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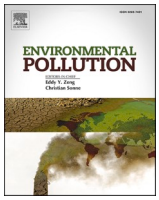

Emerging organic contaminants in the River Ganga and key tributaries in the middle Gangetic Plain, India: Characterization, distribution & controls☆

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ABSTRACT

The presence and distribution of emerging organic contaminants (EOCs) in freshwater environments is a key issue in India and globally, particularly due to ecotoxicological and potential antimicrobial resistance concerns. Here we have investigated the composition and spatial distribution of EOCs in surface water along a ~500 km segment of the iconic River Ganges (Ganga) and key tributaries in the middle Gangetic Plain of Northern India. Using a broad screening approach, in 11 surface water samples, we identified 51 EOCs, comprising of pharmaceuticals, agrochemicals, lifestyle and industrial chemicals. Whilst the majority of EOCs detected were a mixture of pharmaceuticals and agrochemicals, lifestyle chemicals (and particularly sucralose) occurred at the highest concentrations. Ten of the EOCs detected are priority compounds (*e.g.* sulfamethoxazole, diuron, atrazine, chlorpyrifos, perfluorooctane sulfonate (PFOS), perfluorobutane sulfonate, thiamethoxam, imidacloprid, clothianidin and diclofenac). In almost 50% of water samples, sulfamethoxazole concentrations exceeded predicted no-effect concentrations (PNECs) for ecological toxicity. A significant downstream reduction in EOCs was observed along the River Ganga between Varanasi (Uttar Pradesh) and Begusarai (Bihar), likely reflecting dilution effects associated with three major tributaries, all with considerably lower EOC concentrations than the main Ganga channel. Sorption and/or redox controls were observed for some compounds (*e.g.* clopidol), as well as a relatively high degree of mixing of EOCs within the river. We discuss the environmental relevance of the persistence of several parent compounds (notably atrazine, carbamazepine, metribuzin and fipronil) and associated transformation products. Associations between EOCs and other hydrochemical parameters including excitation emission matrix (EEM) fluorescence indicated positive, significant, and compound-specific correlations between EOCs and tryptophan-, fulvic- and humic-like fluorescence. This study expands the baseline characterization of EOCs in Indian surface water and contributes to an improved understanding of the potential sources and controls on EOC distribution in the River Ganga and other large river systems.

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1. Introduction

The prevalence of emerging organic contaminants (EOCs) in aquatic environments is an increasing concern globally (Kasprzyk-Horndern et al. 2008; Pal et al. 2010; Lapworth et al. 2012; Loos et al. 2013; Meffe and de Bustamante, 2014; Lapworth et al. 2015; Sorensen et al. 2015; Kim et al. 2016; White et al. 2019; Yusuf et al. 2021; Morin-Crini et al. 2022; Reberski et al. 2022), including in India (Lapworth et al. 2018; Philip et al. 2018; Sharma et al. 2019; Mathew and Kanmani, 2020; Ghirardelli et al. 2021; Richards et al. 2021; Satyanarayana et al. 2022). A wide range of chemicals compounds can be defined as EOCs (Lapworth et al. 2012), such as pharmaceuticals (human and veterinary) (Kolpin et al. 2002; Richmond et al. 2018), endocrine disrupting compounds, agrochemicals (*e.g.* pesticides, fertilizers) (Solomon et al. 2000), lifestyle products (*e.g.* food and beverage additives (Lange et al. 2012), recreational drugs (Kasprzyk-Horndern et al. 2008) and personal care products (Brausch and Rand, 2011)), and industrial compounds and/or by-products (Garner and Keller, 2014).

As some EOCs have persistent, bio-accumulative and toxic characteristics (Mathew and Kanmani, 2020), known or suspected adverse environmental effects can include the development or promotion of antimicrobial resistance (AMR) (Hawkey, 2008; Kümmerer, 2009; Martinez et al. 2009; Kurunthachalam, 2012; Lupo et al. 2012; Szmolka and Nagy, 2013; Amos et al. 2015) as well as ecotoxicological (Richmond et al. 2017; Barrick et al. 2022; He et al. 2022) and cytotoxic effects (Etteieb et al. 2016). Due to increasing AMR concerns, priority antimicrobials have been identified for both human (World Health Organization, 2018) and veterinary medicine (World Organisation for Animal Health, 2018). As India is one of the world's largest pharmaceutical producers (Greene, 2007) and consumers (The Center for Disease Dynamics, 2015), AMR concerns are particularly pronounced. To address ecotoxicity concerns, the European Commission (EC)'s Water Framework Directive includes regulated and non-regulated Priority Substances (covering many EOCs) in the Environmental Quality Standards Directive 2008/105/EC (European Commission, 2019) and Watch Lists (Carvalho et al. 2015; European Commission, 2018; Lapworth et al. 2019). In addition, predicted no-effect concentrations (PNECs) have been developed on the basis of bacterial resistance selection and ecological toxicity (*e.g.* Tran et al. 2018 and references within) for some EOCs. Given that PNEC values are not always available, a default PNEC of 0.05 $\mu g.L^{-1}$ has been recommended in absence of other data (Vestel et al. 2022).

EOCs enter the hydrological cycle mainly through wastewater discharge (Glassmeyer et al. 2005; Roberts and Thomas, 2006; Kasprzyk-Horndern et al. 2008; Writer et al. 2013; James et al. 2016), industrial production (Lübbert et al. 2017), agricultural runoff (Kay et al. 2005; Kim et al. 2016), livestock (Campagnolo et al. 2002; Watanabe et al. 2010; Kim et al. 2016) and landfill leachate (Wang et al. 2020). In surface waters, spatial and temporal variations in concentrations of EOCs can be substantial and depend, in part, on source loading, catchment characteristics and base-flow conditions (Ascott et al. 2016; Burns et al. 2018). EOCs arising from domestic/residential wastes may contain lifestyle compounds, pharmaceuticals and personal care products, noting that conventional wastewater treatment plants (WWTPs) are often inefficient in complete degradation or removal of EOCs (Glassmeyer et al. 2005; Roberts and Thomas, 2006; Loos et al. 2013; Kosma et al. 2014; Subedi et al. 2015; Anumol et al. 2016; Archer et al. 2017; Mathew and Kanmani, 2020). Wastewater discharge (raw or treated) is thus a major EOC source, even if advanced wastewater treatment processes are implemented, with typical wastewater EOC concentrations at the $ng.L^{-1}$ to $mg.L^{-1}$ level (Loos et al. 2013). EOCs from industrial sources (*e.g.* pulp and paper mills, steel plants, food processing plants) may include intermediates (plasticizers, dyes, resins), food additives, antioxidants, surfactants, and/or detergents (Meffe and de Bustamante, 2014). Hospitals and pharmaceutical manufacturers can be point sources of medical waste including antibiotics and other pharmaceuticals (*e.g.* Lin et al. 2008). Runoff from agricultural areas may contribute pesticides, including fungicides, herbicides, bactericides, and insecticides (Agarwal et al. 2015). Once EOCs are discharged to surface waters through point or non-point sources, dilution and dispersion typically follow, although multiple sources and complex biogeochemical behaviour can lead to difficulties in disentangling the influence of individual inputs. However, the artificial sweetener sucralose has been successfully used as wastewater tracer in aqueous systems (Scheurer et al. 2009; Oppenheimer et al. 2011; Lange et al. 2012; Loos et al. 2013; Tran et al. 2014; Yang et al. 2017; White et al. 2019), because of its widespread occurrence (Batchu et al. 2013; Loos et al. 2013) and environmental persistence (Roberts et al. 2000; Scheurer et al. 2009; Torres et al. 2011; Batchu et al. 2013).

In parts of India, the presence of EOCs is increasingly being investigated in surface water (Mutiyar and Mittal, 2014; Shanmugam et al. 2014; Rayaroth et al. 2015; Sharma et al. 2016; Dwivedi et al. 2018; Khalid et al. 2018; Philip et al. 2018; Sharma et al. 2019; Williams et al. 2019; Mukhopadhyay and Chakraborty, 2021) groundwater (Lapworth et al. 2018; Philip et al. 2018; Sharma et al. 2019; Richards et al. 2021) and riverine sediment (Chakraborty et al. 2019). A recent review of EOCs in Indian surface water has concluded that a wide range of compounds have been detected (Mathew and Kanmani, 2020). However, widespread screening is scarce, and investigations evaluating the spatial distribution of EOCs remain limited, particularly in northern and northeast India (Philip et al. 2018). Further, investigations on temporal variability of EOC concentrations in surface water are very limited, although high seasonal variation in concentrations of some endocrine disrupting compounds (*e.g.* nonylphenol ethoxylates) have been reported previously (Golovko et al. 2014; Gao et al. 2016). Regardless of locality, an inherent challenge with EOC investigations arises from their resource-intensive and complex analytical requirements (Richardson and Ternes, 2014), especially for environmental samples impacted by matrix effects and low level EOC concentrations. In part because of these challenges, other less resource-intensive analytical techniques such as fluorescence excitation emission matrix (EEM) spectroscopy have begun to be explored for potential application in EOC monitoring (Sgroi et al. 2017; Wasswa et al. 2019; Zhang et al. 2019).

The River Ganges (known locally as the Ganga) is of huge religious and cultural significance in India (Kumar 2017) and one of the world's most important river systems, providing water and associated services (*e.g.* agricultural, industrial) to more than 400 million people (Kumar 2017; Dwivedi et al. 2018). The Gangetic Basin is a main contributor to India's agro-economy, with 65% of its area covered by farming land (Ghirardelli et al. 2021) in addition to heavy industrial presence in some areas (Dwivedi et al. 2018). Various types of pollution have been reported in segments of the River Ganga (Lata et al. 2009; Seth et al. 2013; Sinha and Loganathan, 2015; Sharma et al. 2016; Paul, 2017, Central Pollution Control Board, 2019; Bowes et al. 2020; Richards et al. 2022), in part arising from inadequate wastewater infrastructure leading to the majority of wastewaters being discharged untreated into receiving water bodies (Hamner et al. 2006; Satya and Narayan, 2018; Jadeja et al. 2022). This is likely to contribute to widespread presence of EOCs in aqueous environments in this setting, although it has not been widely investigated.

Our work goes beyond previous studies of EOCs in Indian surface waters (Lapworth et al. 2018; Philip et al. 2018; Kumar et al. 2019; Sharma et al. 2019; Williams et al. 2019), and aims to build a detailed mechanistic understanding of the properties, distribution and potential sources of these pollutants through a longitudinal study of a segment of the River Ganga and key tributaries from Varanasi (Uttar Pradesh) to Begusarai (Bihar) in the mid-Gangetic Basin. This topic is particularly relevant in the context of the flagship Namami Gange initiative by the Government of India to clean, conserve and rejuvenate the River Ganga. Here, our objectives are to: (i) quantify and characterize EOCs, and any detected transformation products, including in comparison to priority pollutant lists and available PNECs; (ii) evaluate the spatial distribution

and potential controls impacting concentrations of EOCs in surface water with respect to downstream influences (*e.g.* tributaries, urban and agricultural inputs, surface-groundwater interactions); and to (iii) investigate associations with EEM fluorescence data to identify potential fluorescence-based proxies for surface water EOCs in the Gangetic Basin.

2. Methods

2.1. Study area

The field area is in the Middle Gangetic Plain in northern India (Fig. S1), spanning a ~500 km stretch of the River Ganga and key tributaries (Ghaghara, Sone and Gandak), located between Varanasi (Uttar Pradesh) and Begusarai (Bihar). Surface water samples (n = 11) were collected in November–December 2019 in the post-monsoon season at downstream intervals ranging from ~10 to 100 km, spanning both rural and urban areas (Richards et al. 2022). The post-monsoon season was selected for sampling due to accessibility considerations as well as the post-monsoon season being a period where relatively high groundwater-surface water connectivity is expected (Richards et al. 2022). Whilst there is substantial agricultural activity in rural areas, there are also several rapidly developing cities (*e.g.* Varanasi, Ghazipur, Buxar, Ballia, Chappra, Patna, Barh and Begusarai) intermittently located, all of which have extensive bankside development and effluent inputs (both industrial and municipal). In particular, Patna city (the State capital of Bihar) is a major, rapidly developing urban center and identified as a "Smart City" under the Government of India Scheme for Smart City Project and Atal Mission for Rejuvenation and Urban Transformation. Further details, including estimates of sewage generated from cities within the sampling frame are included in *Supplementary Information*.

2.2. Water sample collection

Surface water samples were collected, using a bucket, from accessible river bank locations (Richards et al. 2022). Unfiltered surface water samples for EOC analyses were collected in 1 L glass bottles, prepared by the UK National Laboratory Service (NLS), and sealed with Parafilm® M. Nitrile gloves were worn during sample collection. Water sub-samples for both EEM and ion chromatography (IC) analysis were filtered on-site using 0.45 μm sterile cellulose nitrate membrane filters (Thermo-Fisher). Water samples for EEM analysis were stored in 20 mL amber glass bottles which had been acid washed (10% nitric acid) and baked; water samples for IC analysis were stored in acid washed (20% hydrochloric acid) Nalgene PTFE bottles. After collection, samples were transported to the UK in non-temperature-controlled airfreight. Upon customs clearance, samples were delivered to the relevant analytical labs as soon as possible, where they were stored in refrigerated conditions prior to analysis.

2.3. Chemical analysis

2.3.1. EOC analysis

Analysis of EOCs was undertaken at the NLS Environment Agency laboratory (Starcross, UK) using methods described elsewhere in (Richards et al. 2021), noting many details are included in the associated Supplementary Information of that manuscript. In brief, solid phase extraction was conducted using cartridges (Waters Oasis HLB SPE cartridges), pre-conditioned with methanol and ultra-high purity water, and spiked with isotopically labelled carbutamide-d9 as an internal standard. Cartridges were loaded, washed and the sorbent dried with high purity nitrogen, followed by two-stage elution with 0.1% formic acid in methanol:acetonitrile (1:1) and dicholoromethane. The combination of elution solvents was selected as it enabled optimal extraction of a wide variety of target compounds with varying chemical characteristics. Eluted fractions were collected separately, with the dicholoromethane eluate evaporated to incipient dryness, and the methanol:acetonitrile eluate evaporated under nitrogen to 100 μL. Ultra-high purity water was added to each vial to a total volume of 1000 μL, vortex mixed and filtered. Procedural blanks were used during extraction and analysis. Semi-quantitative analysis, screening for >750 compounds (see list in Supplementary Information), was undertaken with Ultra-High Definition Liquid Chromatography/Quadrupole-Time-of-Flight Mass Spectrometry (LC/Q-TOF-MS) on an Agilent Q-TOF (model 6545).

2.3.2. EEM and A_{254} analysis

Fluorescence analysis was undertaken at the facilities of the British Geological Survey (Wallingford, UK) using a VarianTM Cary Eclipse fluorescence spectrometer following methods published elsewhere (Lapworth et al. 2009; Richards et al. 2019). Fluorescence indices were calculated using standard peak picking techniques following absorbance correction (Lakowicz, 1991), blank correction and Raman standardization. Here we have considered tyrosine-like fluorescence (TYR), tryptophan-like fluorescence (TLF), fulvic acid-like fluorescence (FA), humic acid-like fluorescence (HA), the humification index (HIX) (Ohno, 2002), the McKnight ratio, the "freshness index" β:α and Gelbstoff (McKnight et al. 2001; Cory and McKnight, 2005; Wilson and Xenopoulos, 2009). Further details are included in *Supplementary Information*.

2.3.3. In-situ water quality measurements and additional hydrochemical parameters

In-situ measurements of pH and electrical conductivity (EC) were taken during sampling using a handheld meter (Myron L Ultrameter II, USA). Chloride (Cl^-) and nitrate (NO_3^-) were analysed using IC (Dionex AS50, Thermo Fisher Scientific) at the UK Center for Ecology & Hydrology. Manganese (Mn) was analysed on acidified (2% analytical grade nitric acid) samples with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; Agilent 5800) at the Manchester Analytical Geochemical Unit at the University of Manchester. Further details on IC analysis and quality assurance/quality control are published elsewhere (Richards et al. 2022).

2.4. Software packages and data analysis

Details of software packages and data analysis are reported in *Supplementary Information*.

3. Results and discussion

3.1. Occurrence and characterization of emerging organic compounds in surface water

A total of 51 EOCs were detected within the 11 surface water samples (Fig. 1, Fig. S2 and Table S1), ranging in concentration from below detection limit to a maximum concentration (C_{max}) of 1.7 $\mu g.L^{-1}$ (sucralose). Detection frequency in surface water (DF_{SW}) ranged from 9% to 100% (diuron), with the highest frequency compounds diuron, sucralose, clopidol and chlorantraniliprole (DF_{SW} = 100%, 91%, 91% and 91%, respectively). For individual surface water samples, the number of detected EOCs ranged from 6 (site T39, River Gandak tributary) to 41 (sites G21 and G22, near Varanasi, noting both concentrations and total number of EOCs detected were higher than previously reported near Varanasi (Lapworth et al. 2018)), with the sum of EOC concentrations ranging from 0.02 (Gandak tributary) to 3.7 $\mu g.L^{-1}$ (site G26, near Buxar). The observed concentration ranges and detection frequencies are broadly similar to other previous studies from India, for example in the wastewater-impacted Ahar River (Rajasthan) EOC (pharmaceutical) concentrations ranged up to ~ 1.9 $\mu g.L^{-1}$ (Williams et al. 2019).

Observed EOCs have been broadly characterized by primary usage

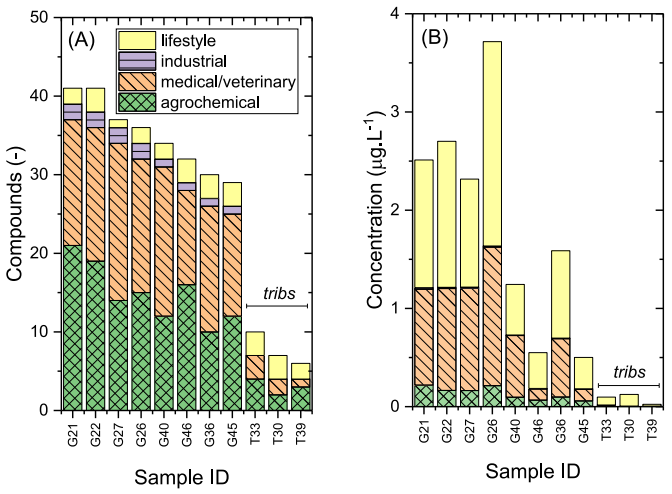

Fig. 1. Main category/usage sub-groups of surface water samples (n = 11 samples) showing (A) number of compounds detected (in total 51 compounds), organized in decreasing order per sample of total compounds in each sub-group, and (B) total EOC concentration per sample ID. Individual samples are represented by a single stack column; IDs beginning with "G" are from River Ganga; "T" are from tributaries (tribs).

(*e.g.* medical/veterinary, agrochemical, industrial and lifestyle) (Fig. 1). The identified compounds were mainly agrochemicals (~47% of compounds) and pharmaceuticals (~41%), with fewer lifestyle (~8%) and industrial (~4%) chemicals detected. By concentration, samples were usually dominated by lifestyle chemicals, with relatively large inputs from pharmaceuticals as well. Despite relatively high numbers of agrochemical compounds, the contribution of agrochemicals to total EOC concentrations was limited. The total number of compounds and EOC concentrations were substantially lower in each of the three tributaries sampled than in the main Ganga body.

3.1.1. Priority Substances

Ten of the detected EOCs are flagged as priority compounds. The antibiotic sulfamethoxazole (DF_{SW} = 73%; C_{max} = 63 ng.L^{-1}) is on the *WHO Highly Important Antimicrobial list* (World Health Organization, 2018). Compounds on the *EC Priority Substance list* (European Commission, 2019) include: diuron (DF_{SW} = 100%; C_{max} = 95 ng.L^{-1}), atrazine (DF_{SW} = 82%; C_{max} = 12 ng.L^{-1}) and chlorpyrifos (DF_{SW} = 9%; C_{max} = 5 ng.L^{-1}), as well as *EC Priority Hazardous Substances* (EC Directive, 2013/39/EU) perfluorooctane sulfonate (PFOS, DF_{SW} = 36%; C_{max} = 2.4 ng.L^{-1}) and related perfluorobutane sulfonate (DF_{SW} = 73%; C_{max} = 12 ng.L^{-1}) (European Commission, 2013; Environment Agency, 2019). Compounds on the *European Commission, 2013 Surface Water Watch list* (European Commission, 2018) include the neonicotinoid insecticides thiamethoxam (DF_{SW} = 73%; C_{max} = 7 ng.L^{-1}); imidacloprid (DF_{SW} = 64%; C_{max} = 6 ng.L^{-1}) and clothianidin (DF_{SW} = 45%; C_{max} = 1 ng.L^{-1}). The pharmaceutical diclofenac (DF_{SW} = 18%; C_{max} = 18 ng.L^{-1}) was included on the first 2015 EC *Watch List* (Carvalho et al. 2015) but was removed upon update. In addition, the fungicide tricyclazole (DF_{SW} = 73%; C_{max} = 24 ng.L^{-1}) although not currently restricted to the authors' knowledge, has recently been proposed to be banned in India (Agro-Pages, 2020).

3.1.2. Agrochemicals

The agrochemicals detected (n = 24) represent a wide range of herbicides, insecticides, fungicides and pesticides. Herbicides were the most frequently detected agrochemicals, including (in decreasing frequency): diuron, atrazine, atrazine-desethyl, metribuzin, metribuzin-diketo, monuron, bentazone and 2,4-dichlorophenoxyacetic acid. Insecticides included chlorantraniliprole, thiamethoxam, imidacloprid, clothianidin, fipronil and chlorpyrifos. Many of these are components of registered herbicides in India (Choudhury et al. 2016). Fungicides include: carbendazim (also used as a chemotherapeutic), tricyclazole, azoxystrobin, propiconazole (also used as veterinary drug), hexaconazole and carboxin. Other detected pesticides and/or pesticide metabolites included metribuzin-desamino, atrazine-desisopropyl, fipronil sulfide and fipronil sulfon (see **Section 3.5**).

3.1.3. Medical and veterinary compounds

Numerous detected compounds (n = 21) are used for a wide variety of medical and veterinary purposes including as poultry anticoccidials (*e.g.* clopidol), anticonvulsants (*e.g.* carbamazepine, lamotrigine and 10,11-dihydroxycarbazepine, the later which is an active metabolite of the antiepileptic drug oxcarbazepine), analgesics (*e.g.* tramadol), antifungals (*e.g.* climbazole, fluconazole and griseofulvin; note both climbazole and fluconazole are also used as pesticides), antihypertensives (*e.g.* telmisartan), antibiotics (*e.g.* sulfamethoxazole), anesthetics (*e.g.* lidocaine/diocaine), antihistamines (*e.g.* cetirizine, fexofenadine), antitussives (*e.g.* dextrorphan), antidiabetics (*e.g.* metformin), antivirals (*e.g.* amantadine), an x-ray contrast media (*e.g.* iohexol), an antimicrobial agent in personal care products (*e.g.* triclosan), anti-inflammatories (*e.g.* diclofenac), a beta-blocker and antihypertensive drug (*e.g.* atenolol) and as an anti-platelet agent (*e.g.* clopidogrel). Previous studies have used carbamazepine as a pollution tracer (Hai et al. 2018; Chakraborty et al. 2019) and have reported significant correlations between atenolol and enterococci counts (Subedi et al. 2015). The relatively high detection frequency of carbamazepine (DF_{SW} = 82%) here is consistent with elevated carbamazepine concentrations previously reported in riverine sediment along the Hooghly, the eastern distributary of the Ganga (Chakraborty et al. 2019).

3.1.4. Lifestyle compounds

The lifestyle compounds detected (n = 4) are heavily dominated by artificial sweeteners, namely sucralose (DF_{SW} = 91%; C_{max} = 1.7 µg.L^{-1}; C_{mean} = 0.9 µg.L^{-1}); saccharin (DF_{SW} = 73%; C_{max} = 35 ng.L^{-1}) and acesulfame (DF_{SW} = 27%; C_{max} = 380 ng.L^{-1}). Cotinine (DF_{SW} = 55%; C_{max} = 45 ng.L^{-1}) is a tobacco biomarker and nicotine metabolite. The high concentrations and frequency of detection of sucralose as a lifestyle compound compared to other types of EOC classes is consistent with, for example, the comparatively high ratio (~540%) of domestic wastewater to industrial sewage discharges in the Ganga (Sharma et al. 2019 and references within). Although caffeine has been widely reported in wastewater in relatively high income countries (Deblonde et al. 2011; Ben et al. 2018; Tran et al. 2018) and elsewhere in India (Sharma et al. 2019; Williams et al. 2019), caffeine was not included in the LCMS screen used and is not reported in this study.

3.1.5. Industrial compounds

The industrial compounds detected (n = 2) were both surfactants: perfluorobutane sulfonate (DF_{SW} = 73%; C_{max} = 12 ng.L^{-1}) and perfluorooctane sulfonate (PFOS; DF_{SW} = 36%; C_{max} = 2.4 ng.L^{-1}). Perfluoroalkyl and polyfluoroalkyl substances widely used in consumer products (Environment Agency, 2019). The concentrations of PFOS detected here (0.4–2.4 ng.L^{-1}) are very similar to previous studies in the Ganga basin (PFOS up to 1.7 ng.L^{-1}) (Sharma et al. 2016).

3.1.6. EOC concentrations in comparison to Predicted No-Effect Concentration (PNEC) values

The exceedances of measured surface water EOC concentrations with regard to published PNEC values for bacteria resistance selection and ecotoxicity (Tran et al. 2018) are shown in Fig. S3. Sulfamethoxazole is below the resistance-based PNEC (16 µg.L^{-1}), yet exceeds the ecotoxicity PNEC (27 ng.L^{-1}) in ~45% of the samples, all located on the Ganga, mostly near Buxar and Varanasi, upstream of the confluences with the major tributaries (one exception is at site G36 just upstream of Patna). Similarly, triclosan exceeds the ecotoxicity PNEC (50 ng.L^{-1}) near Buxar. For the other compounds with available PNEC values (*e.g.*

carbamazepine, diclofenac, atenolol and iohexol), measured concentrations are below the PNEC values, although in some cases are elevated especially in the Ganga as compared to the tributaries. Sulfamethoxazole and triclosan, in addition to other substances, have been previously reported to present moderate risk to aquatic organisms in the Ganga (Sharma et al. 2019). Particularly given limitations regarding the spatial and temporal scope of sampling, this does not represent a comprehensive risk assessment, but rather highlights that risks associated with such compounds may be problematic in some locations and should be considered more fully in the future.

3.2. Spatial distribution of emerging organic compounds in surface water

3.2.1. Longitudinal variations

The distribution of EOCs in surface water in the Ganga and the three major tributaries (Ghaghara, Sone and Gandak) varies widely between

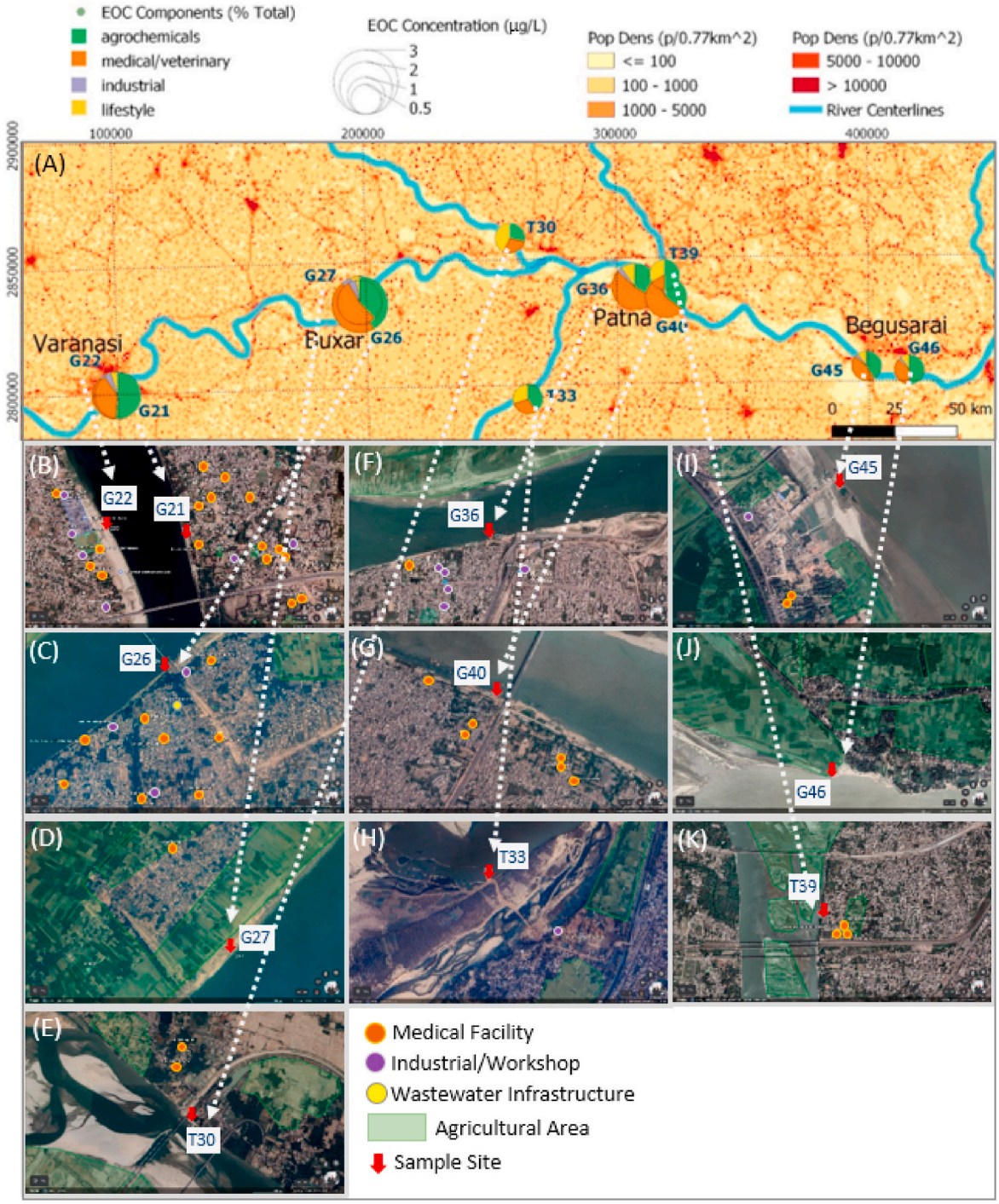

Fig. 2. (A) Distribution of EOCs in surface water with pie charts representing the composition of EOCs on the basis of relative proportions of sub-categories of dominant usage (agrochemicals, medical/veterinary, industrial and lifestyle) of detected compounds and symbol size representing total EOC concentration. Underlying layer shows population density data from the LandScan 2018™ High Resolution Global Population Data Set (Rose et al. 2019). River center lines are not to scale and do not necessarily represent river width. (B–K) Google Earth images of each sampling point with potential nearby pollutant sources marked on the basis of geographical information available through Google Maps and Apple Maps. Map Data: Google, CNES/Airbus and Maxar Technologies.

Varanasi and Begusarai (Fig. 2). Component-type is typically dominated by agrochemicals and medical/veterinary substances, whereas concentration is typically dominated by lifestyle and medical/veterinary components. The relative ratio of components is broadly consistent through the sampling area, although the total number varies. High proportions of agrochemicals are consistent with agricultural runoff throughout the basin, whereas medical/veterinary and lifestyle components would be expected to derive from anthropogenic sources and wastewater inputs. The three tributaries all have considerably lower EOC signatures (both in terms of compounds and total concentrations) than the main Ganga body.

Clear downstream trends were observed in EOC signatures (Fig. 3). Statistically significant downstream reduction in EOCs along the main Ganga body were observed across the total number of compounds (Fig. 3B; slope = −0.02; $t_6 = -5.5$; $p < 0.01$); total EOC concentration (Fig. 3C; slope = −0.005; $t_6 = -3.7$; $p < 0.01$); sucralose (Fig. 3C; slope = −0.002; $t_6 = -3.0$; $p < 0.05$); and EC (Fig. 3C; slope = −0.28; $t_6 = -10$; $p < 0.01$). Dilution from the three tributaries appears to be a major downstream control on EOC signatures, particularly as the number of compounds and total EOC concentrations were substantially lower in all tributaries than in the main Ganga. The distributions of both total number of EOC compounds and concentrations were significantly higher in the main Ganga body as compared to the tributaries ($p < 0.05$, Mann-Whitney test).

A comparison to EC as an indicative tracer of tributary dilution or enrichment effects suggests that dilution is most likely to be the dominant downstream control for the total number of EOC components and concentration (Fig. 3C and D). Note that here EC has been used as a general dilution tracer rather than Cl^- due to possible Cl^- inputs particularly from wastewater, although EC and Cl^- are strongly associated ($t_9 = 13$; $p < 0.01$). However, in addition to dilution effects, concentrations of both lifestyle and medical/veterinary components are also observed to be influenced by localized inputs and in some cases deviate substantially from the general downstream EC trend. For example, these components all show substantial inputs especially near the urban Buxar area (~1650 km from source), which then decrease significantly further downstream of the tributaries. Industrial and agrochemicals follow the same general trend as EC, although downstream patterns are less obvious possibly due to the relatively low concentrations.

Given the potential importance of other processes such as sorption and redox controls on the mobility of some EOCs, other hydrogeochemical differences between the main Ganga body and tributaries were also considered. At the 0.05 level, the two distributions (Ganga versus tributaries) are not significantly different for pH, DO, nor redox-sensitive Mn. This suggest that sorption and/or redox controls are less likely than dilution to be the dominant controlling process impacting downstream trends. Although the distributions are not significantly different, it is noteworthy that both the lowest pH and highest DO encountered both were within tributary samples (Fig. S4), indicating that the geochemical conditions in the tributaries may be distinct even if the distributions are not statistically different, which may still impact EOC behaviour. Specific correlations between the EOC classes (compounds and concentrations) as well as the most frequently detected specific compounds generally did not show statistically significant correlations with pH, DO or Mn (Fig. 4). The only exception to this is for clopidol, which was significantly positively associated with Mn ($t_9 = 3.3$; $p_{FDR} < 0.05$), suggesting that redox controls are particularly important for clopidol. Although the tautomerization of atrazine herbicides is pH-dependent (Zanasi et al. 2021), the association of atrazine-desethyl with pH was positive but marginally insignificant ($t_9 = 2.4$; $p_{FDR} = 0.08$). If only the main Ganga samples are considered (*e.g.* tributaries excluded) (Fig. S5), similarly there are no statistically significant relationships between EOCs and pH, DO or Mn.

3.2.2. Lateral variations

Paired surface water samples collected from similar locations on urban versus non-urban sides of the riverbank show relatively good agreement in EOC composition (Fig. S6). The dominantly urban and

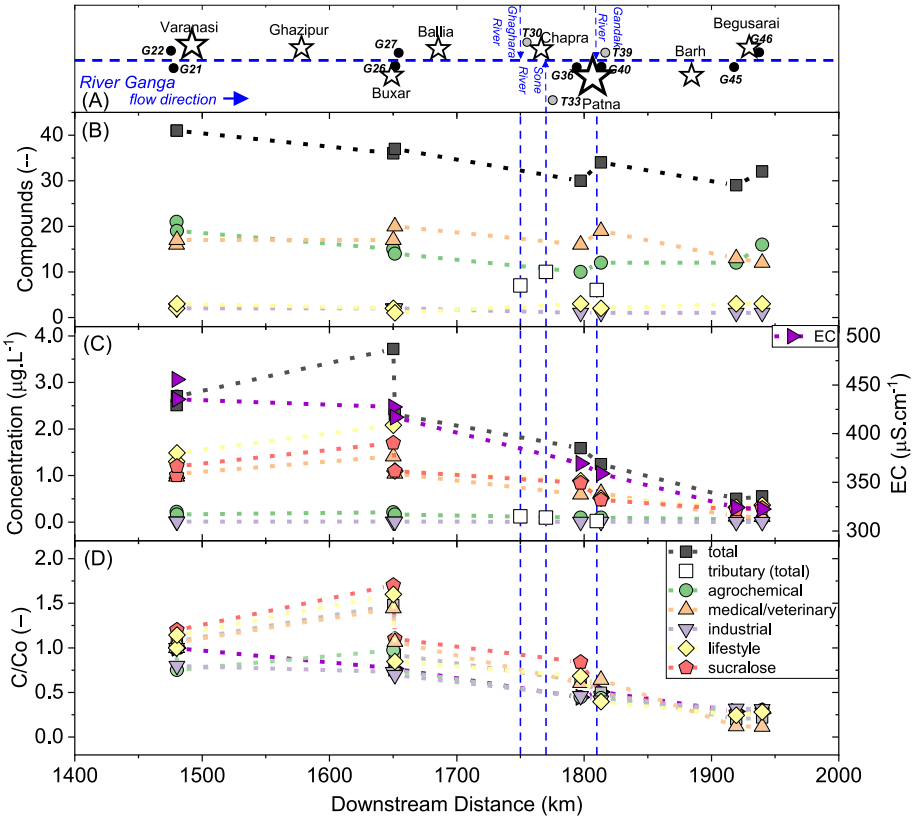

Fig. 3. Spatial distribution of EOCs along a section of the middle River Ganga from Varanasi, Uttar Pradesh to Begusarai, Bihar, with downstream distance in relation to the Himalayan source at Devprayag (Uttarakhand). (A) Simplified (linear) schematic of Ganga with (i) Major tributaries (Ghaghara, Sone and Gandak Rivers) marked as blue arrows and vertical lines on all sub-plots; (ii) Urban centers marked by stars with size corresponding to population; small stars = population ~ 100,000–300,000 people; medium stars (Varanasi) = population ~ 1.2 million; large star (Patna) = population ~ 2.1 million; cities with population < ~ 100,000 are not included; and (iii) sampling points on Ganga (black circles) and tributaries (grey circles; data not included here). (B) Number of EOCs detected and sub-catergorized; (C) concentrations of EOCs detected and sub-catergorized as well as sucralose (wastewater tracer) and electrical conductivity (EC, as a conservative inorganic dilution tracer); (D) Ratios of concentration (C) compared to initial concentration (C_0) using the furthest upstream sample at Varanasi as the reference point. Tributary totals (open squares) shown in B and C are for comparison to main Ganga body and are not included in dotted lines. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

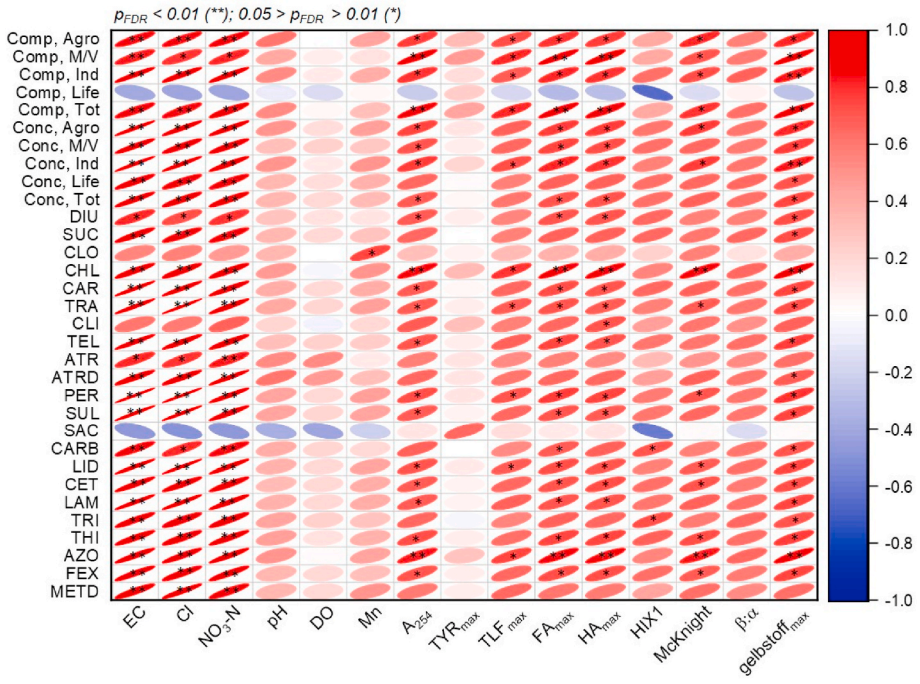

Fig. 4. Pearson's correlation matrix for the full dataset (Ganga and tributaries) of EOCs versus hydrochemical characteristics EC, Cl^-, NO_3–N, pH, dissolved oxygen (DO), Mn, A_{254} and EEM fluorescence based TYR, TLF, FA, HA, HIX, McKnight ratio, β:α and Gelbstoff. EOCs have been included where frequency of detection was >70% and includes, in decreasing order of detection, diuron (DIU), sucralose (SUC), clopidol (CLO), chlorantraniliprole (CHL), carbamazepine (CAR), tramadol (TRA), climbazole (CLI), telmisartan (TEL), atrazine (ATR), atrazine-desethyl (ATRD), perfluorobutane sulfonate (PER), sulfamethoxazole (SUL), saccharin (SAC), carbendazim (CARB), lidocaine (LID), cetrizine (CET), lamotrigine (LAM), tricyclazole (TRI), thiamethoxam (THI), azoxystrobin (AZO), fexofenadine (FEX) and metribuzin-desamino (METD), along with total number of compounds and concentrations of total EOCs, agrochemicals, medical/veterinary chemicals, industrial chemicals and lifestyle chemicals. Concentrations below detection were entered as half of the detection limit. The color scale shows the strength and direction of correlation with statistical significance indicated by False Discovery Rate (FDR)-corrected p (p_{FDR}) values with ** for $p_{FDR} < 0.01$ and * for $0.05 > p_{FDR} > 0.01$; FDR corrections were used to address Type 1 error. For correlation matrix including the main Ganga samples only (*e.g.* tributaries excluded) see Fig. S5. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

non- or peri-urban sides of the bank across the compound sub-categories are strongly correlated for both number of compounds (Fig. S6A; slope 1.0; $t_{10} = 13.9; p < 0.01$) and concentration (Fig. S6B; slope 0.7; $t_{10} = 10.0; p < 0.01$). This indicates that the river was generally well-mixed at these sample locations despite clear inputs from both point and non-point sources which may derive from both banks of the river. The notable exception to this is near Buxar, where the sample collected from the urban bank had much higher concentrations than the opposite side of the river. This supports the hypothesis that urban areas contribute EOCs via urban discharge at certain locations, although these inputs are mixed and diluted with downstream transport. A number of confounding factors contribute to these processes including high variability of river width and flow in various parts of the catchment, noting that typical river width near sample points at Varanasi and Buxar (~500 m and 700 m, respectively) is much narrower than downstream Begusarai (~1.5–2 km).

3.3. Relationship between EOCs and local population density and land use

The relative importance of local geographical conditions in the areas broadly surrounding the sampling sites (*e.g.* within 500 m in width and 2 km upstream distance) (Fig. S7) have been considered in comparison to regional controls such as the tributaries which contribute to dilution impacts (noting that the initial impact of tributary junctions is localized). Population density could plausibly be expected to be associated with sucralose (as a wastewater tracer), lifestyle, medical/veterinary and/or industrial compounds. However, in this case there was no significant overall linear relationship between the surrounding population density and these EOCs, either on the basis of concentration or number of compounds. However, an interesting curve is observed, with total EOCs increasing up until a population density of ~10,000 p. km^{-2}, followed by a steady decrease at higher populations. A similar trend is also seen with sucralose and total lifestyle and medical/veterinary concentrations and may reflect the influence of improved wastewater infrastructure in the highest population density areas.

Similarly, more extensive crop coverage could potentially be associated with runoff associated with agrochemicals. Although a statistically significant relationship at the 0.05 level is not observed, a general trend between grass crops coverage and agrochemicals compounds and concentrations within a 2 km zone upstream was identified (p = 0.15 and 0.14, respective), noting this was most strongly observed in the 2 km buffer zone considered. The lack of overarching relationship between the locally surrounding geographical characteristics with surface water EOC signatures likely reflects numerous confounding factors including multiple upstream influences and degradation and transformation processes which are highly compound-specific. In this case, we observe that the regional controls such as dilution and mixing, as discussed in **Section 3.2**, seem to have a stronger influence on EOC composition than local geographical characteristics. (Lapworth et al. 2009; Richards et al. 2019).

3.4. Comparison between surface water and groundwater EOCs

Surface water EOCs are typically much higher, on the basis of both number of compounds and concentration, than EOCs in groundwater under the rapidly developing city of Patna (Richards et al. 2021) (Fig. S8). In almost all cases, except for industrial EOC concentrations, the median compounds and concentration in surface water are substantially higher than Patna groundwater, with the distributions significantly different ($p < 0.05$; Mann-Whitney test). The exception with industrial chemicals is interesting, and the similarity in surface water and groundwater may reflect the generally low concentrations of these chemicals or potentially localized groundwater influences in Patna, including potential legacy contamination in groundwater. The generally lower concentrations of EOCs in the tributaries as compared to the main Ganga body are more like the groundwater concentrations in Patna, although still usually fall above the Patna groundwater median. This groundwater-surface water comparison indicates that surface water (in particular the River Ganga) are a sink/receptor rather than a source for groundwater EOCs in this area, and consistent with an overall net horizontal flow direction oriented from the aquifers towards the rivers (Lu et al. 2022).

3.5. EOC parent and transformation compounds

Several parent compounds, notably agrochemicals atrazine, metribuzin and fipronil, were detected in addition to their associated transformation products (TPs) (Fig. 5 and Fig. S9), suggesting the occurrence of degradation processes and the presence of an active microbial community. Concentrations of atrazine were higher than its TPs atrazine-desethyl and atrazine-desisopropyl, noting that the adsorption coefficient (i.e. the organic matter-water distribution coefficient K_{OM}) of atrazine is also higher than either detected TP (Brouwer et al. 1990). Atrazine-desisopropyl has a slightly higher adsorption coefficient (K_{OM} ~ 30–60 $dm^3\ kg^{-1}$) and lower measured concentrations than atrazine-desethyl (K_{OM} ~ 20–50 $dm^3\ kg^{-1}$) (Brouwer et al. 1990), suggesting that sorption is likely an important process impacting the fate and transport of atrazine's TPs. However, it is important to note that there are also other factors, such as variation in transfer efficiency, that may also influence the fate and transport. These factors are difficult to disentangle in complex environmental systems in the absence of detailed, compound-specific studies. The observation that atrazine concentrations are higher than atrazine's TPs suggests that there are significant surface runoff sources in the Ganga (Capel and Larson, 2001; Wang et al. 2018). There is a significant positive correlation between atrazine and both atrazine-desethyl ($t_7 = 3.6,\ p < 0.01$) and atrazine-desisopropyl ($t_3 = 3.5,\ p < 0.05$).

The opposite trend is observed with parent compound metribuzin, with concentrations of TPs metribuzin-desamino and metribuzin-diketo (Henriksen et al. 2002; Antonopoulou and Konstantinou, 2014) in some cases being substantially higher than metribuzin, indicating a relatively high degree of biogeochemical processing (Mulbah et al. 2000); other processes such as sorption may also contribute to the observed phenomena. Note the paired dataset is insufficient to determine the association or statistical significance of the direct relationship between metribuzin and its TPs. Similarly, the parent compound fipronil, with a relatively short half-life in water on the order of 10s of days (Chopra and Kumari, 2009), generally had lower concentrations than its more toxic metabolites fipronil sulfon and fipronil sulfide (McMahen et al. 2016), again suggestive of relative high degrees of fipronil processing. The relationship between fipronil and fipronil sulfide is not significant at the 0.05 level (data insufficient to determine the relationship between fipronil and fipronil sulfon). The co-occurrence of parent compounds with TPs is geographically focussed around the Varanasi samples (G21 and G22), although it remains unclear if the transformation processes were occurring locally (either before or after run-off into the Ganga) or if the observed compounds reflected processes further upstream.

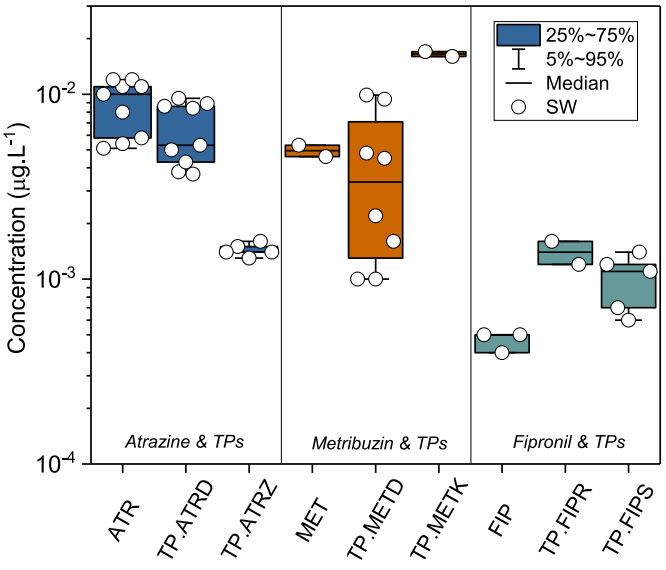

Fig. 5. Box plot of concentration of associated parent and transformation product (TP) compounds detected in surface water, including: parent atrazine (ATR) and TPs atrazine-desethyl (ATRD) and atrazine-desisopropyl (ATRZ); parent metribuzin (MET) and TPs metribuzin-desamino (METD) and metribuzin-diketo (METK); and parent fipronil (FIP) and TPs fipronil sulfon (FIPR) and fipronil sulfide (FIPS). Box plots show 25–75% range, median line and whiskers at 5 and 95% distribution.

In other cases, such as with the parent compound carbamazepine (DF_{SW} = 82%), known TPs included on the LCMS screen were not detected, suggesting that such compounds have not undergone significant degradation and are highly persistent (Jaeger et al. 2019; Posselt et al. 2020). In addition, the metabolite 10,11-dihydroxycarbazepine was detected in three samples although its parent compound oxcarbazepine was not; this may indicate upstream source(s) of oxcarbazepine which has then transformed along downstream flow paths. A number of factors and processes impact relative environmental persistence, including microbial diversity (Posselt et al. 2020), sorption with organic matter (Jaeger et al. 2019), photolysis (Baena-Nogueras et al. 2017), and differences in parent/metabolite transport rates (Gooddy et al. 2002).

Ratios of the concentration of the various transformation product to parent compound (C_{TP}: C_P) pairs are shown for surface water as a function of downstream distance (Fig. S10). Ratios of atrazine's TPs to parent compound are all <1 (*e.g.* $C_P > C_{TP}$) and relatively consistent along the 500 km stretch of the Ganga, and are also consistent with the significant positive relationships observed between atrazine and its TPs. This suggests plausibility that inputs could both be occurring locally/recently as well as much further upstream, noting that atrazine's potential persistence in groundwater and surface water on decadal timescales has been documented (Jablonowski et al. 2010). In contrast, transformation products associated with metribuzin and fipronil are much more localized with ratios usually >1 (*e.g.* $C_{TP} > C_P$). Given that the half-life of these compounds in water is typically much less than that of carbamazepine, this suggests that these samples might derive from a discrete input leading to a concentration plume travelling downstream. Especially given that sampling occurred as a one-off event, the possibility for further interpretation remains limited although results are consistent with a very dynamic system impacted by both point and non-point sources (which may contribute continual or discrete inputs). Detailed investigation of processes controlling the fate and transport of parent compounds and associated transformation products would be an interesting subject of future work.

3.6. Relationship between EOCs and hydrochemical and EEM fluorescence parameters

Lastly, the relationship between surface water EOCs and paired hydrochemical and EEM fluorescence proxies (Fig. 4 and Table S2) has been considered (Sgroi et al. 2017; Wasswa et al. 2019; Zhang et al. 2019), particularly in light of the clear importance of EOC monitoring in wastewater-impacted rivers such as the Ganga, but also the inherent limitations associated with resource-intensive sampling and analytical requirements for broad EOC screening. The total number of EOC compounds in each sample was significantly positively correlated with EC, Cl, NO_3–N, A_{254},TLF, FA, HA, the McKnight ratio and Gelbstoff, whereas the total EOC concentration was significantly correlated with EC, Cl, NO_3–N, A_{254}, FA, HA and Gelbstoff. In general, the majority of the most frequently detected compounds (with the exception of clopidol, climbazole and saccharin) were significantly associated with EC, Cl and NO_3–N, consistent with dilution controls and suggesting the source and/or behaviour of those exceptional compounds were different than the others (the association of Mn with clopidol suggests a redox control as previously discussed).

There are several compound-specific correlations between EOCs and various EEM properties. For example TLF, a wastewater indicator, is significantly positively associated with chlorantraniliprole,

azoxystrobin, perfluorobutane sulfonate, lidocaine and tramadol, in order of decreasing significance, suggestive of wastewater sources of these EOCs. Relationships were generally very similar between specific EOCs and both FA & HA, including significant positive associations with diuron, chlorantraniliprole, carbamazepine, tramadol, telmisartan, perfluorobutane sulfonate, sulfamethoxazole, lidocaine, cetrizine, lamotrigine, thiamethoxam, azoxystrobin and fexofenadine. Each of A_{254}, the McKnight ratio and Gelbstoff had compound-specific correlations with many of the most frequently detected EOCs, although there were no significant correlations with TYR. The EEM humification index HIX was associated with carbadazim and tricyclazole (indeed the only parameter that was for the later). A number of EOCs (*e.g.* diuron, chlorantraniliprole, carbamazepine, tramadol, telmisartan, perfluorobutane sulfonate, sulfamethoxazole, carbendazim, lidocaine, cetrizine, lamotrigine, thiamethoxam, azoxystrobin and fexofenadine) have strong correlations with at least three EEM parameters, indicating that EEM might offer stronger predictive power for these types of compounds. Whilst certain EOCs such as carbamazepine have been reported to quench fluorescence (Wang et al. 2016), the environmental concentrations here are much lower than concentrations where such interactions have been reported; however it may still be possible that EOC-fluorescence interactions may influence some of the specific relationships observed. Note that when only the main Ganga samples are considered (Fig. S5), the compound specific relationships with EEM proxies become much less apparent (except for two significant associations with HIX). This suggest that the overall relationships observed within the combined dataset likely reflect the broader range of surface water chemistry encountered when the tributaries are considered, and thus the sensitivity of EEM proxies for potential predictive power may only be suitable for discriminating lower and higher risk sites for EOC contamination. Detailed investigation of the potential added value of selected fluorescence and absorbance measurements as indicative proxies and as a potential predictive tool to inform EOC monitoring is a subject of ongoing investigation by co-authors.

4. Conclusions

Using a broad screening approach, we have identified and characterized EOCs in surface water along a ~500 km section of the River Ganga and some of its key tributaries in the middle Gangetic Basin in northern India. A total of 51 EOCs were detected in 11 surface water samples, typically at $ng.L^{-1}$ to $\mu g.L^{-1}$ level concentrations. Pharmaceuticals, agrochemicals, lifestyle and industrial chemicals were all identified, with a relatively high number of different pharmaceutical and agrochemical compounds detected. The highest concentrations, however, were of the artificial sweetener sucralose, a persistent lifestyle chemical which can be used as a wastewater tracer. Ten priority compounds were identified (*e.g.* sulfamethoxazole, diuron, atrazine, chlorpyrifos, perfluorooctane sulfonate (PFOS), perfluorobutane sulfonate, thiamethoxam, imidacloprid, clothianidin and diclofenac) which are of particular monitoring and/or regulatory importance. Concentrations of sulfamethoxazole exceeded PNEC values based on ecotoxicity in five samples, suggesting that further systematic investigation on the distribution and environmental impacts particularly of sulphonamide class antibiotics in the River Ganga and surrounding areas should be considered.

EOC concentrations were spatially variable, and a significant downstream reduction in concentration is observed between Varanasi (Uttar Pradesh) to Begusarai (Bihar), likely due to the influence of three major tributaries within this zone, all of which have considerably lower EOC signatures than the main Ganga. Regional downstream trends (*e.g.* dilution from tributaries) appear to be more substantial controls on the distribution of surface water EOCs than the local geographical characterization of the near upstream zone (*e.g.* based on population density and crop cover of the upstream 5 km). Comparison across river bank side locations at selected sites suggests a relatively high degree of mixing of EOCs within surface waters. Parent compounds (notably atrazine, carbamazepine, metribuzin and fipronil) as well as detected associated transformation products suggest the presence of an active microbial community contributing to EOC degradation, as well as other potential confounding processes such as sorption and photolysis. Concentrations of selected EOCs were strongly correlated with EEM-based fluorescence proxies, including TLF, FA and HA which were significantly associated with a number of specific compounds as well as the total number of EOCs detected. The limitations of this study are related to the relatively limited spatial and temporal extent and resolution of sampling, and as such this study does not represent a comprehensive characterization nor risk assessment. Notwithstanding, this study extends the baseline characterization of EOCs in Indian surface water and contributes to an improved understanding of the potential sources and controls on the distribution of these pollutants in the River Ganga and key tributaries, as well as potentially other similar large river systems.

Author contributions

LAR: investigation, formal analysis, visualization, supervision, funding acquisition, writing – original draft; **SG**: formal analysis, software, visualization, writing – original draft; **DJL**: conceptualization, methodology, resources, funding acquisition, writing - review & editing; **DW**: methodology; writing - review & editing; **WC**: investigation; resources; writing - review & editing; **GJLW**: methodology; formal analysis, writing - review & editing; **CL**: software, methodology, writing – review and editing; **AK**: investigation, writing - review & editing; **AG**: conceptualization, funding acquisition; writing - review & editing; **KK**: software; methodology, writing – review and editing; **SK**: conceptualization, methodology, funding acquisition, writing - review & editing; **DAP**: conceptualization, methodology, resources, supervision, project administration, funding acquisition, writing - review & editing; **DCG**: conceptualization, methodology, resources, project administration, funding acquisition, writing - review & editing. All authors have contributed to manuscript reviewing and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2023.121626.

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