Contemporary Contamination of Urban Floodplains in Chennai (India)

Luisa Bellanova · Fabienne Uphoff · Piero Bellanova · Nina Engels · Prabu P. · Yaswanth Pulipatti · Frank Lehmkuhl · Phillip Schulte · Klaus Reicherter · Jan Schwarzbauer

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Abstract Fast growing coastal population centers face an increasing vulnerability to several emission sources of anthropogenic and industrial pollutants. The ongoing industrialization in emerging countries increases the environmental and human risk for people living in coastal megacities, especially in the global south of Asia. Extreme weather events, such as heavy rainfalls and resulting flood events, are projected to increase in frequency in the foreseen future, facing an increasing vulnerability to monsoon-induced floods and the release and distribution of xenobiotics causing harm to communities and the environment along a river’s pathway. To endeavor the unknown risks posed by these toxic floods and to assess the associated contamination distribution, the preserved organic geochemical signature from floodplain sediments is studied.

This investigation evaluates the inorganic and organic pollutant assemblage in ten surface sediments along the Adyar and Cooum river in the urban areas of Chennai (southern India). Potentially toxic elements (Cr, Ni, Cu, Zn, Pb) show a continuous concentration decrease downstream. Four main groups of persistent organic pollutants have been detected: petrogenic pollutants (hopanes, PAHs), urban wastewater pollutants (LABs, DEHA, methyl-triclosan, octocrylene), technical compounds (Mesamoll®, DPE, NBFA), and pesticides (DDX). While most organic compounds show source specific properties, the definite sources for others remain vague based on the multitude of potential sources and diffusiveness of anthropogenic emissions. The chosen approaches have shown that urban wastewater pollutants and several technical compounds are suitable to assess the anthropogenic-induced contamination in floodplain sediments. However, sedimentary archives in fast-growing, urbanized environments are influenced and superimposed by anthropogenic alterations.

Keywords Anthropogenic contamination · Urban rivers · Contamination distribution · Pollution assessment · Toxic flood
1 Introduction

Regarding climate change, low-lying, populous coastal areas experience an increased proneness and vulnerability to floods, sea level rise, or cyclones (Mishra et al., 2015). Coastal areas experience a disproportional increase in population density, culminating to the projection that about 1.4 billion people could live in low-lying coastal zones by 2060 (McGranahan et al., 2007; Vafeidis et al., 2019). Most of the coastal population lives in megacities along estuaries despite environmental challenges enforced by overpopulation (e.g., water shortages, air pollution) coupled climate change effects, such as increased droughts, heavy rainfalls with subsequent flooding, and sea level rise. Coinciding with an increasing economic prosperity are societal and environmental disparities, such as uncontrolled urban growth and associated environmental contamination, which are known from India’s largest cities (i.e., New Delhi, Chennai; Istomina et al., 2005; Mohapatra & Singh, 2003). The pollution associated with a rapidly growing population and industrialization in emerging countries within the twentieth century (Saravanan et al., 2019) affects the ecosystems directly and indirectly by inadequate waste disposals (Mishra et al., 2015), lack of regulations, but also via remobilization of sediment-bounded contaminants (e.g., pharmaceuticals, pesticides, potentially toxic elements; Lammel et al., 2018; Rivetti et al., 2015).

For the current population, insufficient and unmaintained drainage systems together with higher anthropogenically induced sediment rates (e.g., soil erosion, deforestation, agricultural land use) favor urban flooding. Additionally, a poor water, sewage, and waste disposal management increases the general water and soil pollution of Chennai’s rivers (Dhiman et al., 2018; Gupta & Nair, 2010). Associated with flood sediments is a certain (toxic) anthropogenic contamination as it was described for past flash floods and the 2004 tsunami affecting Indian’s coastlines (e.g., Kume et al., 2009; Saravanan et al., 2019; Srinivasalu et al., 2007; Sujatha et al., 2008). This observation implies that even once the short-term and destructive flood event has passed a hazard potential, it remains as contaminated water, and soils accumulate on the floodplains. Various metabolites, xenobiotics, and other (toxic) chemical compounds can persist in the soil for long periods of time, allowing the reconstruction of the recent contamination and the assessment of the remaining hazard potential for human health and the environment.

Most existing case studies from river floods and floodplain sediments across India focus on heavy metal or potentially toxic element contamination, methane effluxes, and water quality (e.g., Haloi & Sarma, 2012; Kumar et al., 2019; Meena et al., 2011; Raja et al., 2019; Singh et al., 2002; Srinivasalu et al., 2007), or on the general impacts and consequences of contaminants to water bodies (e.g., Blöschl et al., 2019; Hilscherova et al., 2007; Ramachandran et al., 2019; Suriya & Mudgal, 2012; Venugopal et al., 2009). Studies investigating the organic contamination distribution and long-term effects of pollutants linked to anthropogenic action and impacts are lacking; thus, the hazardous potential remains underestimated. The 2015 Chennai flood, claiming thousands of lives and causing damages to properties and infrastructure (Lavanya, 2012; Ramachandran et al., 2019), highlights the vulnerability and scientific relevance to gain a better understanding of these toxic floods. For a better awareness of the mechanisms during floods, such as the release, transport, distribution, and longevity of harmful contaminants, it is necessary to study riverine sediments from a (geo-)chemical perspective.

Based on a multi-proxy approach, this study aims to identify the contemporary surface contamination of Chennai’s main river systems (Adyar and Cooum rivers) combined with the distribution of persistent organic pollutants to achieve a better understanding of contamination pathways during flooding events, which helps to lower future pollution. For this purpose, potential contamination sources are detected and connected to the complex morphodynamical distribution and accumulation mechanisms.

2 Materials and Methods

2.1 Study Area

Chennai, located in the north of Tamil Nadu (India) on the Coromandel Coast of the Bay of Bengal (Fig. 1A), features a tropical monsoon climate (mean annual temperature 29 °C) and an annual precipitation of 1200 to 1400 mm with heavy monsoonal rainfalls from October to December (Gowri
et al., 2008; Ramachandran et al., 2019; Fig. 1A). Chennai is characterized by two major river systems, the 42-km-long Adyar river and 65-km-long Cooum river (Fig. 1B), which both act as Chennai’s main drainage system (Dhiman et al., 2018). The approx. 800-km-long coastline parallel running Buckingham canal intersects the two rivers (Shankar et al., 2018).

During the dry summer months (May–July), the reservoirs dams remain closed resulting in a mostly stagnant river waterbody, partly dried-up sections, and clogged river mouths (Raja et al., 2019; Rajkumar et al., 2008). To avoid long-term clogging and to cleanse the rivers, the estuaries are artificially opened on a regular basis during the heavy monsoon rainfalls.

2.2 Sampling

The field survey took place in June and July 2019. This period was deliberately chosen to find the highest possible concentrations and accumulations of organic pollutants in the sediments. However, it coincided with one of the longest droughts and increased water scarcities in the city’s history. During the field survey, rivers and canals in Chennai are virtually stagnant, lakes have dried up, and almost no fresh water reached the catchment areas (Ramesh et al., 2002). Only urban and industrial sewage feed the rivers. At several locations along both rivers (Fig. 1B), sediments of the floodplains were collected with a handheld Geoslicer (Nakata & Shimazaki, 1997). During the fieldwork, temperatures reached a maximum of

Fig. 1 Overview of the study area. (A) NE and SW monsoon drifts over the Indian subcontinent. (B) overview of Chennai metropolitan area with sampling locations, land use, and water ways.
45 °C, and no rainfall occurred. Measures were taken to avoid contamination or microbial alterations (e.g., use of pre-cleaned tools, avoidance of plastic containers, short-term (4 °C) and long-term refrigerated storage at −20 °C).

2.3 Total Organic Carbon Analysis

Total organic carbon (TOC) measurement is performed using a LiquiTOC II device (Elementar Liqui TOC, Elementar Co., Germany). Aliquots of 100 mg dried (30 °C) and ground material per sample are measured for TOC (550 °C) and for TIC (1000 °C). All measurements have been conducted twice for statistical robustness.

2.4 Grain Size and X-Ray Fluorescence Analysis

For grain size analysis, samples were dried at 30 °C and sieved (2 mm). Organic matter was removed using H₂O₂ (30%) (after Allen & Thornley, 2004; Schulte & Lehmkuhl, 2018). To avoid agglutination of (clay) particles, 1.25 mL Na₄P₂O₇ were added, and the samples were treated in an overhead shaker for 12 h (Pye & Blott, 2004). The grain size analysis was performed via a Laser Diffraction Particle Size Analyzer (Beckman Coulter LS 13 320; Beckman Coulter GmbH, Germany; Schulte & Lehmkuhl, 2018). Grain size statistics are calculated using the GRADISTAT software (V9, Blott & Pye, 2001) based on Folk and Ward (1957).

For XRF elemental analysis, samples are dried (30 °C), sieved (<63 µm), and pellets of ca. 8 g material and 2 g wax (FLUXANA CEREOX Lico-wax) were pressed. Measurements were performed on a Spectro Xeps XRF device (Spectro Analytical Instruments GmbH, Germany). Each sample was measured twice with a 90° rotation (Nottebaum et al., 2020).

2.5 Sample Extraction and Treatment

Organic compounds were extracted from the sediment using solid–liquid extraction with different organic solvents after Franke et al. (1998). Aliquots of 10 g wet sample material were extracted with a high-speed dispersion tool (Ultra-Turrax®) at 16,000 rpm. Different mixtures of acetone and n-hexane were added for the each 3-min extraction step: (I) 30 mL acetone, (II and III) 30 mL acetone/n-hexane (50:50), and (IV and V) 30 mL n-hexane. After each dispersion, extracts were separated by centrifugation and combined in a separatory funnel. Through volume reduction via rotary evaporation (300 mbar) and a surplus of n-hexane, the aqueous phase was separated from the extract. Afterwards, the extract was dried over anhydrous granulated Na₂SO₄ and desulphurized using copper powder activated with hydrochloric acid through sonication (Bellantova et al., 2020).

Sediment extracts were separated into six fractions by column chromatography (Franke et al., 1998). Each column with 2 g silica gel (Baker, 40 µm) was activated at 200 °C. Different mixtures of n-pentane, dichloromethane (DCM), and methanol (MeOH) were used as eluents (Franke et al., 1995; Schwarzbauer et al., 2000). Fractions B1 to B5 were spiked with 50 µL internal surrogate standard (5.8 ng/µL fluoracetophenone, 6.28 ng/L d₁₀-benzophenone, and 6.03 ng/µL d₃₄-hexadecane) and evaporated to a volume of 50 µL.

2.6 GC–MS Analysis

The subsequent gas chromatography-mass spectrometry (GC–MS) analyses were performed on a quadrupole Trace MS mass spectrometer (Thermo Finnigan, Germany) connected to a Mega Series HRGC 5160 gas chromatograph (Thermo Finnigan, Germany), supplied with a ZB-5 fused silica capillary column (Phenomenex, Aschaffenburg, Germany, 30 mÅ~0.25-mm ID Å~0.25-µm film thickness) and helium as carrier gas (velocity 30 cm/s). A temperature program ranging from 60 to 310 °C with a heating rate of 3 °C per minute was used for the measurement. The initial temperature of 60 °C was held for 3 min, and 310 °C was retained for 20 min. The MS was operated in a full-scan mode (EL⁺, 70 eV), detecting m/z from 50 to 650. For injection, 1 µL of each sample fraction was injected at an injector temperature of 270 °C and a splitless time of 60 s. Compound identification was accomplished by mass spectral comparison with standard reference materials and the NIST MS database (National Institute of Standards and Technology—US Department of Commerce).
2.7 Quality Control (QA/QC)

While established quality control measures (duplicate samples, blanks, reference material) result in negligible analytical inaccuracies and the determination of the detection limits, it must be considered that natural variations on small spatial scales (e.g., TOC content and grain size) across a specific sampling location can lead to alterations in concentration of pollutants. To reduce adverse effects, bulk samples of larger samples have been homogenized before extraction and normalized to TOC content.

3 Results and Interpretation

3.1 Grain Size and Potentially Toxic Elements

Floodplain sediments of both rivers (Fig. 1B) reveal a great variation in grain size distribution ranging from very coarse silt to very coarse sand (Table A1). Few sediments also contained pebbles, anthropogenic rubble, and shell hash. While the upstream sections of the Adyar and Cooum river (AD8; CO5) are dominated by silty to fine sands (Table A1), the sediment downstream are composed of increasing grain sizes (Table A1) and experience ultimately marine influences (e.g., shell hash) in the estuary (AD2; CO1).

For potentially toxic element contamination assessment of the floodplains, five trace metals have been selected: Cr, Cu, Ni, Zn, and Pb. All elements are known to originate from industrial activities and are well-suited to determine the environmental pollution (Dhamodharan et al., 2019; Veerasingam et al., 2014). Chromium (Cr) is a frequent pollutant in effluent discharges of the automobile industry, and copper (Cu) is attributed to the electroplating industries (Tanner & Leong, 2000). The presence of nickel (Ni) in the Adyar estuary has been correlated by Veerasingam et al. (2014) to petroleum-related activities and the combustion of fossil fuels. Zinc (Zn) is known for its usage in liquid manure and agrochemical industries (Mantovi et al., 2003; Romic & Romic, 2003). Lead (Pb) contamination is ubiquitously distributed due to the aerial deposition from urban environments and its long-distance atmospheric transport (Veerasingam et al., 2014). Lead and zinc are also well-known pollutants in Chennai’s rivers to originate from the paint industries (Raj & Jayaprakash, 2008).

The heavy metal distribution within the sediments shows a general concentration decrease downstream, except for CO6 (Fig. 2). This implies that heavy metal emission sources can be correlated to the industry in Chennai’s inland located urban outskirts. This is supported by observations of Veerasingam et al. (2014). The downstream decrease can be connected to the heavy metal’s sediment-association properties and the lower amount of fine-grained sediments in the estuaries (AD7, AD2, CO1). The observation of a downstream decrease in heavy metal contamination (Fig. 2) favors the hypothesis of a washing-out and dilution effect by monsoonal floods. Therefore, a likely pollutant sink is the continental shelf. However, analyses on the continental shelf (e.g., Nisha & Achyuthan, 2014; Veerasingam et al., 2014) report relatively low heavy metal concentration, which might hint towards the ocean’s dilution potential.

To further assess the environmental contamination and to determine the distribution of persistent organic pollutants, four major compound groups are analyzed in detail: (1) petrogenic and pyrogenic contamination indicators, (2) urban wastewater contamination indicators, (3) technical compounds, and (4) pesticides.

3.2 Petrogenic and Pyrogenic Contamination Indicators

Hopanes and polycyclic aromatic hydrocarbons (PAHs) are well-studied organic indicators frequently applied to assess petrogenic contamination and corresponding emission sources (Goswami et al., 2016; Samelak et al., 2018; Schwarzbauer et al., 2000). Here, the homologue series of $C_{29-35}$ hopanes stereoisomers, $18\alpha$-trisnorneohopane (Ts), and $17\alpha$-trisnorhopane (Tm) have been analyzed (Table A2). Total hopane concentrations range between 2600 and 105,000 ng/g TOC with peak concentrations in CO1 (Fig. 3A). Potential sources range from oil spills (e.g., 2017 Ennore oil spill; Han et al., 2018) to oiling of river systems in the present and past (Watson, 1921). The occurrence of oil in Chennai’s river systems is supported by the predominance of $\alpha,\beta$-hopanes, which indicate petrogenic material of higher maturity, such as crude oil or petroleum products (Nytoft & Bojesen-Koefoed, 2001). For further source classification, two ratios have been analyzed: $\text{Ts}/(\text{Ts} + \text{Tm})$ and $22\text{S}/(22\text{S} + 22\text{R})$ of the $C_{31}$ homohopanes (Fig. 3B). Values of all samples for
Ts/(Ts + Tm) range between 0.30 and 0.68 and for the 22S/(22S + 22R) ratio between 0.52 and 0.64 pointing to mature organic material and therefore indicating fossil matter (Fig. 3B). Within surface sediments of riverine floodplains oil generation and a natural reaching of the equilibrium cannot be expected, but these ratios implicate the release and distribution of petrogenic pollutants.

Aside hopanes, the ∑EPA16 PAHs, originating from different natural and anthropogenic pyrogenic, petrogenic, and diagenetic sources (Goswami et al., 2016; Sanders et al., 2002) are identified. Related to their lipophilic and semi-volatile properties, PAHs undergo long-range transports in the atmosphere (Balmer et al., 2019) and are known to accumulate in river sediments (Abdel-Shafy & Mansour, 2016; Alves et al., 2011; González-Pérez et al., 2014). High levels of PAHs (average 604,500 ng/gTOC; Table A2) were identified in all surface sediments (Fig. 3A), with the highest concentrations in CO2 and AD7 (1,700,000 and 1,560,000 ng/gTOC) and lowest concentrations in AD2 and CO6 (34,000 and 29,600 ng/gTOC). The detected concentrations are significantly higher than in previous studies of Chennai (e.g., Goswami et al., 2016; Rajan et al., 2019) and other rivers in India (e.g., Agarwal et al., 2006; Tripathi et al., 2006).

Fig. 2 Contemporary surface pollution by heavy metals (Pb, Zn, Cu, Ni, Cr; in mg/kg) for Cooum and Adyar river.
2009 or Dhananjayan et al., 2012). High concentrations in CO2 and AD7 can be explained by uncontrolled incineration of waste on the floodplains and the inlet of the Buckingham Canal further upstream. AD10, located close to Chennai’s airport, has unexpectedly low concentrations (55,500 ng/gTOC) caused by the Nandambakkam check dam (ca. 100 m upstream of AD10), acting as a sediment trap and subsequently a sediment-associated pollutant trap. The same observations of a sediment trap can be seen for CO5 (58,000 ng/gTOC), where canalized bridge piers cause a similar accumulation. Overall lowest concentrations in AD2 and CO6 are linked to the lack of direct emission sources and a generally more natural environment.

To differentiate between pyrogenic and petrogenic emission sources, different diagnostic ratios are applied: An/(An + Phe); Fl/(Fl + Pyr); Phe/An (Fig. 3C; e.g., Sanders et al., 2002; Yunker et al., 2002). PAHs in all surface samples originate predominantly from pyrogenic sources (Fig. 3C) of assorted incomplete petrogenic and pyrogenic combustion (petroleum, petroleum products, coal, wood). The pyrogenic origin as principal emission source is supported by the high density of motorized vehicles and industry (Shanmugam et al., 2007). As Chennai is known for its bad air quality and atmospheric pollution (Krishnan et al., 2019), overall PAH concentrations are linked to predominantly pyrogenic input. However, specific (point) sources of PAHs remain vague, and PAHs rather reflect the general atmospheric contamination.

### 3.3 Urban Wastewater Contamination Indicators

Linear alkylbenzenes (LABs) are known as environmental pollutants released through municipal, industrial, and domestic wastewater (Eganhouse, 1986; Takada et al., 1990). They tend to accumulate in sediments due to their enhanced lipophilicity and high environmental stability. Based on their persistent properties (e.g., Heim et al., 2004), they are a well-suited anthropogenic marker for household effluents and municipal sewage discharge (Eganhouse, 1986).

LABs have been detected in all analyzed samples (Fig. 4) with concentrations ranging between 1900 ng/gTOC in CO6 and 7,700,000 ng/gTOC in AD8. Elevated concentrations in AD7 (114,000 ng/gTOC) are supported by field observations of untreated municipal wastewater discharging into the Adyar by the upstream located Buckingham canal.

Furthermore, microbial degradation of LABs can be indicated by changes in the isomeric composition (e.g., Alkhadher et al., 2020; Eganhouse et al., 2000; Heim et al., 2004). Therefore, the internal to external isomer ratio (I/E-ratio) is considered. I/E-ratio values of 0.7 indicate untreated wastewater, while higher values illustrate progressive degrees of degradation (Takada & Eganhouse, 1998; Takada et al., 1997). The ratios determined show degraded LAB compositions (0.51–1.02; Table A2), thus supporting the observation of the presence of raw, relatively untreated, or only primarily treated wastewater affecting the floodplains.

Hexanedioc acid 2-ethylhexylester (DEHA), an additive in soaps and washing agents, has been detected in all surface sediments of the Adyar river (10–710 ng/gTOC) but not in the Cooum river (Fig. 4). DEHA concentrations are significantly lower than those of LABs, caused by the water insolubility of DEHA (logKOW = 6.3; WHO, 2004). Highest concentrations in AD2 coincide with observations for LABs and are further supported by the presence of a hospital and dense urban area discharging effluents directly into the Adyar river near the AD2 sampling location.

Methyl-triclosan, a persistent metabolite of triclosan (Coogan et al., 2007), originates either from biomethylation of triclosan during wastewater treatment processes (e.g., Bester, 2003; Halden & Paull, 2005; Singer et al., 2002; Waltman et al., 2006) or from natural biomethylation of untreated wastewater in aquatic systems (e.g., Balmer et al., 2004; Lindström et al., 2002). Despite its high persistence, methyl-triclosan has only been detected in low concentrations (n.d.–65 ng/gTOC; Table A1). This is related to the rather coarse sediment type with low contents of organic material, where preferred (bio-) accumulation takes place.

As a last wastewater indicator, the UV-absorber octocrylene was detected in all surface sediments, entering the environment through direct input (e.g., leisure activities) or through the discharge of untreated wastewater (cosmetic products; Amine et al., 2012; de Groot & Roberts, 2014; Rodríguez et al., 2015). Concentrations range between 5 and 3400 ng/gTOC in the floodplain sediments with peak concentrations in CO2 (Fig. 4; Table A1).
All urban wastewater proxies analyzed in this study reflect the contamination impact by the densely populated districts, both rivers pass. The predominance of LABs indicates a widespread release of untreated effluents into the environment. The quantified contamination by DEHA, methyl-triclosan, and octocrylene supports the evidence of significant urban wastewater contamination in Chennai’s major river systems.

3.4 Technical Compounds

Mesamoll®, an alkylsulfonic acid phenyl ester known for ca. 65 years (Haslam et al., 1951), can be related to anthropogenic industrial pollution (plasticizer in PVC, polymers, nitrocellulose lacquers; Franke et al., 1998). Mesamoll® has been identified in all surface samples (Fig. 5) with peak concentrations in AD8 and CO1 (17,600 and 16,600 ng/gTOC). The downstream accumulation of Mesamoll® along the Cooum river correlates with the increasing number of tributaries, draining Chennai’s industrial areas (Fig. 1B). The highest concentration was detected in AD8, which is related to a local point source of a large uncontrolled waste dump site close to the sampling location.

1,2-Diphenoxyethane (DPE), originating from untreated wastewater of the paper and pulp industry, has been identified (Dzikowiczky et al., 2015; Latorre et al., 2005; Munkittrick et al., 2013). Industrial contamination is known to contribute significantly to water and soil pollution of Chennai’s main river systems, which is reflected by the detection of DPE. Except for AD8 (Fig. 5), DPE has been detected in all samples, with concentrations ranging between 60 and 4100 ng/gTOC and peak concentrations in the Adyar estuary (AD2).

N-Benzylformamide (NBFA), used as a synthetic intermediate (Martinez et al., 2005), has been identified in all surface sediment samples except for AD8. However, this compound’s environmental behavior and effects are virtually unstudied. Concentrations in the floodplain sediments range between 15 and 6100 ng/gTOC with a peak contamination in AD2 (Fig. 5). The wide distribution along the rivers implies the technical application and subsequent environmental release of NBFA or synthetized products in which NBFA acts as a chemical intermediate. NBFA is also known in the synthesis of antitubercular agents (Martinez et al., 2005). As India has experienced a wide distribution of tuberculosis in the past (Khatri & Frieden, 2002), an increased usage of NBFA-containing antitubercular agents was needed. This leads to a general increased NBFA release by untreated urban wastewater along the rivers or through point sources, such as the medical facilities in the vicinity of AD2.

The quantified contamination by technical compounds (Mesamoll®, DPE, and NBFA) supports the observation that the release of untreated urban and industrial wastewater into Chennai’s river systems contributes to the floodplains surface pollution.

3.5 Pesticides

DDT and its metabolite derivates (DDD and DDE) have been analyzed as representatives for pesticide pollution (Pereira et al., 1996). While DDT is environmentally unstable, its metabolites are persistent and show environmental risks by their high bio- and geo-accumulative rates (Eganhouse et al., 2000). Once released to the environment, DDT follows one of two degradation pathways depending on the aerobic (DDE) or anaerobic (DDD) conditions (Yu et al., 2011). For this study, the summarized quantities of the detected DDX metabolites have been considered to assess the contemporary pesticide contamination and remobilization of environmentally stable old burdens. DDX have been detected in all samples (Fig. 6) with highest concentrations in AD8 (10,000 ng/gTOC) and CO2 (33,000 ng/gTOC) indicating point sources or a distinct re-mobilization of old burdens near these locations. In most of the surface sediments DDD makes up the largest proportion indicating anaerobic conditions in the river, which is supported by documented low oxygen levels in both rivers (Mishra et al., 2015), coinciding with a high methane emission through anaerobic microbial activities (Rajkumar et al., 2008).

4 Discussion

Meandering through Chennai’s densely populated urban and industrial metropolitan area, the major
river systems are exposed to severe contamination by numerous direct emission sources, but also to (re-) mobilizing (canal/wastewater inlets, embankments, dredging) and sediment-trapping (e.g., dams, bridges) anthropogenic modifying activities. Both, contamination sources and anthropogenic modifications, on and off the floodplains imply the complexity of the observed distribution of pollutants. The heavy metal contamination in both rivers follows a rather static downstream decrease with lowest concentrations in the estuaries (AD2, CO1). This contamination can further be extended onto the continental shelf of the Bay of Bengal. Even 15 km offshore of the Adyar River mouth, Veerasingam et al. (2014) observed low but remaining heavy metal concentrations. Thus, the continental shelf acts as a major sink for pollutants discharging from the rivers. The lower concentrations are explained by the wider distribution over a large area (e.g., by ocean currents) and the dilution capabilities of the ocean. The rather punctual emission of the heavy metals from the inland located industry or old burden remobilization and the subsequent dilution along the rivers courses do not correlate to the distribution pattern of the persistent organic pollutants.
No generalized organic pollutant distribution trend across the river's course from the metropolitan outskirts, Chennai’s urban, and industrial areas and both estuaries can be postulated. Diffuse entry of organic pollutants into a complex and dynamic river system is evident. But our evaluation of persistent organic contaminants revealed higher concentrations in the floodplain sediments than detected in previous studies (e.g., Goswami et al., 2016; Rajan et al., 2019).

The numerous inlets and canals into the two major river systems provide additional diffuse sources of wastewater and subsequently contribute to the complexity of contamination distribution. The exception are few compounds (DPE, NBFA, DEHA, and LABs), which can be linked to punctual wastewater emission sources. Further do uncertainties regarding the preservation and anthropogenic alterations to the floodplains, and the contamination sources of certain compounds remain. Nonetheless, concerning contamination originates from PAHs, hopanes, LABs, octocrylene, Mesamoll®, NBFA, DPE, and DDX, which all have been detected in distinctive concentration within the floodplain sediments. Therefore, urban wastewater, pesticide, and technical contamination indicators have proven to be well-suited to assess the contemporary surface contamination of the Adyar.
and Cooum rivers which are both known for their poor water quality (e.g., Jayaprakash et al., 2012; Rajkumar et al., 2008; Ramesh et al., 1997). Lower concentrations in the estuary (especially Adyar river) correlate to dilution effects of the larger water mass in the widened river mouth and coarser grain sizes.

Results and field observations have shown substantial anthropogenic modifications (e.g., dams, dikes, dredging), strengthening the assumption that most of the surface sediments are anthropogenically superimposed or altered.

Contrary to the general assumption that major flooding events cause an overall increased contamination in the rivers, the concentration distribution implies rather a washing- or flushing-out effect by the increased volume of water. The naturally deposited finer sediments, especially the most recent ones, showed the most significant contamination, while no definitive evaluation of the contamination distribution can be made. Furthermore, the identification of all contamination sources remains difficult based on the vastness of tributaries, inlets, numerous other diffuse contamination sources, and the influence of disruptive anthropogenic forces.

Fig. 6 Contemporary surface pollution by DDX as sum of DDT metabolites (in ng/gTOC) for Cooum and Adyar river
5 Conclusion

The results of this study show that the main river systems of Chennai, Tamil Nadu state, experience severe contemporary contamination through the discharge of industrial and urban wastewaters, but also by the contribution of waste dumping on or near the floodplains. The overall contamination of the rivers is contributed by a complex interaction between contamination sources, water level and dynamic, dilution effects by flood events, and anthropogenic actions. The consequences for the adjacent ecosystems, their surroundings, remain ultimately unknown.

The multiproxy analysis of surface sediments along the Adyar and Cooum river revealed the severe contemporary contamination of the Adyar and Cooum rivers by potentially toxic elements, urban and industrial wastewater, petrogenic contaminants, and pesticides. This study attempts to unveil the widespread distribution of pollutants contained in floodplain sediments. The chosen approaches and contaminants are well-suited to characterize the present contamination of a (sub-)tropical urban river system. However, several analytical and evaluation pitfalls have also been discovered, mainly emanating from anthropogenic disturbance, modification (e.g., dredging, damming), and overprinting of the natural deposition. In addition, washing-out and dilution effects by flood events and the cleansing of the rivers contamination onto the shelf have the most notable impact on the contamination distribution in both rivers. Nonetheless, severe consequences for both river ecosystems and their surroundings by the high contamination levels remain virtually unknown.

Supplementary information.

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Data Availability All data generated or analyzed during this study are included in this published article (and its supplementary information files).

Declarations

Competing Interests The authors declare no competing interests.

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