A9 in Adyar river and stations C3, C7 and C9 in Cooum river is greater than 0.35, as the sources are coming from vehicular emission and the ratio IcdP/(IcdP+ BghiP) is not present in Adyar river and station C3, C5, C7, C8 and C9 are equivalent values from the range of > 0.50 as presenting in the downstream station of Cooum rivers.

6.8.3 Comparison between the Cross Plot of Diagnostic Source Ratio before and after 2015 Flood

The cross plot of multiple characteristic ratio for comparison between before and after 2015 flood sediment samples are illustrated in the Figure 6.22 for Adyar river and Figure 6.23 for Cooum river. In this illustration label for Adyar river, A station a indicates sample before flood 2015 and A station b indicates sample after flood 2015. Similarly, Cooum river C station a and C station b specifies samples before and after 2015 flood respectively.

Table 6.8 Diagnostic ratios of PAHs in post flood deposited sediments samples of Chennai megacity rivers

Station		FLA / (FLA + PYR)	ANT / (ANT + PHE)	BaA / (BaA + CHR)	IcdP / (IcdP+BghiP)
		<0.4 Petrogenic	<0.1 Petrogenic	<0.2 Petrogenic	<0.2 Petrogenic
		0.4 - 0.5 Fossil Fuel	**>0.1 Pyrogenic**	0.2-0.35 Coal Combustion	0.2 – 0.5 Petroleum combustion
		>0.5 Grass, Wood, Coal combustion	**-**	**>0.35 Vehicular Emission**	**>0.5 Grass, wood and coal combustion**
Adyar River	A1	**-**	**-**	**-**	**-**
	A2	**-**	**0.42**	**-**	**-**
	A3	**-**	**0.42**	**-**	**-**
	A4	**-**	**0.30**	**-**	**-**
	A5	0.37	**0.44**	**0.40**	**-**
	A6	**0.63**	**0.29**	**0.54**	**-**
	A7	**0.55**	**0.38**	**-**	**-**
	A8	0.46	**0.58**	**-**	**-**
	A9	**0.53**	**0.52**	**0.55**	**-**
Coum River	C1	**-**	**-**	**-**	**-**
	C2	0.49	**0.35**	**-**	**-**
	C3	**0.52**	**0.38**	**0.39**	0.46
	C4	0.48	**0.44**	**-**	**-**
	C5	0.46	**0.42**	0.29	**0.57**
	C6	0.41	**0.55**	**-**	**-**
	C7	0.44	**0.65**	**0.41**	**0.64**
	C8	**0.50**	**0.39**	0.14	0.36
	C9	0.29	**0.67**	**0.59**	0.41

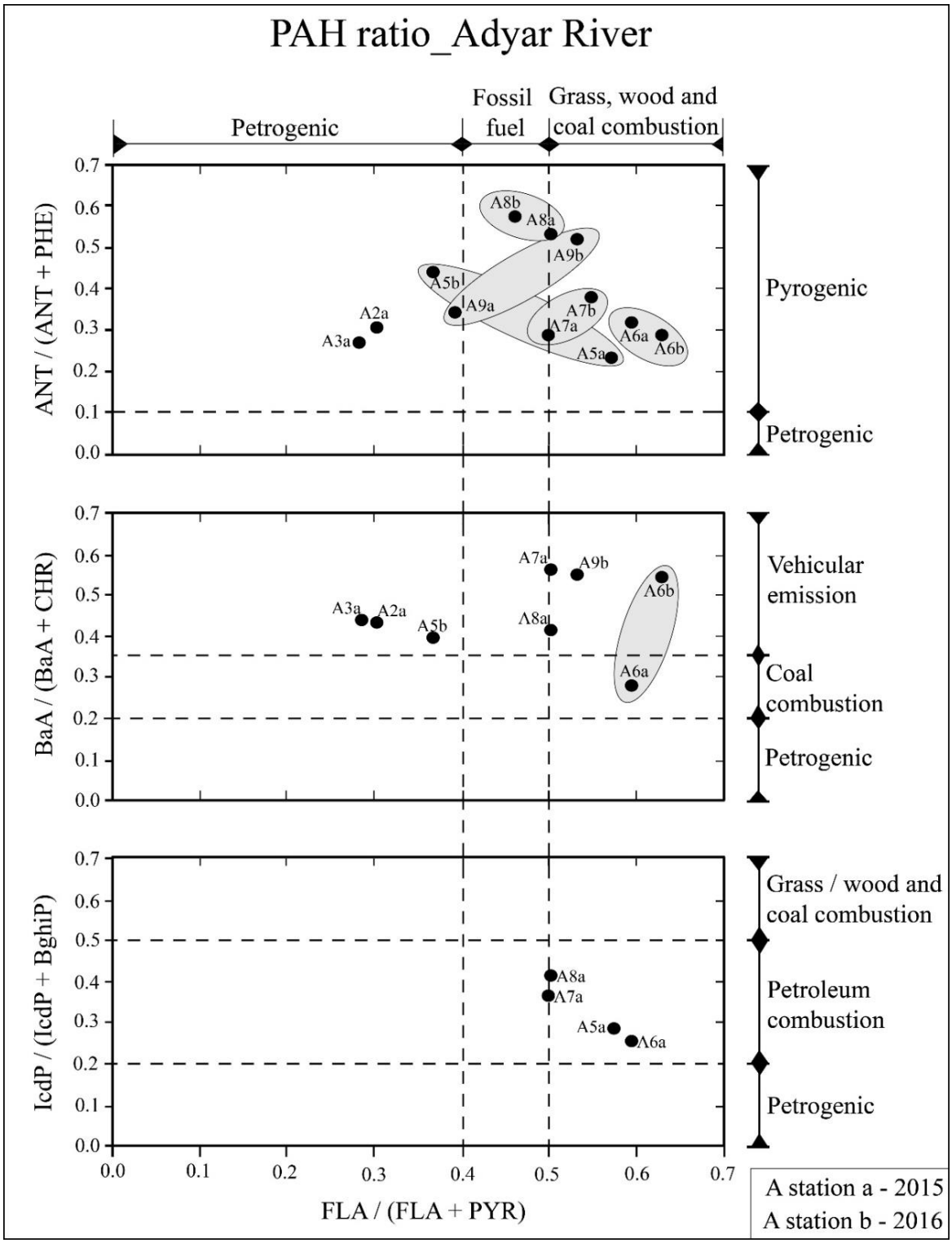


Figure 6.22 Comparison between the cross plots of multiple characteristic ratio before and after the flood of 2015 for sediment samples in Adyar river

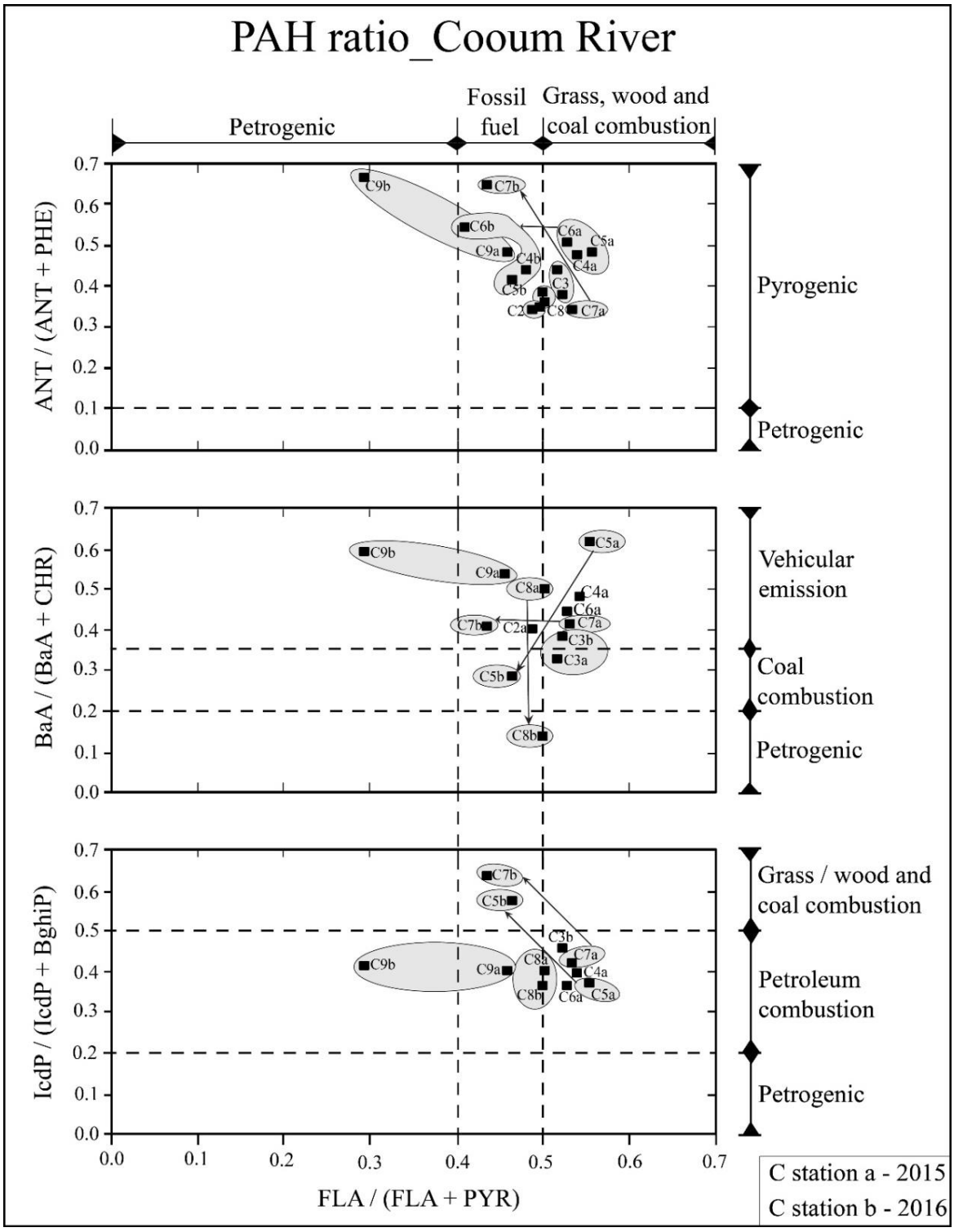


Figure 6.23 Comparison between the cross plots of multiple characteristic ratio before and after the flood of 2015 for sediment samples in Cooum river

In Adyar river the Cross plot of diagnostic sources ratio of comparative sediment samples (Figure 6.22) before and after 2015 flood, the ratios FLA/(FLA+PYR) and ANT/(ANT+PHE) represent the mixed pyrogenic sources in the stations A5 to A9. Similarly, the ratio between FLA/(FLA+PYR) and BaA/(BaA+CHR) in station A6 also represents pyrogenic sources. However, due to the 2015 flood influence these sources are transformed from coal combustion to vehicular emission. The ratio of FLA/(FLA+PYR) and IcdP/(IcdP+ BghiP) are not influenced in 2015 flood.

Correspondingly, in Cooum river sediment sample (Figure 6.23) between the ratio of FLA/(FLA+PYR) and ANT/(ANT+PHE) at the stations C3 to C9 are strongly influenced for mixed pyrogenic sources compared before 2015 flood. Especially in the downstream stations the level is very high due to the back water from sea to river. For the ratio between FLA/(FLA+PYR) and BaA/(BaA+CHR) in stations C3, C5, C7, C8 and C9 are influenced by coal combustion and vehicular emission. But except C9, remaining stations are very strongly influenced by vehicular emission compared before 2015 flood. Also, the ratio between FLA/(FLA+PYR) and IcdP/(IcdP+ BghiP) in station C5, C7, C8 and C9 are influenced by petroleum and fossil fuel combustion before 2015 flood. After the 2015 flood the sources are transformed into coal combustion especially, station C5 and C7. However, multiple characteristic ratio for comparison of PAHs in this Cooum river, the hotspots of PAHs were observed at downstream stations. The higher concentrations are likely to originate from wastewater washed out (Figure 6.3 (c)) from residential and industries (stations C6 to C9 are located lot of automobile service stations (workshops) discharging waste products, waste engine oil, automobile spare parts etc.,) via drainage in Chennai megacity.

6.8.4 Pollution and Toxicity Levels of Organic Contaminants (PCBs, Phthalates and PBDEs)

The pollution and toxicity levels of organic contaminants (PCBs, Phthalates and PBDEs) of sediment samples in Chennai megacity rivers are reported in Table 6.9.

As per PCBs, after the 2015 flood in Adyar river PCBs congeners (mg/kg) were not detected anywhere in the sampling locations. In Cooum river station C3 is detected with PCB 153 = 0.005; station C7 is detected with PCB 28 = 0.010 and PCB 52 = 0.007; and PCB 101 is detected at station C3 = 0.009, C4 = 0.013, C5 = 0.009, C6 = 0.005 and C7 = 0.010. Due to the flood effect, these detected PCBs congener sources are coming from commercial products (electrical products) being washed out from residential and industries and deposited in the river. Figure 6.24 shows floating debris accumulated after 2015 flood.



Figure 6.24 Floating debris accumulated after 2015 post flood

Table 6.9 Post flood deposited sediment concentrations (mg/kg) of PCBs, Phthalates and PBDEs in Chennai megacity rivers – see Figure 6.1 for locations

Station	Adyar River				Cooum River						
	A1 to A4	A5	A6	A7 to A9	C1 to C2	C3	C4	C5	C6	C7	C8 to C9
PCB 28	-	-	-	-	-	-	-	-	-	0.010	-
PCB 52	-	-	-	-	-	-	-	-	-	0.007	-
PCB 101	-	-	-	-	-	0.009	0.013	0.009	0.005	0.010	-
PCB 118	-	-	-	-	-	-	-	-	-	-	-
PCB 138	-	-	-	-	-	-	-	-	-	-	-
PCB 153	-	-	-	-	-	0.005	-	-	-	-	-
PCB 180	-	-	-	-	-	-	-	-	-	-	-
Σ PCB	**-**	**-**	**-**	**-**	**-**	**0.014**	**0.013**	**0.009**	**0.005**	**0.027**	**-**
BBP	-	-	0.91	-	-	-	0.58	-	-	-	-
DBP	-	-	-	-	-	-	-	-	-	-	-
DEHP	-	4.34	41.20	-	-	-	-	-	-	-	-
DEP	-	-	0.41	-	-	-	0.40	-	-	-	-
DiBP	-	-	-	-	-	-	-	-	-	-	-
DiNP	-	-	13.99	-	-	-	-	-	-	-	-
Σ Phthalate	**-**	**4.34**	**56.52**	**-**	**-**	**-**	**0.98**	**-**	**-**	**-**	**-**
BDE 47	-	-	-	-	-	-	-	-	-	-	-
BDE 85	-	-	-	-	-	-	-	-	-	-	-
BDE 99	-	-	-	-	-	-	-	-	-	-	-
BDE 100	-	-	-	-	-	-	-	-	-	-	-
BDE 153	-	-	-	-	-	-	-	-	-	-	-
Σ PBDE	**-**	-	-	-	-	-	-	-	-	-	-

Similarly, phthalates congeners (mg/kg) in Adyar river station A5 is detected in DEHP = 4.34 and station A6 is detected in BBP = 0.91, DEHP = 41.20 (16 times higher concentration compared to before 2015 flood (Table 6.4)), DEP = 0.41 and DiNP = 13.99 (5.5 times higher concentration compared to before 2015 flood). Also, in Cooum river only one station C4 is detected with BBP = 0.58 and DEP = 0.40. The higher concentrations occurred due to the effect of flood, commercial products of plasticizers are deposited in the river body (Figure 6.24). The sediment concentration of PBDEs congeners are not detected anywhere in the Chennai megacity river samples.

6.9 CONCLUSION

The unusual intense monsoon in December 2015 triggered huge floods in Chennai and was completely overflooded due to increased discharge from major upstream reservoir in Adyar river. The February 2016 sediment sample results were compared to the previous survey of February 2015. The effect of 2015 flood on I_{geo} level of Adyar river sediment contamination level has no change in Chennai peri-urban area and downstream side of the Chennai city has changed between extremely polluted to moderately polluted in the trace elements of Cd and Hg. Similarly, in Cooum river sediments Ag has changed between extremely polluted to moderately polluted on the upstream side of the river and downstream has no changes between February 2015 and 2016 samples.

Sediment contamination in the megacity scale for special Index of GUFI in Adyar river has decreased between high to moderate contamination in the downstream stations A6 and A8. But in Cooum river, contamination has increased from moderate to high contamination between the stretches C3 and C9. This is due to an urban effect after the floods. The comparison of organic composition in Chennai river sediments from the influence of 2015 flood showed that the pollution and toxicity level of organic contaminants are reduced between February 2015 and 2016 samples.

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CHAPTER 7

SUMMARY AND CONCLUSION



CHAPTER 7

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7.1 SUMMARY

Fast developing cities are highly affected by multiple sources of contamination. The pollutants also get deposited in rivers sediments due to anthropogenic sources of domestic and industrial effluents create major quality issues in many urban areas. Chennai megacity is taken as an example to study the impact of the pollutants in its urban river sediments. Chennai megacity is one of the most comprehensive industrial and commercial metropolitan cities in India. The Adyar and Cooum rivers are the two important rivers among four rivers in Chennai megacity which plays a vital role in flood control and drainage of urban waste water. Many reasons can be attributed to the present condition such as population explosion, discharge of untreated domestic sewage and industrial effluents, sand bar at the river mouth etc. This study investigates the geochemical urban footprint of Chennai megacity on the river sediments from upstream to downstream of rivers using sedimentological characteristics.

In order to understand the geochemical urban foot print, surface sediment and flood deposit samples were collected at a depth of 0 – 15 cm using an uwitec coring device. The samples were collected before and after the 2015 flood over 18 locations from upstream to downstream of both the rivers and from 6 locations of some major drains. These samples were analysed for the trace elements and organic components at the national CNRS-SARM laboratory, Nancy, France and LERES laboratory Rennes, France.

The analysis of results are used to develop the geochemical index namely Geoaccumulaion Index (I_{geo}) (Muller 1969). The results of I_{geo}, is used to develop new index such as Geochemical Urban Footprint Index (GUFI) for identify the pollution

status of Chennai Megacity rivers. Also, to compare the trace element level of Chennai city contamination to that of worldwide megacities was compared to the Sediment Quality Guidelines (SQGs). The organic components of the river sediments were estimated based on the Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), Polybrominated Diphenyl Ethers (PBDEs) and phthalates or Alkylphenols. The summary of results is discussed broadly in three parts (i) Trace element urban footprint; (ii) Occurrence of endocrine disruptor and (iii) Influence of 2015 flood hazard on distribution of pollutants.

7.1.1 Trace Element Urban Footprint

The spatial variations of the upstream-downstream concentrations of trace elements are presented in surface sediments and to quantify the present pollution level of the two urban rivers studied and the major drains which connect with these rivers. Sediment concentrations of trace elements are presented in in Table 5.1 according to kilometric points.

For both rivers, the minimum concentrations of Ag, Cd, Cu, Hg, Pb and Zn were always found in sediment samples collected at the most upstream stations (A1 and C1, Table 4.1). Concentrations at these stations were in the same range of magnitude to the ones in sediments collected in the most upstream drain, the station A-CSC at the Chembarambakkam Surplus Channel in the Chennai peri-urban area (Figure 3.2). These concentrations indicate that the upstream stations can be considered as not influenced by any anthropogenic activity for Ag, Cd, Cu, Hg, Pb and Zn levels. On the opposite, As, Cr and Ni, the minimum concentrations were measured in more downstream reaches.

In the Adyar river, the highest sediment concentrations were found at station A6 for Ag, Cd, Cu and at station A8, 6 km downstream from A6 (Figure 3.2), for As, Hg, Pb. These results indicate an increase of these trace element concentrations (Ag, As, Cd, Cu, Hg and Pb) from upstream downstream of the Adyar river. For Cr and Ni, the minimum concentrations were found at station A5 and their concentrations maximum were measured at different stations: A2 for Cr and A4 for Ni.

In the Cooum river, the station C6 presented the highest levels of Ag, Cd, Hg and Zn, the station C9 for Cu, indicating an up-downstream gradient of contamination along the river for these trace elements as for the Adyar river. For As, Cr and Ni, the lowest concentrations were measured in the middle of the river length at station C7 and their maxima at station C9, the most downstream station. For both rivers, all trace element concentrations in sediments decreased at the most downstream station in the estuarine part (stations A9 and C9) except for As, Cr, Ni and Pb in Cooum sediments.

Therefore, several drains were sampled in order to quantify trace element levels from some potential punctual pollution sources as they are considered as representative of specific urban inputs. The drain stations A-BC, A-YMCA and A-NMR are 3 main urban drains of Chennai city, collecting waste water from various urban areas. A comparison of trace element levels in drains and in the 2 studied rivers shows that drain maxima were in the same range of concentrations than studied river sediments, presenting even more elevated concentrations for Cd, Cu, Ni and Zn.

The most widely adopted pollution index, Geoaccumulation Index (I_{geo}) is used to classify the peri-urban area and urban area (city limit) with the trace element concentration levels. The classifications are described with six I_{geo} classes (0 to 6) which vary from unpolluted to extremely polluted (Table 4.3). The upstream basins of both rivers mean $I_{geo,}$ are lower than 3 as unpolluted to moderately polluted, with trace elements of As, Cd, Cu, Hg, Ni, Pb and Zn except Cr in Adyar river and Ag in Cooum river sediment concentrations. This is due to multi sources of industrial discharge of effluents without any treatment.

Similarly, at downstream stations of both the rivers as Ag, Cd and Hg are strongly to extremely polluted in urban area. These pollution levels are exceeding I_{geo} class 6 (Figure 4.3 from stations A6 to A9 in Adyar river). The same trend is observed in the urban limit of Cooum river but the I_{geo} class for the trace element of Ag concentration reaches class 8 (Figure 4.4). This may be due to the influence of urban activities and emerging contaminations. There is a significant level of Cr sediment

concentration, indicate an extremely polluted state in the most upstream part of the Adyar river (Figure 4.3) due to the influence of the tanning region. The presence of chromium may be an industrial signal. However, Cooum river is free from Cr pollution. These trace elements, namely Ag, Cd and Hg are used as an urban tracer of Chennai city and Cr is considered as industrial signals.

The upstream and downstream concentrations of urban foot print are specifically developed a new index called GUFI. This study is to identity the contamination levels of three main urban tracers, Ag, Cd and Hg which are considered on the basis of I_{geo} analysis results. The GUFI is classified to six classifications based on the level of contamination from extreme low to extreme high (Table 4.5). The sediment contamination level on the upstream side of the river Adyar and Cooum are found to be extremely less contaminated. In downstream (urban area) side, the concentration reveals that it is moderate to extremely contaminated at stations A6 to A9 of Adyar river and C3 to C7 in Cooum river. However, this type of contamination is most complex for multiple sources of pollution. For this reason, sediment samples taken from major drains in Chennai city were useful to identify sources of pollution and their respective levels of contamination. Inside the city, all the sampled drains were contaminated from moderate to extreme levels. The results clearly show that pollution sources came directly from the urban area and related to different urban activities

Socioeconomic data was collected to identify the causes of these pollution hotspots. However, these most polluting hotspots which discharge huge amounts of effluent. With levels of Geochemical Urban Footprint Index (GUFI), socioeconomic data, level of pollution are correlated to the global trend of population and industrial hotspots which do not reveal anything in Chennai city because of non-channelized drains. Baud *et al.* (2009) mentioned that Chennai is a complex city and a straight comparison is less valid than in other Indian megacities due to population density and industrial hotspots. This is one of the reasons why pollution levels have been unpredictable at the urban scale.

The comparative analysis of megacity pollution level is aimed to correlate the worldwide megacity population versus sediment concentration with the help of Sediment Quality Guidelines (SQGs)**.** These SQGs are used to correlate the Chennai megacity pollution levels with the worldwide megacities. The comparison of ubiquitous trace elements are Cr, Cu, Ni, Pb, and Zn pollution of megacities is was compared using PEC values (Table 4.6).

The results of comparative analysis carried out from megacities of worldwide reveal that the PEC of Cr, Cu, Ni, Pb and Zn exceeds in the megacities of Lagos in Nigeria, Guangzhou in China, Kinshasa in DR Congo, Paris in France and Ho Chi Minh city in Vietnam respectively. However, in India, Delhi and Mumbai river trace elements concentrations of Zn, Cr, Cu, Pb and Ni (except Pb in Delhi) are higher than the proposed PEC levels. Similarly, in Chennai megacity rivers Cr, Cu and Ni sediment concentrations are exceeding the PEC level in selected locations. This may be due to presence of tanning industries and anthropogenic activities around the rivers Adyar and Cooum.

Based on the surface sediment concentrations of ubiquitous trace elements (Cr, Cu, Ni, Pb, Zn) in various rivers and drains of megacities worldwide were compared according to pollution ranking using the mean PEC quotient. According to this megacity pollution ranking, Chennai is ranked fifth, with the first six rankings all being megacities in Asian countries. The result of this study shows that Chennai is on a par level with Ho Chi Minh City (Vietnam) and Guangzhou (China).

7.1.2 Occurrence of Endocrine Disruptor

The result of endocrine disruptor occurrence provides information on the priority hazard of PAHs in surface sediments of Adyar and Cooum rivers are reported in the Table 5.1. A total of 13 PAHs in sediment samples of Adyar river are analyzed and the results indicate that the total concentration of PAHs (Σ_{13} PAHs) ranges from 0.136 to 2.032 mg/kg. Similarly, in Cooum river it ranges from 0.471 to 3.753 mg/kg. This shows that the Cooum river has more concentration than Adyar river. The minimum concentration of Σ_{13} PAHs are observed along the upstream sides of both the

rivers, except station A2 in Adyar river. The higher concentration of Σ_{13} PAHs are observed in the downstream side stations A6 to A8 of Adyar River and C4 to C9 of Cooum river. However, station A9 in Adyar river has less concentration due to the influence of tidal variations.

The Principal Component Analysis (PCA) has been applied to evaluate a variety of samples in Adyar and Cooum Rivers. The analysis result reveals that the PC 1 contributes with 81.98% of the variance in Adyar river and 80.25% in Cooum river. The PCA observe the formation of two clusters with negative and positive scores which can be characterized as petrogenic in the upstream of Adyar river and Cooum river and pyrogenic in the downstream.

The PAHs diagnostic ratio is a tool to identify the pollution emitting sources. There are many ratios used to obtain the likely point source originating locations. In this study the ratios between FLA/(FLA+PYR), ANT/(ANT+PHE), BaA/(BaA+CHR) and IcdP/(IcdP+ BghiP) are used to identify the petrogenic and pyrogenic (gasoline, petro, diesel, grass, wood and coal combustion) sources respectively (Table 5.3).

The cross plot is prepared for three different ratios between FLA/(FLA+PYR) and ANT/(ANT+PHE); FLA/(FLA+PYR) and BaA/(BaA+CHR); FLA/(FLA+PYR) and IcdP/(IcdP+ BghiP) to identify the source based hotspot locations (Figure 5.4) in both the rivers of Chennai megacity. The results of three cross plot ratios indicate that sediment samples represent the mixed pyrogenic sources (vehicular emission and grass, wood and coal combustion) from the stations A2 to A9 in Adyar river and C2 to C9 in Cooum river. However, the upstream stations A2, A3 is influenced by SIPCOT industry and station A9 at the sea mouth is tidal action. However, this diagnostic ratio reveals that the hotspots of PAHs were observed in the downstream stations because of high density population and industrial sectors.

The other sources of pollution from electric, electronic and other commercial products are estimated using the congeners of PCBs (seven major PCBs

such as 28, 52, 101, 118, 138, 153 and 180 are considered), Phthalates (six compounds such as BBP, DBP, DEHP, DEP, DiBP and DiNP) and PBDEs (five compounds of BDE such as 47, 85, 99, 100 and 153) for Chennai megacity river sediments (Table 5.5). The ΣPCBs is detected only one station (A6) in Adyar river and three stations (C4, C5 and C6) in Cooum river. These stations are most common hotspot locations as per the result of PAHs (Table 5.5). The common PCB present in both the rivers sediments of Chennai megacity is PCB101 and the source may be electric and electronic products from commercial. However, PCB101 is considered as one of the indicators of PCBs pollution.

Similarly, the sediment concentrations based on phthalates DiNP and DBP in river Adyar and Cooum river respectively. The total sediment concentration of all phthalates work out to 2.33 mg/kg, 4.98 mg/kg, 2.90 mg/kg, 2.63 mg/kg and 2.02 mg/kg in stations A5, A6, A7, A8 and A9 of Adyar river, and 3.20 mg/kg, 14.46 mg/kg, 2.06 mg/kg, 2.80 mg/kg and 8.27 mg/kg in stations C4, C5, C6, C7 and C8 of Cooum river respectively. The sources for DiNP and DBP are due to plasticizer (toys, erasers etc.) from commercial and industrial products. Also, the sediment concentration of PBDEs congeners are not detected in both river sediments.

7.1.3 Influence of 2015 Post Flood Hazard on Distribution of Pollutants

The sediment concentration of trace elements and organic component pollution levels of two main rivers are estimated, it is essential to understand the influence of 2015 December flood. This comparison is part of the present study considering February 2015 (pre-flood) and 2016 (post flood) samples to assess the gochemical composition of river sediments using I_{geo} and newly developed index GUFI. Also, the organic toxic levels were also analysed and compared.

The results of post flood on sediment quality of river Adyar indicates that the sediment concentrations (Table 4.1 and 6.1) of the trace elements Ag, As, Cd, Cu, Hg, Pb and Zn a decreasing trend except Cr at station A4 and Ni at station A2 (4331 mg/kg and 110 mg/kg for Cr and Ni). The increase in concentrations of trace elements

Cr and Ni due to industrial and commercial products (electronic, plastic etc) which are washed out and deposited during the flood 2015. The high concentrations at stations A2 to A4 are due to the reduction in flow velocity due to the construction of check dam and causeways. Also, the stations A8 and A9 show higher concentrations of sediments due to tidal effect. Similarly, in Cooum river sediment the trace element concentrations of As, Cd, Cr, Hg and Pb show a declining trend and Ag, Cu, Ni and Zn sediment concentrations are as before the 2015 flood.

The values of I_{geo} sediment concentrations before and after the December 2015 flood (2015 February and 2016 February) were compared for both the rivers (Table 4.3 and 6.3). The results reveal that there are no changes in I_{geo} class from stations A1 to A4 and C3 to C9 in Adyar and Cooum rivers respectively. The I_{geo} class for stations A5 to A9 of Cd and Hg concentrations in Adyar river and stations C1 to C2 of Ag concentrations in Cooum river are changed from 3-6 (strongly to extremely polluted) to 0-3 (unpolluted to strongly polluted).

The effect of 2015 flood on selected urban trace elements such as Ag, Cd and Hg on river sediments are studied using I_{geo} (Figures 6.6 to 6.13). The study reveals that there is an increase in I_{geo} values of Ag in stations A4, A5, A8 and A9 of Adyar river and C3, C7 and C9 of Cooum river. As for Cd, at station A2, A5 and A9 in Adyar river and C3, C7, C8 and C9 in Cooum river show an increase in I_{geo} value. The I_{geo} value of Hg is also increased in stations A5 and A9 in Adyar River and C5 and C9 in Cooum river.

The other trace element which confirms the industrial signal is Cr, which has significant influence of I_{geo} sediment concentrations in Adyar river from stations A2 to A9 except A6 and in Cooum river stations C3 to C8. The higher concentrations of trace elements are due to industrial and commercial products (electronic, plastic products) accumulated during flood deposited in both rivers. The downstream side of the Cooum river has lot of automobile used spare parts (shops and service stations) which are the main sources of deposit of sediments. In general, 2015 flood influence

on sediment concentrations in Chennai Megacity Rivers are moderately reduced compare to before flood.

Geochemical Urban Footprint Index (GUFI) is a newly developed index in this study to compare the level of contamination in the upstream and downstream of Chennai megacity rivers (Table 6.5). The level of contamination in the upstream stations of both the rivers are extremely low and in downstream stations are moderate contaminated in Adyar river stations A5, A6, A8 and A9. Also, in Cooum river, stations C3 to C9 are contaminated strongly to high.

The contamination levels of GUFI indicate that there is a decrease in sediment contamination from high to moderate in the river Adyar (Stations A6 to A8) and moderate to high in Cooum river sediments (stations C3 to C9). The reason for decreased level of sediment contamination in Adyar river may be due to high runoff from more open lands whereas in Cooum the level is increased due to more urban runoff with less upstream flow.

The effect of 2015 flood on the endocrine disruptor of PAHs in both river sediment is that, the concentration of PAHs is reduced to a greater extent except in the river mouth (A9 and C9 in Adyar and Cooum river). This higher concentration in river mouth is due to the influence of sea tide/sand bar. The molecular structure compounds comparison indicates that the percentage of LPAHs is increased from 32% to 45% and HPAHs is decreased from 68% to 55% in Adyar river sediment. Similarly, in Cooum river sediment LPAHs and HPAHs are in same percentage (30%) but, 4 ring compounds have increased from 38% to 47% compared to the 2015 flood. The influence of 2015 flood shows that the molecular compounds in Adyar river sediment pollution levels are reduced and in Cooum river it is increased for specific compounds (4 rings).

The cross plot of multiple characteristic ratio of mixed pyrogenic sources is estimated and compared before and after the 2015 flood with the ratio of FLA/(FLA+PYR) and ANT/(ANT+PHE). These ratios are predominant in the stations

A5 to A9 of Adyar river and C3 to C9 of Cooum river. Similarly, the ratio of pyrogenic sources (coal combustion and vehicular emission) is deduced from FLA/(FLA+PYR) and BaA/(BaA+CHR). The presences of pyrogenic sources are observed in station A6 of Adyar river and C3, C5, C7, C8 and C9 of Cooum river. These ratios indicate that the downstream portions of both the rivers are strongly influenced by vehicular emission.

Also, the ratio between FLA/(FLA+PYR) and IcdP/(IcdP+ BghiP) in stations C5, C7, C8 and C9 of Cooum river are influenced by petroleum and fossil fuel combustion before 2015 flood. But after 2015 flood the diagnostic source ratio are transformed into grass, wood and coal combustion. However, there are no evidence of such sources in Adyar river. The ratio of PAHs hotspots were observed to have higher concentrations at downstream stations of Cooum river. The reasons for higher concentrations are likely the disposal of wastewater from residential, industrial and automobile sectors.

The pollution and toxicity levels of organic compounds such as PCBs, Phthalates and PBDEs are compared before and after 2015 flood for their sources. The comparison indicates that the PCBs congeners are not deducted in Adyar river after the 2015 flood. The organic compounds such as PCB 28 and PCB 52 at station C7, PCB 101 at stations C3 to C7 and PCB 153 at station C3 detected respectively. This congener of PCBs are expected from the sources such as commercial, residential / industrial activities.

Similarly, phthalates congeners DEHP, BBP, DEP and DiNP are detected in station A6 whereas station A5 is detected with DEHP only. However, it is observed that the congener concentration of DEHP is increased to 16 times and DiNP 5.5 times compared to that before 2015 flood. Similarly, in Cooum river station C4 is detected with BBP and DEP. The cause for increase in concentration is due to the 2015 flood whereas the sediment concentration of PBDEs congeners are not detected anywhere in the megacity rivers of Chennai.

7.2 CONCLUSION

Based on the above studies, the following results and conclusions are arrived at:

- The result of trace elements Ag, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn footprint of Chennai megacity rivers, sediment concentrations indicate an extremely polluted urban fluvial system.

- The Geoaccumulation Index (I_{geo}) revealed that concentration of trace elements Ag, Cd and Hg were present at levels indicating a highly to extremely polluted level for sediments in the urban area compared to other trace elements such as As, Cr, Cu, Ni, Pb, and Zn. Concentration of Cr, however, did indicate an extremely polluted state in the most upstream part of the Adyar river due to the influence of the tanning region.

- This study shows that the extreme pollution of I_{geo} trace elements such as Ag, Cd and Hg concentrations can be used as urban tracers and Cr concentration can be considered as an industrial signal in Chennai megacity.

- The GUFI is specifically developed in this study, was calculated by combining the concentrations of these three key trace elements (Ag, Cd and Hg).

- The analysis of GUFI reveals that the upstream side of the sediment has an extremely low level of contamination, indicating that these stations are not influenced by urban activity. Downstream in Chennai city, GUFI trends for both rivers and drains are moderately to extremely high contamination, particularly for sediment concentrations at stations A6 and A8 on the Adyar river where levels were very high to extremely high.

- This increase in GUFI levels in the urban area is directly related to overflow of combined sewers as shown with the analysis of highly impacted sediments in sampled urban drains. It can also be linked to an overall trend of population and industrial increases. However, this correlation could not be direct as no upstream to downstream gradient could be evidenced with population density nor the number of identified point pollution hotspots.

- The comparative analysis of ubiquitous trace element (Cr, Cu, Ni, Pb, Zn) concentration in various rivers and drains of megacities worldwide were compared according to pollution ranking using the mean PEC quotient. According to this megacity pollution ranking, Chennai is ranked fifth among the worldwide megacities. However, it should be noted the population of Chennai megacity is considerably less and the pollution level is on a par with highly populated worldwide megacities.

- The analysis of spatial distribution of sediments organic component of both the rivers show less concentration in upstream and high concentration in the downstream stations of the rivers. The results of Σ_{13} PAHs sediment concentration are greater in Cooum river than Adyar river due to influence of tidal variations.

- The diagnostic ratio of PAHs cross plots between FLA/(FLA+PYR) and ANT/(ANT+PHE); FLA/(FLA+PYR) and BaA/(BaA+CHR); FLA/(FLA+PYR) and IcdP/(IcdP+ BghiP) reveal that the hotspots of PAHs in upstream stations are polluted by petrogenic and downstream stations are mixed pyrogenic sources in both the rivers due to high density of population and industrial sectors.

- The analysis of PCBs sediment concentrations reveal that the values are low or below the detection limits compared to the international standards except PCB 101.

- The phthalates analysis of sediment concentrations show that DiNP and DBP are the predominant compounds in the downstream stations of river Adyar and Cooum. The source could be plasticizer products. However, the sediment concentrations of PBDEs are not detectable in both the river sediments.

- The results of post flood on sediment quality of Adyar river indicate that the concentrations of trace elements in sediment have reduced except Cr concentration at station A4 and Ni at station A2. Similarly, in Cooum river As, Cd, Cr, Hg and Pb have reduced and Ag, Cu, Ni and Zn remain same as before the 2015 flood.

- The Geoaccumulation Index (I_{geo}) revealed that concentration of trace elements Ag, Cd and Hg were present at levels indicating a highly to extremely polluted.

- The Geoaccumulation Index (I_{geo}) of trace elements estimated in post flood deposited sediments show concentrations level same in upstream of both the rivers as before the 2015 flood. However, the trace element Cd and Hg pollution level has decreased from extreme to moderate in the downstream of Adyar river and Ag in the upstream of Cooum river.

- The influence of 2015 flood on GUFI indicates that the contamination level of the sediment is high to moderate in Adyar river and moderate to high in Cooum river. These variations of sediment concentrations are due to the availability or non-availability of open lands within the urban area.

- The effect of 2015 flood on the endocrine disruptor of PAHs in both the river sediment concentrations show a decline in concentration in the downstream of both the rivers compared to pre-flood of 2015 due to the influence of sea tide at river mouth.

- The influence of 2015 flood molecular structure compounds indicate that the percentage of LPAHs and HPAHs show that in Adyar river sediment pollution levels are reduced and Cooum river has increased with specific compounds (4 rings).

- The comparative analysis of diagnostic source ratio cross plots FLA/(FLA+PYR) and ANT/(ANT+PHE) reveal that the downstream side of the both rivers are polluted with mixed pyrogenic sources. Similarly, the ratios of FLA/(FLA+PYR) and BaA/(BaA+CHR) show pollution of coal combustion and vehicular emission.

- However, the ratios of FLA/(FLA+PYR) and IcdP/(IcdP+ BghiP) reveal that the Cooum river is influenced by coal combustion and there is no evidence of such sources in Adyar river. The comparison of organic composition of 2015 floods, diagnostic source ratio shows that the river sediment pollution and toxicity levels are reduced.

- The comparison of 2015 flood indicate that the PCBs congeners are not detected in Adyar river and detected in downstream stations of Cooum river due to commercial, residential / industrial activities.

- Similarly, phthalates congeners of DEHP are increased to 16 times and DiNP 5.5 times than the 2015 pre-flood levels. The increase concentration due to flood, plasticizer from commercial and industrial products deposited in river sediment.

- However, the sediment concentration of PBDEs congeners are not detected anywhere in the megacity rivers of Chennai.

- Hence, the newly developed Index GUFI is useful over the I_{geo} to assess and quantify the pollution severity status of any Megacity river influenced by emerging contamination due to urbanisation.

7.3 RECOMMENDATIONS FOR THE FUTURE STUDY

The following are the recommendations deduced from the results of this study:

- The present situation can be linked to population explosion associated with unplanned growth of the city and non-controlled point sources of pollution in Chennai's waterways.
- The monitoring of urban river contamination is essential to avoid further potentially toxic metal pollution of river sediment.
- The appropriate pollution hotspot need to identified and concern authority to take necessary steps to control the pollution entering in to the river by means of proposing additional STPs.
- The river restoration activities should be carried out based on the based on the level of pollution in the river stretch.
- The public awareness program should be conducted periodically to emphasise the importance urban rivers for the urban ecosystem sustainability.

ANNEXURE A

GEOCHEMMICAL ANALYSIS DATA

Table A1.1 Geochemical Analysis (Trace elements and Major elements) concentration of sediment sample (before 2015 flood) in Chennai Megacity rivers and drains

Station		Kilometric point (km)	Ag	As	Ba	Be	Bi	Cd	Ce	Co	Cr
			mg/kg								
Adyar River	A1	0.0	0.1	3.1	750.8	1.6	0.1	0.2	75.8	27.5	140.7
	A2	3.0	0.8	3.1	669.6	1.2	0.3	0.8	100.0	45.4	1517.0
	A3	6.6	0.6	2.4	698.8	1.4	0.3	0.4	91.8	20.6	924.9
	A4	12.0	0.2	1.8	525.0	1.2	0.2	0.4	85.6	25.1	700.1
	A5	14.7	1.8	1.8	825.3	0.8	0.1	0.8	41.1	8.3	74.2
	A6	15.9	18.8	3.7	829.7	1.1	0.7	4.8	56.3	16.7	348.3
	A7	18.4	7.1	2.9	796.3	1.2	0.5	1.5	56.4	13.7	163.9
	A8	21.9	12.1	4.1	700.2	1.3	0.3	2.3	96.9	18.8	359.2
	A9	23.7	4.4	3.1	763.3	1.0	0.4	1.1	64.6	9.8	166.9
	Min.		**0.1**	**1.8**	**525.0**	**0.8**	**0.1**	**0.2**	**41.1**	**8.3**	**74.2**
	Max.		**18.8**	**4.1**	**829.7**	**1.6**	**0.7**	**4.8**	**100.0**	**45.4**	**1517.0**
Coum River	C1	0.0	1.2	4.9	564.3	1.7	0.1	0.4	111.9	19.8	109.0
	C2	4.1	9.3	3.8	880.6	1.5	0.2	1.1	113.0	14.4	185.0
	C3	9.2	2.6	4.5	746.9	1.5	0.2	0.9	120.3	15.6	122.5
	C4	12.8	17.7	3.9	985.7	1.5	0.5	9.9	83.9	12.5	113.3
	C5	14.6	22.4	4.3	797.1	1.4	0.4	16.2	67.5	14.8	119.1
	C6	15.8	31.0	3.7	925.9	1.4	0.3	17.4	75.0	11.6	105.0
	C7	17.4	16.1	3.5	794.7	1.4	0.2	7.3	71.8	12.4	95.3
	C8	19.8	15.4	4.0	898.1	1.4	0.3	10.1	80.3	11.6	103.9
	C9	23.5	9.0	10.8	1146.0	1.5	1.1	7.8	108.8	15.7	225.9
	Min.		**1.2**	**3.5**	**564.3**	**1.4**	**0.1**	**0.4**	**67.5**	**11.6**	**95.3**
	Max.		**31.0**	**10.8**	**1146.0**	**1.7**	**1.1**	**17.4**	**120.3**	**19.8**	**225.9**
Drains	A_CSC		0.1	2.6	684.0	1.2	0.1	0.4	60.7	16.1	95.9
	A_RP		7.2	3.9	1018.4	1.5	0.4	0.7	71.6	17.7	267.1
	A_BC		9.7	3.0	776.9	1.2	0.3	0.9	72.8	15.0	225.5
	A_YMCA		14.3	3.9	820.0	1.4	0.4	10.0	64.7	13.9	131.1
	C_NMR		14.5	4.3	808.3	1.3	0.3	37.6	64.1	12.9	94.9
	C_GR		5.9	4.4	823.4	1.2	0.4	0.5	92.8	13.4	92.6
	Min.		**0.1**	**2.6**	**684.0**	**1.2**	**0.1**	**0.4**	**60.7**	**12.9**	**92.6**
	Max.		**14.5**	**4.4**	**1018.4**	**1.5**	**0.4**	**37.6**	**92.8**	**17.7**	**267.1**

Table A1.1 (Continued)

Station		Kilometric point (km)	Cs	Cu	Dy	Er	Eu	Ga	Gd	Ge	Hf	Hg
			mg/kg									
Adyar River	A1	0.0	1.7	68.0	3.9	2.1	1.7	22.8	4.4	1.4	6.0	0.0
	A2	3.0	1.0	236.6	4.0	2.2	1.2	18.8	5.1	1.3	17.6	0.1
	A3	6.6	1.4	81.6	3.9	2.0	1.3	22.4	5.4	1.4	8.2	0.1
	A4	12.0	1.2	82.5	3.2	1.8	1.2	19.5	4.1	1.4	9.6	0.1
	A5	14.7	0.7	73.7	1.8	0.9	0.7	12.0	2.2	0.9	5.1	0.3
	A6	15.9	1.1	325.0	2.4	1.3	0.9	14.4	3.1	1.0	5.9	1.4
	A7	18.4	1.2	181.8	2.7	1.5	0.9	16.0	3.2	1.1	6.7	0.5
	A8	21.9	1.3	191.9	3.5	1.8	1.2	18.9	4.7	1.2	12.6	1.8
	A9	23.7	0.9	84.9	2.3	1.2	0.9	14.6	3.0	0.9	9.3	0.5
	Min.		**0.7**	**68.0**	**1.8**	**0.9**	**0.7**	**12.0**	**2.2**	**0.9**	**5.1**	**0.0**
	Max.		**1.7**	**325.0**	**4.0**	**2.2**	**1.7**	**22.8**	**5.4**	**1.4**	**17.6**	**1.8**
Coum River	C1	0.0	2.2	60.8	4.1	2.1	1.4	21.8	5.7	1.4	6.7	0.1
	C2	4.1	1.3	188.0	4.2	2.3	1.4	20.1	5.7	1.4	20.2	0.1
	C3	9.2	1.6	85.6	4.8	2.7	1.4	19.9	6.1	1.4	24.1	5.7
	C4	12.8	1.4	179.0	3.5	1.9	1.1	18.3	4.4	1.2	14.9	3.7
	C5	14.6	1.5	254.3	2.9	1.6	1.0	16.9	3.6	1.2	7.2	1.7
	C6	15.8	1.4	222.5	3.2	1.8	1.0	17.6	4.0	1.2	12.2	6.6
	C7	17.4	1.3	154.8	3.1	1.7	1.0	17.5	3.9	1.2	9.3	4.3
	C8	19.8	1.3	173.3	3.3	1.8	1.0	17.6	4.3	1.2	14.7	1.5
	C9	23.5	1.8	302.0	4.1	2.2	1.3	20.1	5.5	1.5	18.4	0.8
	Min.		**1.3**	**60.8**	**2.9**	**1.6**	**1.0**	**16.9**	**3.6**	**1.2**	**6.7**	**0.1**
	Max.		**2.2**	**302.0**	**4.8**	**2.7**	**1.4**	**21.8**	**6.1**	**1.5**	**24.1**	**6.6**
Drains	A_CSC		0.6	45.1	2.8	1.5	1.2	19.0	3.4	1.2	11.8	0.0
	A_RP		1.5	159.1	3.3	1.7	1.1	18.1	4.0	1.2	8.1	1.7
	A_BC		1.1	335.7	2.9	1.6	1.0	15.5	3.8	1.1	12.9	1.8
	A_YMCA		1.3	238.7	3.0	1.6	1.0	17.2	3.7	1.1	8.4	1.4
	C_NMR		1.3	345.6	2.9	1.6	1.0	16.1	3.6	1.1	8.8	1.5
	C_GR		1.1	104.3	3.7	2.1	1.1	17.5	4.9	1.1	18.2	1.0
	Min.		**0.6**	**45.1**	**2.8**	**1.5**	**1.0**	**15.5**	**3.4**	**1.1**	**8.1**	**0.0**
	Max.		**1.5**	**345.6**	**3.7**	**2.1**	**1.2**	**19.0**	**4.9**	**1.2**	**18.2**	**1.8**

Table A1.1 (Continued)

Station		Kilometric point (km)	Ho	In	La	Lu	Mo	Nb	Nd	Ni	Pb	Pr
			mg/kg									
Adyar River	A1	0.0	0.8	0.1	37.9	0.3	0.6	7.8	29.1	65.6	21.9	8.0
	A2	3.0	0.8	0.0	49.9	0.4	1.8	11.7	40.0	67.5	55.4	11.0
	A3	6.6	0.8	0.0	44.3	0.3	1.1	8.1	38.3	62.0	27.5	10.3
	A4	12.0	0.7	0.0	43.0	0.3	0.9	8.2	32.8	76.4	23.7	9.1
	A5	14.7	0.4	0.0	19.9	0.1	1.0	3.4	15.6	17.9	25.9	4.3
	A6	15.9	0.5	0.3	28.4	0.2	6.0	6.6	21.9	55.2	54.1	5.9
	A7	18.4	0.6	0.1	28.8	0.2	2.9	6.7	22.6	43.8	60.0	6.2
	A8	21.9	0.7	0.1	47.2	0.3	4.2	9.2	37.6	56.3	65.2	10.3
	A9	23.7	0.5	0.0	31.6	0.2	3.2	5.2	23.9	27.9	33.5	6.7
	Min.		**0.4**	**0.0**	**19.9**	**0.1**	**0.6**	**3.4**	**15.6**	**17.9**	**21.9**	**4.3**
	Max.		**0.8**	**0.3**	**49.9**	**0.4**	**6.0**	**11.7**	**40.0**	**76.4**	**65.2**	**11.0**
Coum River	C1	0.0	0.8	0.0	56.1	0.3	2.1	9.1	43.2	45.6	38.1	12.1
	C2	4.1	0.8	0.0	55.5	0.4	2.3	9.2	44.3	46.4	339.7	12.3
	C3	9.2	1.0	0.0	60.3	0.5	2.4	10.9	47.0	44.4	51.9	13.1
	C4	12.8	0.7	0.0	42.8	0.3	4.5	8.0	33.3	42.3	78.6	9.3
	C5	14.6	0.6	0.0	33.3	0.2	6.7	7.8	26.1	47.0	70.8	7.3
	C6	15.8	0.7	0.0	37.1	0.3	3.8	7.5	29.4	39.4	83.6	8.1
	C7	17.4	0.6	0.0	36.0	0.3	4.3	7.1	28.6	36.3	58.0	7.9
	C8	19.8	0.6	0.1	41.0	0.3	4.7	7.4	31.8	36.4	70.7	8.8
	C9	23.5	0.8	0.1	54.0	0.4	4.8	10.3	40.4	49.4	145.1	11.5
	Min.		**0.6**	**0.0**	**33.3**	**0.2**	**2.1**	**7.1**	**26.1**	**36.3**	**38.1**	**7.3**
	Max.		**1.0**	**0.1**	**60.3**	**0.5**	**6.7**	**10.9**	**47.0**	**49.4**	**339.7**	**13.1**
Drains	A_CSC		0.6	0.0	29.2	0.3	0.5	7.9	23.7	37.0	17.4	6.4
	A_RP		0.6	0.1	36.9	0.3	5.8	7.5	28.1	60.5	59.4	7.7
	A_BC		0.6	0.0	37.2	0.3	3.1	7.3	29.0	56.0	75.1	8.0
	A_YMCA		0.6	0.1	33.7	0.3	4.1	7.2	26.1	44.4	65.0	7.1
	C_NMR		0.6	0.1	34.2	0.3	4.9	7.3	25.2	39.6	53.7	6.9
	C_GR		0.7	0.1	46.9	0.3	3.2	8.6	36.9	36.1	59.5	10.1
	Min.		**0.6**	**0.0**	**29.2**	**0.3**	**0.5**	**7.2**	**23.7**	**36.1**	**17.4**	**6.4**
	Max.		**0.7**	**0.1**	**46.9**	**0.3**	**5.8**	**8.6**	**36.9**	**60.5**	**75.1**	**10.1**

Table A1.1 (Continued)

Station		Kilometric point (km)	Rb	Sc	Sb	Sm	Sn	Sr	Ta	Tb	Th
			mg/kg								
Adyar River	A1	0.0	51.4	20.1	0.3	5.3	2.4	278.4	0.6	0.6	11.6
	A2	3.0	49.5	16.7	1.2	6.8	304.0	305.8	0.9	0.7	25.5
	A3	6.6	57.6	16.5	0.8	7.1	5.5	258.0	0.7	0.7	13.7
	A4	12.0	59.8	17.1	0.4	5.5	3.4	299.9	0.6	0.6	19.8
	A5	14.7	68.1	5.6	0.3	2.8	3.7	323.4	0.3	0.3	12.3
	A6	15.9	58.9	9.3	1.3	3.9	17.2	302.4	0.6	0.4	11.7
	A7	18.4	59.8	10.7	2.8	4.1	8.5	333.2	0.5	0.5	14.0
	A8	21.9	69.0	13.2	0.9	6.5	11.5	318.7	0.8	0.6	23.5
	A9	23.7	72.6	7.3	0.4	4.1	5.3	303.9	0.4	0.4	17.0
	Min.		**49.5**	**5.6**	**0.3**	**2.8**	**2.4**	**258.0**	**0.3**	**0.3**	**11.6**
	Max.		**72.6**	**20.1**	**2.8**	**7.1**	**304.0**	**333.2**	**0.9**	**0.7**	**25.5**
Coum River	C1	0.0	86.1	13.9	0.5	7.6	5.2	300.4	0.8	0.8	28.0
	C2	4.1	74.9	12.5	10.2	7.9	17.7	462.4	0.8	0.8	34.6
	C3	9.2	74.3	13.0	0.7	8.3	7.0	361.8	0.9	0.9	37.9
	C4	12.8	80.1	10.2	1.2	5.9	16.1	411.8	0.7	0.6	27.3
	C5	14.6	68.1	10.4	1.7	4.7	14.1	322.6	0.7	0.5	16.1
	C6	15.8	78.3	9.9	1.3	5.3	15.5	360.3	0.6	0.6	22.6
	C7	17.4	70.9	10.3	1.1	5.1	10.4	378.1	0.6	0.5	20.3
	C8	19.8	77.5	9.7	1.4	5.6	15.0	469.2	0.7	0.6	23.2
	C9	23.5	72.0	14.1	2.9	7.2	32.2	335.7	0.8	0.8	30.0
	Min.		**68.1**	**9.7**	**0.5**	**4.7**	**5.2**	**300.4**	**0.6**	**0.5**	**16.1**
	Max.		**86.1**	**14.1**	**10.2**	**8.3**	**32.2**	**469.2**	**0.9**	**0.9**	**37.9**
Drains	A_CSC		49.8	14.3	0.0	4.4	1.7	425.2	0.7	0.5	15.1
	A_RP		62.9	11.8	1.8	5.1	12.9	325.5	0.7	0.6	15.5
	A_BC		55.6	10.6	1.5	5.2	163.4	336.6	0.7	0.5	18.8
	A_YMCA		62.3	11.4	1.6	4.8	11.9	323.0	0.6	0.5	15.4
	C_NMR		64.2	9.3	1.2	4.7	10.2	358.1	0.6	0.5	15.3
	C_GR		61.4	11.7	1.7	6.4	11.6	350.0	0.6	0.7	30.5
	Min.		**49.8**	**9.3**	**0.0**	**4.4**	**1.7**	**323.0**	**0.6**	**0.5**	**15.1**
	Max.		**64.2**	**14.3**	**1.8**	**6.4**	**163.4**	**425.2**	**0.7**	**0.7**	**30.5**

Table A1.1 (Continued)

Station		Kilometric point (km)	Tm	U	V	W	Y	Yb	Zn	Zr
			mg/kg							
Adyar River	A1	0.0	0.3	1.8	141.5	1.2	21.0	2.1	114.7	236.7
	A2	3.0	0.3	2.5	131.5	2.0	21.2	2.3	1392.0	643.8
	A3	6.6	0.3	2.0	110.5	1.8	20.2	2.0	155.4	323.8
	A4	12.0	0.3	2.1	116.2	0.9	17.9	2.0	144.5	391.4
	A5	14.7	0.1	1.3	46.1	1.1	9.5	0.9	121.5	195.5
	A6	15.9	0.2	3.2	88.1	9.6	13.4	1.3	721.6	223.6
	A7	18.4	0.2	2.1	79.4	3.2	14.9	1.5	307.6	262.7
	A8	21.9	0.3	3.4	104.8	3.0	18.3	1.8	320.7	508.5
	A9	23.7	0.2	2.1	56.0	1.2	11.8	1.2	154.6	377.2
	Min.		**0.1**	**1.3**	**46.1**	**0.9**	**9.5**	**0.9**	**114.7**	**195.5**
	Max.		**0.3**	**3.4**	**141.5**	**9.6**	**21.2**	**2.3**	**1392.0**	**643.8**
Coum River	C1	0.0	0.3	3.7	105.4	1.6	21.1	1.9	147.5	262.8
	C2	4.1	0.3	3.4	87.3	2.7	22.5	2.3	381.2	712.0
	C3	9.2	0.4	4.2	90.0	5.1	26.4	2.8	202.7	892.9
	C4	12.8	0.3	5.6	80.9	5.7	19.6	2.0	517.0	544.6
	C5	14.6	0.2	5.8	88.7	5.4	16.2	1.6	586.1	278.5
	C6	15.8	0.3	4.6	77.0	3.4	17.9	1.8	595.1	488.2
	C7	17.4	0.2	3.7	77.4	3.9	16.4	1.6	381.9	374.7
	C8	19.8	0.3	4.5	74.6	5.9	17.9	1.8	470.7	530.2
	C9	23.5	0.3	4.2	124.6	2.5	22.0	2.3	402.0	647.6
	Min.		**0.2**	**3.4**	**74.6**	**1.6**	**16.2**	**1.6**	**147.5**	**262.8**
	Max.		**0.4**	**5.8**	**124.6**	**5.9**	**26.4**	**2.8**	**595.1**	**892.9**
Drains	A_CSC		0.2	1.9	89.4	0.9	14.9	1.6	65.2	498.5
	A_RP		0.2	3.1	101.6	3.8	17.2	1.7	776.2	325.2
	A_BC		0.2	3.3	84.2	3.1	16.0	1.6	456.7	512.7
	A_YMCA		0.2	3.5	92.4	2.2	16.6	1.7	415.0	324.9
	C_NMR		0.2	4.3	76.6	1.9	15.8	1.6	442.0	346.9
	C_GR		0.3	4.2	97.1	3.2	20.2	2.1	358.2	667.4
	Min.		**0.2**	**1.9**	**76.6**	**0.9**	**14.9**	**1.6**	**65.2**	**324.9**
	Max.		**0.3**	**4.3**	**101.6**	**3.8**	**20.2**	**2.1**	**776.2**	**667.4**

Table A1.1 (Continued)

Station		Kilometric point (km)	Si	Al	Fe	Mn	Mg	Ca	Na	K
			Percentage (%)							
Adyar River	A1	0.0	22.63	9.31	6.72	0.06	0.86	1.99	1.12	0.99
	A2	3.0	23.08	7.61	5.58	0.07	1.01	3.45	1.40	1.32
	A3	6.6	22.40	8.64	5.07	0.04	0.83	2.73	1.24	1.43
	A4	12.0	23.95	7.71	4.91	0.05	1.04	2.75	1.33	1.42
	A5	14.7	32.19	5.46	2.22	0.03	0.42	3.00	1.42	2.30
	A6	15.9	22.52	6.13	3.88	0.05	1.12	3.77	1.27	1.59
	A7	18.4	22.66	6.75	3.60	0.06	1.22	5.21	1.73	1.65
	A8	21.9	24.66	7.64	5.14	0.05	0.95	1.91	1.68	1.69
	A9	23.7	30.41	6.25	3.15	0.03	0.58	1.13	1.96	2.34
	Min.		**22.40**	**5.46**	**2.22**	**0.03**	**0.42**	**1.13**	**1.12**	**0.99**
	Max.		**32.19**	**9.31**	**6.72**	**0.07**	**1.22**	**5.21**	**1.96**	**2.34**
Coum River	C1	0.0	24.29	8.29	5.29	0.12	0.79	2.44	1.15	1.62
	C2	4.1	26.07	8.05	4.63	0.06	0.78	3.03	1.99	1.86
	C3	9.2	25.83	8.13	4.48	0.06	0.97	2.99	1.57	1.83
	C4	12.8	24.72	7.38	3.72	0.05	1.11	3.48	1.81	2.03
	C5	14.6	22.70	7.04	3.94	0.05	1.06	3.01	1.41	1.62
	C6	15.8	23.96	7.19	3.80	0.05	1.19	2.93	1.68	1.95
	C7	17.4	24.34	7.35	3.70	0.05	1.03	3.99	1.78	1.83
	C8	19.8	24.89	7.18	3.43	0.05	1.11	3.66	1.84	2.00
	C9	23.5	23.07	7.73	6.00	0.04	1.14	1.77	2.11	1.61
	Min.		**22.70**	**7.04**	**3.43**	**0.04**	**0.78**	**1.77**	**1.15**	**1.61**
	Max.		**26.07**	**8.29**	**6.00**	**0.12**	**1.19**	**3.99**	**2.11**	**2.03**
Drains	A_CSC		27.71	8.24	4.01	0.06	0.54	3.54	2.13	1.68
	A_RP		23.15	7.43	4.44	0.05	0.91	2.64	1.56	1.61
	A_BC		20.49	6.38	3.99	0.06	1.20	5.60	1.43	1.46
	A_YMCA		22.62	7.02	3.93	0.05	1.16	4.16	1.58	1.59
	C_NMR		21.63	6.45	3.60	0.05	1.13	4.51	1.53	1.58
	C_GR		23.88	7.07	4.36	0.05	0.95	3.83	1.70	1.67
	Min.		**20.49**	**6.38**	**3.60**	**0.05**	**0.54**	**2.64**	**1.43**	**1.46**
	Max.		**27.71**	**8.24**	**4.44**	**0.06**	**1.20**	**5.60**	**2.13**	**1.68**

Table A1.1 (Continued)

Station		Kilometric point (km)	Ti	P	PF	Total	CO2 total	Corg	S total
			Percentage (%)						
Adyar River	A1	0.0	0.46	0.03	15.14	98.80	5.36	1.18	0.27
	A2	3.0	0.72	0.05	14.41	97.85	11.35	2.45	1.32
	A3	6.6	0.43	0.04	17.35	98.53	11.53	2.59	0.90
	A4	12.0	0.45	0.03	15.88	98.88	13.76	2.98	0.96
	A5	14.7	0.18	0.03	6.76	99.34	7.86	1.40	0.28
	A6	15.9	0.30	0.11	20.49	97.93	26.38	6.22	1.26
	A7	18.4	0.35	0.07	17.27	98.49	21.32	4.02	0.88
	A8	21.9	0.49	0.04	14.96	99.27	14.29	3.36	2.37
	A9	23.7	0.27	0.02	9.50	99.61	9.05	2.25	1.37
	Min.		**0.18**	**0.02**	**6.76**	**97.85**	**5.36**	**1.18**	**0.27**
	Max.		**0.72**	**0.11**	**20.49**	**99.61**	**26.38**	**6.22**	**2.37**
Coum River	C1	0.0	0.42	0.03	14.86	99.39	12.56	2.46	0.94
	C2	4.1	0.48	0.05	9.95	99.30	9.24	2.11	0.55
	C3	9.2	0.54	0.03	10.83	99.25	8.04	1.49	0.73
	C4	12.8	0.39	0.09	14.41	99.52	17.84	3.71	0.91
	C5	14.6	0.36	0.10	20.03	98.78	27.20	5.99	1.13
	C6	15.8	0.37	0.10	16.14	98.53	19.39	4.53	1.26
	C7	17.4	0.36	0.07	14.65	98.97	16.67	3.42	1.47
	C8	19.8	0.37	0.08	14.16	99.01	17.34	3.65	0.87
	C9	23.5	0.53	0.06	16.03	99.12	13.35	3.30	2.06
	Min.		**0.36**	**0.03**	**9.95**	**98.53**	**8.04**	**1.49**	**0.55**
	Max.		**0.54**	**0.10**	**20.03**	**99.52**	**27.20**	**5.99**	**2.06**
Drains	A_CSC		0.50	0.01	6.52	98.95	3.14	0.36	0.08
	A_RP		0.39	0.24	18.73	99.22	21.38	4.98	1.04
	A_BC		0.40	0.33	22.00	98.68	27.14	5.27	0.91
	A_YMCA		0.38	0.23	18.54	98.91	23.69	5.43	0.86
	C_NMR		0.35	0.26	21.42	98.52	27.61	6.49	1.31
	C_GR		0.48	0.23	15.58	98.96	20.67	4.54	0.55
	Min.		**0.35**	**0.01**	**6.52**	**98.52**	**3.14**	**0.36**	**0.08**
	Max.		**0.50**	**0.33**	**22.00**	**99.22**	**27.61**	**6.49**	**1.31**

Table A1.2 Geochemical Analysis (Trace elements and Major elements) concentration in After 2015 flood (Post deposited sediments sample of Chennai Megacity rivers and drains

Station		Kilometric point (km)	Ag	As	Ba	Be	Bi	Cd	Ce	Co	Cr
			mg/kg								
Adyar River	A1	0.0	0.0	4.0	835.9	1.7	0.2	0.1	84.1	32.8	138.4
	A2	3.0	0.6	3.8	550.3	1.4	0.2	1.1	72.4	31.1	3345.5
	A3	6.6	0.0	2.3	781.1	1.6	0.3	0.4	114.1	22.7	944.1
	A4	12.0	0.8	2.4	678.4	1.1	0.4	0.2	81.2	26.2	4331.5
	A5	14.7	6.7	2.8	598.6	1.1	0.2	1.2	54.2	14.7	406.8
	A6	15.9	6.2	2.5	434.3	0.6	0.3	1.2	28.3	8.7	245.6
	A7	18.4	1.8	3.4	672.3	1.4	0.2	0.4	86.6	24.9	198.1
	A8	21.9	14.4	4.1	705.0	1.5	0.3	1.4	91.4	20.2	411.7
	A9	23.7	10.8	2.4	631.6	1.4	0.3	3.1	82.9	16.1	278.2
	Min.		**0.0**	**2.3**	**434.3**	**0.6**	**0.2**	**0.1**	**28.3**	**8.7**	**138.4**
	Max.		**14.4**	**4.1**	**835.9**	**1.7**	**0.4**	**3.1**	**114.1**	**32.8**	**4331.5**
Coum River	C1	0.0	0.3	3.8	603.1	2.0	0.2	0.2	111.4	22.3	114.9
	C2	4.1	0.0	2.6	795.5	1.5	0.1	0.5	122.0	15.0	103.4
	C3	9.2	14.2	4.4	807.3	1.4	0.3	1.2	73.4	18.4	171.6
	C4	12.8	8.4	4.0	766.4	1.4	0.3	9.2	77.6	14.8	125.9
	C5	14.6	8.3	4.1	743.2	1.6	0.3	10.4	89.9	16.7	124.8
	C6	15.8	24.2	4.2	830.8	1.5	0.3	15.5	79.7	14.1	122.1
	C7	17.4	38.2	5.5	936.9	1.5	0.3	15.9	81.6	14.9	124.0
	C8	19.8	8.8	4.5	697.7	1.5	0.2	11.2	78.4	17.7	131.5
	C9	23.5	12.0	8.8	853.5	1.6	1.0	9.0	78.9	16.4	203.8
	Min.		**0.0**	**2.6**	**603.1**	**1.4**	**0.1**	**0.2**	**73.4**	**14.1**	**103.4**
	Max.		**38.2**	**8.8**	**936.9**	**2.0**	**1.0**	**15.9**	**122.0**	**22.3**	**203.8**

Table A1.2 (Continued)

Station		Kilometric point (km)	Cs	Cu	Dy	Er	Eu	Ga	Gd	Ge	Hf	Hg
			mg/kg									
Adyar River	A1	0.0	2.2	64.4	4.5	2.5	1.6	23.5	5.0	1.4	6.5	0.0
	A2	3.0	1.8	138.6	3.6	2.0	1.2	19.4	4.2	1.3	5.6	0.1
	A3	6.6	1.5	109.1	4.5	2.5	1.3	21.5	5.9	1.5	15.8	0.1
	A4	12.0	1.1	60.3	3.0	1.7	1.1	15.8	4.0	1.0	7.9	0.0
	A5	14.7	1.2	143.0	2.3	1.2	0.9	13.9	2.9	0.9	3.6	0.7
	A6	15.9	0.7	158.5	1.2	0.7	0.5	7.2	1.5	0.5	1.8	0.6
	A7	18.4	1.5	107.0	3.3	1.8	1.3	22.2	4.4	1.3	7.1	0.3
	A8	21.9	1.8	202.2	3.8	2.0	1.3	19.1	4.8	1.3	9.9	0.8
	A9	23.7	1.5	177.7	3.4	1.8	1.2	18.3	4.5	1.1	11.2	1.0
	Min.		**0.7**	**60.3**	**1.2**	**0.7**	**0.5**	**7.2**	**1.5**	**0.5**	**1.8**	**0.0**
	Max.		**2.2**	**202.2**	**4.5**	**2.5**	**1.6**	**23.5**	**5.9**	**1.5**	**15.8**	**1.0**
Coum River	C1	0.0	2.8	53.7	4.6	2.4	1.7	24.5	6.1	1.5	6.2	0.0
	C2	4.1	1.4	62.2	4.8	2.6	1.6	21.9	6.3	1.4	25.8	0.1
	C3	9.2	1.6	226.0	3.3	1.8	1.1	17.3	4.2	1.2	9.9	2.6
	C4	12.8	1.4	186.2	3.3	1.8	1.1	17.8	4.2	1.2	11.9	1.0
	C5	14.6	1.8	178.3	3.7	1.9	1.3	20.2	4.6	1.3	10.3	2.0
	C6	15.8	1.6	248.9	3.3	1.9	1.1	18.1	4.3	1.2	8.4	1.5
	C7	17.4	1.5	309.8	3.4	1.8	1.1	16.7	4.4	1.2	11.4	3.4
	C8	19.8	1.8	198.3	3.4	1.8	1.3	18.8	4.3	1.3	6.7	0.9
	C9	23.5	1.9	353.9	3.5	2.0	1.2	18.4	4.3	1.3	10.3	2.3
	Min.		**1.4**	**53.7**	**3.3**	**1.8**	**1.1**	**16.7**	**4.2**	**1.2**	**6.2**	**0.0**
	Max.		**2.8**	**353.9**	**4.8**	**2.6**	**1.7**	**24.5**	**6.3**	**1.5**	**25.8**	**3.4**

Table A1.2 (Continued)

Station		Kilometric point (km)	Ho	In	La	Lu	Mo	Nb	Nd	Ni	Pb	Pr
			mg/kg									
Adyar River	A1	0.0	0.9	0.1	42.6	0.4	0.6	9.3	32.5	67.4	23.0	8.8
	A2	3.0	0.7	0.1	36.4	0.3	1.3	7.2	27.9	110.7	21.4	7.7
	A3	6.6	0.9	0.1	56.5	0.4	1.1	10.4	46.0	64.8	27.2	12.6
	A4	12.0	0.6	0.0	41.8	0.3	0.6	7.6	31.2	69.9	21.7	8.7
	A5	14.7	0.4	0.1	28.1	0.2	3.8	5.3	21.2	49.7	26.7	5.9
	A6	15.9	0.3	0.1	14.7	0.1	3.6	3.3	10.6	34.7	28.2	3.0
	A7	18.4	0.7	0.1	43.2	0.3	1.5	7.8	32.7	66.9	47.6	9.0
	A8	21.9	0.8	0.1	45.6	0.3	4.0	8.6	35.3	67.1	76.3	9.7
	A9	23.7	0.7	0.1	42.1	0.3	6.1	8.1	32.8	48.9	54.1	9.0
	Min.		**0.3**	**0.0**	**14.7**	**0.1**	**0.6**	**3.3**	**10.6**	**34.7**	**21.4**	**3.0**
	Max.		**0.9**	**0.1**	**56.5**	**0.4**	**6.1**	**10.4**	**46.0**	**110.7**	**76.3**	**12.6**
Coum River	C1	0.0	0.9	0.1	57.5	0.3	0.6	10.5	43.9	54.3	30.2	12.2
	C2	4.1	1.0	0.1	62.1	0.4	0.8	9.2	48.2	35.3	227.9	13.4
	C3	9.2	0.7	0.0	38.2	0.3	8.0	7.6	29.4	54.6	92.8	8.1
	C4	12.8	0.7	0.1	39.6	0.3	6.8	7.3	30.8	41.6	85.9	8.5
	C5	14.6	0.7	0.1	45.6	0.3	3.7	8.7	34.1	44.4	101.8	9.4
	C6	15.8	0.7	0.1	40.0	0.3	3.3	7.4	31.5	45.8	71.2	8.7
	C7	17.4	0.7	0.1	40.3	0.3	7.5	7.4	32.0	50.5	92.5	8.8
	C8	19.8	0.7	0.1	38.8	0.3	4.1	7.5	30.6	48.9	91.3	8.4
	C9	23.5	0.7	0.1	38.5	0.3	4.8	8.6	30.3	52.1	130.7	8.3
	Min.		**0.7**	**0.0**	**38.2**	**0.3**	**0.6**	**7.3**	**29.4**	**35.3**	**30.2**	**8.1**
	Max.		**1.0**	**0.1**	**62.1**	**0.4**	**8.0**	**10.5**	**48.2**	**54.6**	**227.9**	**13.4**

Table A1.2 (Continued)

Station		Kilometric point (km)	Rb	Sc	Sb	Sm	Sn	Sr	Ta	Tb	Th
			mg/kg								
Adyar River	A1	0.0	62.1	19.9	0.3	6.1	2.4	291.1	0.7	0.7	12.9
	A2	3.0	57.6	17.8	0.7	5.2	4.8	312.1	0.6	0.6	13.6
	A3	6.6	62.1	17.4	0.8	8.0	5.1	330.0	0.8	0.8	27.3
	A4	12.0	48.5	12.8	0.5	5.3	2.6	417.4	0.6	0.5	19.4
	A5	14.7	52.5	9.5	0.6	3.9	5.9	444.9	0.5	0.4	9.8
	A6	15.9	26.2	4.9	1.4	2.0	6.6	301.4	0.3	0.2	5.3
	A7	18.4	61.0	17.6	0.9	5.8	5.5	280.7	0.6	0.6	14.6
	A8	21.9	74.4	14.0	1.1	6.4	15.4	299.8	0.8	0.7	19.8
	A9	23.7	68.1	13.2	0.8	5.9	10.6	306.0	0.7	0.6	20.8
	Min.		**26.2**	**4.9**	**0.3**	**2.0**	**2.4**	**280.7**	**0.3**	**0.2**	**5.3**
	Max.		**74.4**	**19.9**	**1.4**	**8.0**	**15.4**	**444.9**	**0.8**	**0.8**	**27.3**
Cooum River	C1	0.0	95.0	17.0	0.3	8.0	3.3	298.6	0.9	0.8	21.9
	C2	4.1	75.8	13.5	2.1	8.7	5.4	545.0	0.8	0.8	33.4
	C3	9.2	70.1	11.1	1.5	5.4	13.4	331.7	0.9	0.6	18.5
	C4	12.8	68.1	10.5	1.1	5.7	9.4	395.7	0.6	0.6	21.5
	C5	14.6	76.9	12.2	1.3	6.1	12.3	374.8	0.8	0.6	23.2
	C6	15.8	74.0	11.3	1.4	5.6	13.4	324.0	0.7	0.6	18.9
	C7	17.4	72.7	10.4	1.6	5.8	20.1	327.0	0.7	0.6	18.6
	C8	19.8	72.0	12.4	1.2	5.6	10.3	327.0	0.7	0.6	13.8
	C9	23.5	72.0	13.8	2.4	5.5	31.7	267.4	0.7	0.6	17.6
	Min.		**68.1**	**10.4**	**0.3**	**5.4**	**3.3**	**267.4**	**0.6**	**0.6**	**13.8**
	Max.		**95.0**	**17.0**	**2.4**	**8.7**	**31.7**	**545.0**	**0.9**	**0.8**	**33.4**

Table A1.2 (Continued)

Station		Kilometric point (km)	Tm	U	V	W	Y	Yb	Zn	Zr
			mg/kg							
Adyar River	A1	0.0	0.3	1.8	145.9	1.2	24.2	2.4	107.2	260.8
	A2	3.0	0.3	3.0	136.6	1.1	20.1	2.0	472.6	212.9
	A3	6.6	0.4	3.3	120.0	2.9	24.5	2.5	177.3	583.8
	A4	12.0	0.2	1.8	95.3	1.3	16.4	1.6	148.4	309.3
	A5	14.7	0.2	2.8	79.8	2.0	12.4	1.2	333.7	139.8
	A6	15.9	0.1	1.4	42.7	5.2	7.1	0.7	366.1	67.5
	A7	18.4	0.3	1.9	132.6	2.0	18.0	1.8	204.6	282.0
	A8	21.9	0.3	3.2	109.5	2.9	19.9	1.9	479.3	381.5
	A9	23.7	0.3	3.3	97.8	2.1	18.0	1.8	359.2	432.5
	Min.		**0.1**	**1.4**	**42.7**	**1.1**	**7.1**	**0.7**	**107.2**	**67.5**
	Max.		**0.4**	**3.3**	**145.9**	**5.2**	**24.5**	**2.5**	**479.3**	**583.8**
Cooum River	C1	0.0	0.3	2.7	116.8	1.0	24.2	2.3	101.8	229.2
	C2	4.1	0.4	3.9	91.2	1.1	25.5	2.7	145.3	878.7
	C3	9.2	0.3	4.4	88.6	20.2	18.3	1.8	704.5	386.1
	C4	12.8	0.3	4.4	86.6	7.3	17.8	1.8	439.7	466.6
	C5	14.6	0.3	4.0	95.2	3.8	19.6	2.0	397.1	400.7
	C6	15.8	0.3	4.1	96.2	3.6	18.3	1.9	583.7	325.6
	C7	17.4	0.3	5.3	88.3	4.8	18.0	1.8	669.0	428.3
	C8	19.8	0.3	3.4	94.8	3.8	17.8	1.7	424.6	247.8
	C9	23.5	0.3	3.2	110.9	1.8	19.8	2.0	435.4	401.0
	Min.		**0.3**	**2.7**	**86.6**	**1.0**	**17.8**	**1.7**	**101.8**	**229.2**
	Max.		**0.4**	**5.3**	**116.8**	**20.2**	**25.5**	**2.7**	**704.5**	**878.7**

Table A1.2 (Continued)

Station		Kilometric point (km)	Si	Al	Fe	Mn	Mg	Ca	Na	K
			Percentage (%)							
Adyar River	A1	0.0	21.8	9.2	6.4	0.2	0.9	2.6	0.8	1.0
	A2	3.0	19.8	7.8	5.1	0.1	1.0	4.4	1.0	1.0
	A3	6.6	23.8	8.5	5.1	0.1	0.9	2.4	1.6	1.4
	A4	12.0	20.7	6.3	4.1	0.1	1.0	7.6	1.1	1.2
	A5	14.7	17.3	5.7	3.4	0.1	1.0	7.5	1.0	1.2
	A6	15.9	9.5	2.9	2.3	0.1	0.8	6.0	0.6	0.8
	A7	18.4	23.6	8.8	5.6	0.1	0.9	3.2	1.4	1.5
	A8	21.9	22.9	7.8	4.9	0.0	1.1	2.2	1.5	1.6
	A9	23.7	23.2	7.7	4.3	0.0	1.1	2.1	2.3	1.7
	Min.		**9.5**	**2.9**	**2.3**	**0.0**	**0.8**	**2.1**	**0.6**	**0.8**
	Max.		**23.8**	**9.2**	**6.4**	**0.2**	**1.1**	**7.6**	**2.3**	**1.7**
Coum River	C1	0.0	24.0	9.6	5.3	0.1	0.8	1.5	1.2	1.6
	C2	4.1	27.7	8.5	3.9	0.1	0.6	2.5	2.2	1.9
	C3	9.2	21.0	7.1	4.5	0.1	1.2	3.9	1.4	1.5
	C4	12.8	22.8	7.1	4.0	0.1	0.9	3.4	1.7	1.6
	C5	14.6	23.5	7.8	4.2	0.1	0.9	2.9	1.6	1.6
	C6	15.8	23.5	7.7	4.2	0.0	1.0	2.2	1.5	1.8
	C7	17.4	22.4	7.2	4.6	0.1	1.2	2.7	1.5	1.7
	C8	19.8	21.5	7.7	5.3	0.1	0.9	2.9	1.4	1.5
	C9	23.5	22.3	7.8	5.7	0.1	1.2	2.2	1.7	1.6
	Min.		**21.0**	**7.1**	**3.9**	**0.0**	**0.6**	**1.5**	**1.2**	**1.5**
	Max.		**27.7**	**9.6**	**5.7**	**0.1**	**1.2**	**3.9**	**2.2**	**1.9**

Table A1.2 (Continued)

Station		Kilometric point (km)	Ti	P	PF	Total	CO2 total	Corg	S total
			Percentage (%)						
Adyar River	A1	0.0	0.5	0.1	18.5	100.7	6.6	1.4	0.1
	A2	3.0	0.4	0.1	23.8	99.8	18.1	3.6	0.6
	A3	6.6	0.6	0.1	15.7	99.9	10.5	2.4	0.5
	A4	12.0	0.4	0.2	20.2	98.9	18.6	2.6	0.4
	A5	14.7	0.3	0.3	30.0	98.9	36.5	7.3	0.8
	A6	15.9	0.2	0.9	55.8	98.9	94.3	14.6	1.1
	A7	18.4	0.4	0.1	13.5	99.5	7.9	1.6	0.2
	A8	21.9	0.4	0.2	18.1	98.9	17.1	4.4	1.9
	A9	23.7	0.4	0.1	18.0	99.4	14.9	3.6	1.6
	Min.		**0.2**	**0.1**	**13.5**	**98.9**	**6.6**	**1.4**	**0.1**
	Max.		**0.6**	**0.9**	**55.8**	**100.7**	**94.3**	**14.6**	**1.9**
Cooum River	C1	0.0	0.5	0.1	13.8	99.0	5.1	1.3	0.3
	C2	4.1	0.5	0.1	7.5	99.0	4.6	1.1	0.2
	C3	9.2	0.4	0.2	20.8	98.0	25.4	5.8	1.6
	C4	12.8	0.4	0.2	18.7	98.5	22.7	5.3	1.4
	C5	14.6	0.4	0.2	16.3	98.5	18.7	4.5	0.9
	C6	15.8	0.4	0.3	17.8	99.1	20.6	4.8	0.6
	C7	17.4	0.4	0.3	19.6	99.0	24.6	5.8	2.3
	C8	19.8	0.4	0.2	20.7	99.1	20.2	4.8	2.0
	C9	23.5	0.5	0.2	18.4	99.5	15.7	4.1	2.3
	Min.		**0.4**	**0.1**	**7.5**	**98.0**	**4.6**	**1.1**	**0.2**
	Max.		**0.5**	**0.3**	**20.8**	**99.5**	**25.4**	**5.8**	**2.3**

ANNEXURE B

LIST OF PUBLICATIONS

INTERNATIONAL JOURNALS

Saravanan, SP, Ambujam, NK, Grosbois, C, Saravanan, R, Manikandabharath, K, Rukkumany, RH & Desmet, M 2019, 'Spatial distribution of trace element into a fluvial urban system in Chennai, India', International Journal of Ecology and Development, vol. 34, issue 2, p.no 38-46.

Saravanan, SP, Desmet, M, Ambujam, NK, Saravanan, R, Shumskikh, N & Grosbois, C 2019, 'Geochemical footprint of megacities on river sediments: A case study of the fourth most populous megacity in India, Chennai', Minerals (under review)

Saravanan, SP, Desmet, M, Ambujam, NK, Saravanan, R & Grosbois, C 2019, 'Endocrine distruptor occurrence: Preliminary study for PAHs, PCBs, Phthalates and PBDEs', Sustainablity (under review)

CONFERENCE / SEMINAR/ WORKSHOP (INTERNATIONAL / NATIONAL)

Desmet, M, Grosbois, C, **Saravanan, SP,** Ambujam, NK, Saravanan, R & Nirmala, K 2018, 'What kind of tools can we use to outline the urban river pollution in an emerging megacity? Example of Chennai (Tamil Nadu, India)', 3rd International Conference Integrative science and sustainable development of rivers (I.S. RIVERS), (4 – 8 June 2018), **Lyon, France.**

Saravanan, SP, Ambujam, NK, Desmet, M & Grosbois, C 2017, 'Relationship between particle size and characterization of fluvial sediment in the urban river: case study of Chennai city', ICASEM 2017 (International Conference on Advances in Science, Engineering and Management), 30 – 31st March 2017, Organized by Jay Shriram Group of Institutions, **Tirupur, Tamil Nadu, India.**

Saravanan, SP, Ambujam, NK, Desmet, M, Grosbois, C, Thenmozhi, D, Nirmala, K & Manikandabharh, K 2017, 'What are the water science tools to outline the river quality of Chennai megacity?', Urban waters ARCUS workshop (15 – 18 February 2017), **Anna University, Chennai, India.**

Saravanan, SP, Desmet, M, Grosbois, C, Ambujam, NK, Thenmozhi, D, Nirmala, K & Manikandabharh, K 2017, 'Geochemical Pollution Index vs. Geochemical Urban Footprint Index: the case studies of large rivers in Chennai (India)', Urban waters ARCUS workshop (15 – 18 February 2017), **Anna University, Chennai, India.**

Saravanan, SP, Desmet, M, Grosbois, C, Ambujam, NK, Thenmozhi, D, Nirmala, K & Manikandabharh, K 2017, 'Geochemical composition of river sediments before and after the 2015 monsoon hazard in Chennai', Urban waters ARCUS workshop (15 – 18 February 2017), **Anna University, Chennai, India.**

Shumskikh, N, Viet V Ngo, **Saravanan, SP**, Grosbois, C, Ambujam NK & Desmet, M 2016, 'Mobility of trace metals between contaminated urban sediments and surface waters: an experimental study from 2 urban rivers in Chennai (India)', RST 2016: Reunion Sciences de la Terre (Earth Science). International Conference (24-28 October 2016), **Centre de Congres, Caen, France.**

Saravanan, SP, Desmet, M, Ambujam, NK, Thenmozhi, D, Manikandabharath, K, Rukkumany, RH & Grosbois, C 2015, 'Upstream – Downstream contamination gradient of fluvial urban system in Chennai, India', International conference on Water, Megacities and Global Change, (1 – 4 December 2015), **UNESCO HQ- Paris, France.**

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Spatial Distribution of Trace Element into a Fluvial Urban System in Chennai, India

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ABSTRACT

The present study was conducted to investigate the trace element contamination of urban river sediments of the Adyar and Cooum River, Chennai, Tamil Nadu, India. Both are the major source of urban irrigation and water supply system. An intensive sampling and analysis of bed sediments and flood deposits is done to find out the sources and transfer of trace elements across the river stream. The bed sediments and flood deposit samples were collected from 19 different stations along the course of both rivers using standard sampling methods and concentrations of multi trace elements were determined on the <63 µm fraction. Grain size analysis was performed on fresh bulk sediments using a laser diffraction microgranulometer Mastersizer 3000, Grain size analysis reveals that Adyar River and Cooum river consists of coarse sand, silt and clay. It is also found that the trace elements are linked with organic sediment matrix. Concentrations of total carbon (TC) content in the Adyar River range between 3.1% to 26.4% and 8.0 % to 27.2% in the Cooum River respectively. Trace element concentrations are asses with the geoaccumulation index (I_{geo}), results indicate that the river basin is moderately to extremely polluted. Especially Ag, Cd and Hg are present at alarming level and use as Urban tracer. This may be ascertained to the various pollutants discharge via diffuse urban and punctual industrial sources operating in and around the river bed. It was concluded that the sediment in the Adyar and Cooum rivers were severely polluted and should be monitored of different pollutants adversely affecting the environment.

keywords: Chennai, urban river, bed sediment, trace element, pollution index.

Mathematics Subject Classification: 92B05, 92E99

Journal of Economic Literature (JEL) Classification: Q52, Q53, R12

1. INTRODUCTION

Urban areas are extremely important for the development of social, economic and culture. Large towns and cities are disturbed from the natural landscape (Miguel et al. 2005; Khadse et al. 2008; Mohiuddin et al. 2011; Lyons and Harmon 2012). Fast developing cities are highly affected by multiple sources of contamination, the effects of which pollution overlap in space and time. Urbanization and industrialization puts deep and irreversible impact on our aquatic systems which are the life supporting tools of our generation, need to protect them is the need of the hour. It is therefore, very important to systematically study the status of river pollution in relation to various anthropogenic activities (Kaushik et al., 2009). Chennai's population density creates thrust on the drainage system and also woe to the treatment plant operations.

Geochemical footprint of megacities on river sediments: A case study of the fourth most populous area in India, Chennai

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ABSTRACT

This study presents the Geochemical Urban Footprint Index (GUFI) an index developed to determine the pollution status of any megacity river influenced by urban development. The GUFI was applied to the Adyar and Cooum Rivers, which are two important rivers among the six main waterways in the megacity of Chennai, Tamil Nadu, India, an area which has experienced extensive urbanisation over the last three decades. An intensive surface sediment survey was carried out over 24 locations from the upstream to downstream sections of the river during the February dry season of 2015. Concentrations of multi trace elements were determined on the <63 μm fraction. Trace element concentrations for Chennai megacity were assessed using the geoaccumulation index (I_{geo}) and the new GUFI. Sediment quality of Chennai was also compared to worldwide megacity pollution using sediment quality guidelines (SQGs) and a new megacity pollution ranking was determined. The I_{geo} results indicate that the Chennai rivers studied are strongly to extremely polluted regarding trace element concentrations of sediment. silver (Ag), cadmium (Cd) and mercury (Hg) are the most significant tracers of urban contamination. Chromium (Cr) concentrations show an industrial contamination gradient in relation to levels of other trace elements (As, Cu, Ni, Pb, Zn) at the Chennai megacity scale. The GUFI ranges from moderate to extreme contamination, particularly in the downstream stretches of the two rivers. This spatial trend is related to various point sources, identified at specific sampling stations and a lack of identifiable buffer zones. According to the worldwide comparison of megacity pollution, Chennai is ranked in fifth position. The present position can be attributed to a number of explanations: population explosion associated with unplanned growth of the city and non-controlled point sources of pollution in Chennai's waterways.

Keywords: *megacities; urban river; sediment; pollution; geochemical index*

Endocrine disruptor occurrence: Preliminary Study for PAHs, PCBs, Phthalates and PBDEs

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ABSTRACT

Endocrine disruptor occurrence of, thirteen individual Polycyclic Aromatic Hydrocarbons (PAHs) in the list of US Environmental Protection Agency (EPA) priority pollutants, seven PCBs, six Phthalates and five PBDEs were analyzed in surface sediment samples (0 – 15 cm) collected from eighteen stations in the two main urban rivers (Adyar and Cooum river) during dry session of February 2015 in Chennai megacity, Tamil Nadu, India to investigate the levels of concentration, possible sources and ecological risk. Results indicated that the concentrations of PAHs in the sediments varied greatly across the rivers. The sediment concentration of Σ_{13}PAHs ranged from 0.136 to 2.032 mg/kg in Adyar river and 0.471 to 3.753 mg/kg in Cooum river. The higher concentration Σ_{13}PAHs are sited in the downstream station (A6 to A8 in Adyar river and C4 to C9 in Cooum river). Also, the total concentrations of Σ_{13} PAH in sediment samples are greater in Cooum river than in the Adyar river. Higher molecular weight of PAHs (4-6 rings) were predominant in the sediment sample than the Lower molecular weight of PAHs (3 rings). Considering the different diagnostic ratios of PAHs, such as FLA/(FLA+PYR)), (ANT/(ANT+PHE)), (BaA/(BaA+CHR)) and (IcdP/(IcdP+ BghiP)) and the principal component analysis results, the sediments were likely attributed to mixed pyrogenic sources (vehicular emission and grass, wood and coal combustion). Similarly, in this study clearly indicates that polychlorinated biphenyls (PCBs) and phthalates concentration in sediments are very low values or below the detection limits in the international standards except PCB 101 and phthalates (DiNP and DBP). Also, PBDEs concentrations are not detected in anywhere of the Chennai megacity river sediment samples.

Keywords: *Endocrine disruptor; sediment; source identification; diagnostic ratios; hazard levels*

What kind of tools can we use to outline the urban river pollution in an emerging megacity? Example of Chennai (Tamil Nadu, India)

De quels outils dispose-t-on pour caractériser la pollution d'un fleuve urbain dans une mégapole émergente? Exemple de la ville de Chennai (Tamil Nadu, Inde)

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RÉSUMÉ

Deux fleuves côtiers, Cooum et Adyar, drainent la mégapole de Chennai (Tamil Nadu, Inde, 12 millions d'habitants). Ils reçoivent à la fois les eaux usées non traitées, celles des stations d'épuration après traitement, des égouts issus de différentes infrastructures de la ville et du lessivage de chaussées. Des sédiments de fond ont été échantillonnés dans ce gradient urbain sur une distance de plusieurs kilomètres depuis la zone amont semi-rurale jusqu'à la zone estuarienne à travers la zone la plus urbanisée de Chennai. Les concentrations en éléments majeurs ont été analysées tout comme plusieurs paramètres sédimentologiques. Un nouvel indice géochimique urbain est proposé pour expliciter ce développement urbain et industriel, bien souvent anarchique. Les variations spatiales des concentrations d'éléments tels que l'argent, le chrome, le cadmium sont des traceurs représentatifs de ce gradient de contamination d'origine urbaine. De plus, une mousson centennale a eu lieu en Décembre 2015. Le réseau de la Cooum a complétement été inondé et celui de l'Adyar a vu son niveau augmenter à plein bord à cause des lâchers depuis le réservoir principal situé en amont. La comparaison des concentrations dans les sédiments de 2015 et 2016 permet de mieux identifier les facteurs contrôlant ce gradient longitudinal de contamination urbaine

ABSTRACT

Two main rivers, Cooum and Adyar rivers, drain the growing megacity area of Chennai (Tamil Nadu, India; 12 million inhabitants). These rivers are discharging sewage, waste water and runoff water conveyors and several smaller outputs of untreated waters. Bed sediments of both urban rivers were collected in a urban gradient over a distance of several kilometers from semi-rural upstream location to the mouth of the rivers and crossing the most urbanized part of the city (major and trace elements, grain size and sedimentological preliminary measurement were detected). A new proposed Grosbois/Geochemical Urban Footprint Index is triggered by the development of non-planned urbanization and urban industry. Silver, chromium, cadmium, mercury are the most significant tracers of an urban contamination gradient at the Chennai megacity scale. Samples were collected in 2015 and 2016 during the dry season. However, unusual centennial intense monsoon in December 2015 provided huge flood events in Chennai. The Cooum urban basin was completely overflooded and water level of the Adyar river increased due to high discharge of the major upstream reservoir. The comparison between the 2 sediment surveys made it possible to identify main factors controlling the longitudinal gradient of contamination.

MOTS CLES

Pollution, fleuves urbains, mégapoles, empreinte géochimique – pollution, urban waters, megacities, geochemical footprint

Relationship Between Particle Size and Characterization of Fluvial Sediment in The Urban River: Case Study of Chennai City

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Abstract:

In this study, an attempt is made to relationship between particle size and fluvial sediment in the urban river. which are the important rivers (Adyar and Cooum) in Chennai, Tamil Nadu, India. The study area is the most conspicuous relief of the ferricrete surfaces regolith is derived from charnockite bedrock formed due to more or less fragmental decomposed matter drifted by wind, water or other source of erosion. Almost the entire area is covered by Pleistocene/ Recent alluvium, deposited by the two rivers. An intensive sampling and analysis of bed sediments and flood deposits is done to find out the sources and transfer of trace elements across the river stream. The prime aim of this study is to establish an upstream-downstream characterization of the fluvial system. The bed sediments and flood deposit samples were collected from 21 different stations along the course of both rivers using standard sampling methods and concentrations of multi trace elements were determined on the <63 µm fraction. Grain size analysis was performed on fresh bulk sediments using a laser diffraction microgranulometer Mastersizer 3000, Malvern after been sieved by <2000 µm. H_2O_2 treatment was also applied to bulk sediments in order to determine detrital fraction. The detrital fraction of sampled sediments in the Adyar River are generally coarse sand, with sand content ranging from 32 % to 86 % with an average sand content as 71.29 %. The finest fractions are not really important (silt content up to 22 % and the clay content ranging from 0.7 % to 47%) although these fractions are usually highly concentrated in trace elements. Similarly, for Cooum River, sand content varied from 23 % to 83 % (silt content up to 31 % and the clay content up to 51%). For both rivers, any upstream to downstream gradient could be evidenced although several specific samples were particularly clayey. Therefore, the sampling was considered as random and no trace element signal trend should be attributed to a texture variation of the sediment deposits. This may be ascertained to the various pollutants discharge via diffuse urban and punctual industrial sources operating in and around the river bed.

Keywords: *urban river, sediment, fluvial system, particle size, gradient*



S.P. Saravanan
Research Scholar, Anna University, Chennai & University of Tours, France

Title : What are the water science tools to outline the river quality of Chennai megacity?

Abstract : Two main rivers, Cooum and Adyar rivers drain the growing megacity area of Chennai (10 million inhabitants). These rivers are discharging sewage, waste water and runoff water conveyors and several smaller outputs of untreated waters. In 2015 and in 2016, two bed sediment surveys were carried out, aiming to reconstruct the upstream to downstream quality of the waterbodies. Major and trace element composition and associated geochemical indexes were one of the used tools to compare Chennai river quality to other megacities, either in India and all over the world.

Title: Geochemical composition of river sediments before and after the 2015 monsoon hazard in Chennai

Abstract : Unusually intense monsoon in December 2015 triggered huge flood events in Chennai. The Cooum urban basin was completely overflooded and water level of the Adyar river increased due to high discharge of the major upstream reservoir. The February 2016 sediment survey was compared to the previous survey in February 2015. In order to quantify the potential influence of such a natural event on the contamination gradient, two main questions were investigated: (i) how will urban tracer levels, calculated by the Geochemical Urban Footprint Index (GUFI) evolve at the megacity scale? (ii) What are the main factors controlling the longitudinal gradient of contamination ?

Title : Geochemical Pollution Index vs. Geochemical Urban Footprint Index : the case studies of large rivers in Chennai (India)

Abstract : Bed sediments of both urban rivers (Coum and Adyar) of the Chennai megacity were collected in 2015 and 2016 during the dry season. Over a distance of several kilometers from semi-rural upstream location to the mouth of the rivers and crossing the most urbanized part of the city, the collected samples were analyzed (major & trace elements, organic compounds, grain size and sedimentological preliminary measurement). A new proposed Geochemical Urban Footprint Index is triggered by the development of non-planned urbanization and urban industry. Silver, Cadmium, Mercury and PAH are the most significant tracers of the megacity of Chennai.

Sédiments urbains ***Urban sediments***	Chairmen : Jérémy JACOB (ISTO Orléans), Marc DESMET (GéHCO - Tours)
Le milieu urbain se singularise par la nature des matières qui y sont produites, transportées, et sédimentées. Les teneurs et rapports élémentaires, isotopiques, moléculaires qui y sont mesurés sont significativement distincts de ceux qui prévalent dans les milieux sentinels. Cette session est dédiée à la sédimentologie urbaine et aux matériaux accumulés dans les hydrosystèmes urbains (lacs naturels ou artificiels, fleuves et rivières, canaux, fosses, réseaux d'assainissement) au cours de périodes et sur des durées variées. Les champs disciplinaires ciblés sont variés et peuvent concerner les études liées à la gestion des sédiments urbains, à leur dynamique et mode de mise en place, à la caractérisation (sédimentologie, géochimie, datation), ou à leur potentiel d'archivage environnemental.	

UPSTREAM - DOWNSTREAM CONTAMINATION GRADIENT OF THE FLUVIAL URBAN SYSTEM IN CHENNAI, INDIA

Saravanan S.P. [1 2], *Desmet. M.* [3], *Ambujam N.K.* [4], *Thenmozhi D.* [5], *Manikandabharath K.*[6], *Rukkumany R.H.b, Grosbois. C*[7].

KEYWORDS

Chennai, urban river, bed sediment, trace element, pollution index, geochemical urban tracers.

ABSTRACT

In this study, an attempt is made to ascertain the present pollution status of the Adyar and Cooum River, which are the important rivers in Chennai, Tamil Nadu, India. Both are the major source of urban irrigation and water supply system. An intensive sampling and analysis of bed sediments and flood deposits is done to find out the sources and transfer of trace elements across the river stream. The prime aim of this study is to (i) establish an upstream-downstream characterization of the fluvial system, (ii) identify potential industrial and urban sources of incoming pollution, (iii) correlate the state of sediment contamination to the industrial, waste areas and urban planning. The bed sediments and flood deposit samples were collected from 21 different stations along the course of both rivers using standard sampling methods and concentrations of multi trace elements were determined on the <63 µm fraction. The geoaccumulation index (Igeo) results indicate that the river basin is moderately to extremely polluted. Especially Ag, Cd and Hg are present at alarming level and used as urban tracers. This may be ascertained to the various pollutants discharge via diffuse urban and punctual industrial sources operating in and around the river bed.

INTRODUCTION

Urban areas are extremely important for the development of social, economic and culture. Large towns and cities are disturbed from the natural landscape (Berry and Russell, 2012). Rapid urbanization and industrial development during last decades have provoked some serious concerns in waterbodies. Trace element contamination of rivers is one of the major quality issues in many fast developing cities, which are highly affected by multiple sources of contamination over the last decades. Most of the urban population in India still depends on the river water source for their day to day consumption purpose. It is therefore, very important to systematically study the status of river pollution in relation to various anthropogenic activities (Kaushik et al., 2009). Chennai's population density creates thrust on the drainage system and also woe to the treatment plant operations.

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Saravanan SUKKAMPATTI PALANISAMY

Empreinte géochimique urbaine dans la mégapôle de Chennai sur les sédiments de rivière : gradient amon-aval, sources et résilience

Geochemical urban footprint of Chennai megacity onto river sediment: upstream – downstream gradient, sources and resilience

Résumé

Dans cette étude, l'état **actuel de la pollution des rivières Adyar et Cooum**, a été déterminé. Ce sont les deux rivières importantes parmi les six voies navigables principales de la mégapole de Chennai (Tamil Nadu, Inde) qui a connu une urbanisation importante au cours des trois dernières décennies. Cette étude vise trois objectifs principaux: (i) **empreinte géochimique de la mégapole** sur les sédiments des rivières (ii) **apparition de perturbateurs endocriniens**: étude préliminaire sur les HAP, les PBDE, les PCB et les phtalates (iii) **Influence du risque de mousson de 2015** sur le niveau de pollution par les oligo-éléments de 2 principaux cours d'eau.

Mots clés : *mégapole; riviére urbaine; sédiments; pollution; index géochimique; sources et résilience; perturbateurs endocriniens.*

Abstract

In this study, an attempt is made to ascertain the **present pollution status of Adyar and Cooum River**, which are the two important rivers among the six main waterways in the Chennai Megacity, Tamil Nadu, India and greatly influenced by urbanisation in the past three decades. This study is designed 3 main objectives (i) **Geochemical footprint of megacity** onto river sediments (ii) **Endocrine disruptor occurrence:** Preliminary study for PAHs, PBDEs, PCBs and Phthalates (iii) **Influence of 2015 monsoon hazard** onto trace element pollution level of 2 main rivers.

Keywords : *megacities; urban river; sediment; pollution; geochemical index; sources and resilience; endocrine disruptor*.