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Emerging organic contaminants in groundwater under a rapidly developing city (Patna) in northern India dominated by high concentrations of lifestyle chemicals☆

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ABSTRACT

Aquatic pollution from emerging organic contaminants (EOCs) is of key environmental importance in India and globally, particularly due to concerns of antimicrobial resistance, ecotoxicity and drinking water supply vulnerability. Here, using a broad screening approach, we characterize the composition and distribution of EOCs in groundwater in the Gangetic Plain around Patna (Bihar), as an exemplar of a rapidly developing urban area in northern India. A total of 73 EOCs were detected in 51 samples, typically at ng.L^{-1} to low μg.L^{-1} concentrations, relating to medical and veterinary, agrochemical, industrial and lifestyle usage. Concentrations were often dominated by the lifestyle chemical and artificial sweetener sucralose. Seventeen identified EOCs are flagged as priority compounds by the European Commission, World Health Organisation and/or World Organisation for Animal Health: namely, herbicides diuron and atrazine; insecticides imidacloprid, thiamethoxam, clothianidin and acetamiprid; the surfactant perfluorooctane sulfonate (and related perfluorobutane sulfonate, perfluorohexane sulfonate, perfluorooctanoic acid and perfluoropentane sulfonate); and medical/veterinary compounds sulfamethoxazole, sulfanilamide, dapson, sulfathiazole, sulfamethazine and diclofenac. The spatial distribution of EOCs varies widely, with concentrations declining with depth, consistent with a strong dominant vertical flow control. Groundwater EOC concentrations in Patna were found to peak within ~10 km distance from the River Ganges, indicating mainly urban inputs with some local pollution hotspots. A heterogeneous relationship between EOCs and population density likely reflects confounding factors including varying input types and controls (*e.g.* spatial, temporal), wastewater treatment infrastructure and groundwater abstraction. Strong seasonal agreement in EOC concentrations was observed. Co-existence of limited transformation products with associated parent compounds indicate active microbial degradation processes. This study characterizes key controls on the distribution of groundwater EOCs across the urban to rural transition near Patna, as a rapidly developing Indian city, and contributes to the wider understanding of the vulnerability of shallow groundwater to surface-derived contamination in similar environments.

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1. Introduction

Aquatic pollution from legacy and emerging organic contaminants (EOCs) is of increasing attention and concern in India (Lapworth et al., 2018; Philip et al., 2018; Sharma et al., 2019) and globally (Kasprzyk-Horndern et al., 2008; Kim et al., 2016; Lapworth et al., 2012, 2015a; Loos et al., 2013; Pal et al., 2010; Sorensen et al., 2015; White et al., 2019). EOCs represent a broad range of agrochemicals (Solomon et al., 2000), human and veterinary pharmaceuticals (Kolpin et al., 2002; Richmond et al., 2018), lifestyle products (Kasprzyk-Horndern et al., 2008; Lange et al., 2012) and personal care products (Brausch and Rand, 2011). Numerous sources can contribute to aqueous EOCs, including raw or treated wastewater discharge (Kasprzyk-Horndern et al., 2008; Writer et al., 2013), run-off from agricultural, farming and livestock activities (Lapworth et al., 2012; Lupo et al., 2012), industrial processes (Lübbert et al., 2017), urban drainage (You et al., 2015) and spills (Gavrilescu et al., 2015). The removal of EOCs via wastewater treatment remains difficult, costly and highly process-dependent (Glassmeyer et al., 2005; Loos et al., 2013; Subedi et al., 2015). As analytical techniques evolve (Richardson and Ternes, 2014), the ability to detect additional compounds at lower concentrations improves.

EOCs have been used to trace the fate and transport of pollutants in aqueous systems (Glassmeyer et al., 2005; James et al., 2016; White et al., 2019) including to determine groundwater vulnerability in northern India (Lapworth et al., 2018). Commonly used artificial sweeteners (Lange et al., 2012; Tran et al., 2014a) and the pharmaceutical carbamazepine (Chakraborty et al., 2019; Hai et al., 2018) have been used as indicators of wastewater inputs. Sucralose, in particular, has been used as a reliable wastewater tracer (Loos et al., 2013; Oppenheimer et al., 2011; Scheurer et al., 2009; White et al., 2019; Yang et al., 2017) due to environmental persistence (Batchu et al., 2013), lack of bioaccumulation (Roberts et al., 2000), minimal degradation during wastewater treatment (Scheurer et al., 2009; Torres et al., 2011) and widespread occurrence (Batchu et al., 2013; Loos et al., 2013).

A major concern regarding EOCs in aqueous environments is the potential development of antimicrobial resistance, exacerbated by the presence of low-concentration antimicrobials (Amos et al., 2015; Hawkey, 2008; Lupo et al., 2012; Martinez et al., 2009; Szmolka and Nagy, 2013). The World Health Organisation (WHO) has developed a ranking and categorization of priority antimicrobials used in human medicine and associated risk management guidelines (World Health Organization, 2018); prioritized antimicrobials for veterinary medicine are similarly categorized (World Organisation for Animal Health (OIE), 2018).

Further, disruptions to ecological processes and functions in freshwater ecosystems due to EOCs is a growing concern (Richmond et al., 2017). The European Commission (EC)'s Water Framework Directive includes 33 regulated Priority Substances, as well as 8 other pollutants included in the Environmental Quality Standards Directive 2008/105/EC (European Commission, 2019), amended by Directive (2013)/39/EU (European Commission, 2013). The EC's dynamic surface water Watch List, initially published in 2015 (Carvalho et al., 2015) and updated in 2018 (European Commission, 2018), targets pollutants for high priority monitoring and regulatory consideration. The development of a voluntary groundwater watch list has been recently proposed to be viable (Lapworth et al., 2019) with an associated prioritization framework (Gaston et al., 2019). Additionally, highest priority pharmaceuticals for monitoring in China have recently been identified (Li et al., 2020). Predicted no-effect concentrations (PNECs) have been developed for some compounds on the basis of bacterial resistance selection and ecological toxicity (Tran et al., 2018 and references within), and some health-based drinking water advisory levels are in place (Cordner et al., 2019; US EPA, 2016).

This is particularly important in India as one of the world's largest antibiotics consumers (The Center for Disease Dynamics, 2015) and as a globally leading pharmaceutical producer (Greene, 2007). A recent review highlighted that EOC screening in India remains relatively scarce and especially focussed in the south (Philip et al., 2018), although there is increasing attention on northern India (Duttagupta et al., 2020; Kumar et al., 2019; Lapworth et al., 2018; Sharma et al., 2019; Williams et al., 2019). Given that groundwater demand in India is high and increasing, and most drinking water supplies are derived from groundwater in the Ganges Basin (MacDonald et al., 2016), the vulnerability of groundwater to surface-derived contamination is of key importance (Lapworth et al., 2015b, 2017, 2018), particularly in rapidly developing urban areas. Geochemical conditions in groundwater near rapidly developing cities are uniquely defined particularly by inputs from urban wastewaters and high organic content (Lawrence et al., 2000), perhaps also leading to unique EOC signatures reflecting emerging (Lapworth et al., 2018), rather than legacy, contaminants.

The aim of this paper is thus to systematically characterize, for the first time, the spatial distribution of groundwater EOCs in and around the rapidly developing urban center of Patna (Bihar), as an exemplar of a rapidly developing urban center in northern India. Using a broad screening approach, the specific objectives are to: (i) quantify and characterize groundwater EOCs, including in comparison to EC, WHO and/or OIE priority lists and PNEC/health advisory values; (ii) analyze the spatial distribution of groundwater EOCs with respect to depth, distance from the River Ganges, distance from urban centers, and seasonality, along the geographical transition from rapidly developing urban areas to peri-urban and rural areas (including a separate control site in Ballia (Uttar Pradesh)); and (iii) identify relationships between any detected parent compounds and associated transformation products.

2. Methods

2.1. Field area

The field area is in the Middle Gangetic Plain, India (Fig. 1). Groundwater sampling sites (Richards et al., 2020) were focussed near and around the urban center in Patna District (Bihar, Eastern region) (n = 37), with additional limited sites in a relatively rural area in Ballia District (Uttar Pradesh, Central region) (n = 7) as a control comparison with low urban growth. Sample locations were selected to represent multi-depth transects (T1, T2 and T3 in Patna, and T4 in Ballia) in incremental, increasing distance from the River Ganges (Figure S1), and, in Patna, transitions from dominantly urban to peri-urban to rural areas. Patna city (Bihar capital) is a rapidly developing "Smart City" under the Government of India Scheme for Smart City Project and Atal Mission for Rejuvenation and Urban Transformation, with the Patna District urban population of ~2.5 million (Government of India, 2011) heavily centered within ~5–10 km of the Ganges River. The Ballia transect T4 is ~10 km from Ballia city (subdistrict population of ~140,000) (Government of India, 2011), further covering a transition between relatively new and old alluvial deposits between the Ganges and Ghagara Rivers. Hydrogeological characterization of Bihar (Saha, 2009; Saha et al., 2011) and Ballia (Chauhan et al., 2009), and typical seasonal groundwater level fluctuations in Varanasi (Lapworth et al., 2018), have been reported by other authors.

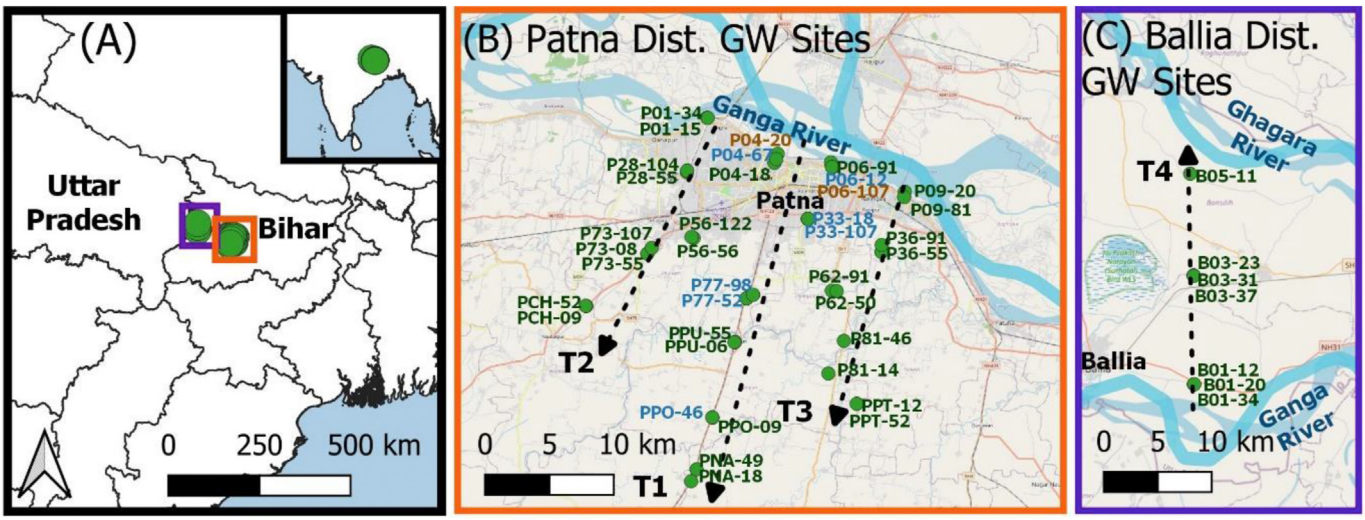

Fig. 1. Field site map (A) in Bihar and Uttar Pradesh, northern India; zoom to (B) main Patna District groundwater (GW) EOC sampling sites (green dots); and (C) Ballia District sampling sites. Sample IDs are XXX-YY where XXX is a site ID and YY is depth (m); green ID = post-monsoon sampling; blue ID = paired post- and pre-monsoon sampling of identical well; brown ID = pre-monsoon sampling only. Open-access layers obtained from OpenStreetMap (www.openstreetmap.org) and Natural Earth (https://www.naturalearthdata.com/). River centerlines have been exaggerated and do not represent river width. Transects (T1, T2, T3, T4) and arrow heads are oriented in increasing direction from the River Ganges; depths of sampling sites are shown on Figure S1. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2.2. Water sample collection

Groundwater sampling was conducted during two seasons: (i) pre-monsoon in July 2019 (n = 9 samples, Patna only) and (ii) post-monsoon in November–December 2019 (n = 42 samples, Patna and Ballia). The seasonal split was allocated according to sampling priorities and logistic feasibility. Groundwater was typically collected, after flushing, from handpumps or submersible pumps connected to private or public wells (predominantly used for drinking), at representative depths ranging from ~6 to 120 m (Richards et al., 2020). Site/sample IDs are coded as XXX-YY-(PRE), where XXX is a site code (beginning with P or B for Patna or Ballia, respectively), and YY is well depth (in m); "PRE" indicates pre-monsoon.

Water samples (unfiltered) for EOC analyses were collected in 1 L glass bottles prepared by the UK National Laboratory Service (NLS), sealed using Parafilm M airtight sealing film to prevent leakage. Nitrile gloves were worn at all times during sample collection. Prior to use, bottles were stored closed and away from potential sources of contamination. After collection, samples were transported to the UK in non-temperature controlled airfreight and delivered to NLS as soon as possible upon customs clearance. Upon arrival at NLS samples were stored at 5 ± 3 °C prior to analysis.

2.3. Chemical analysis

Chemical analysis was conducted at the NLS Environment Agency laboratory (Starcross, UK). Solid phase extraction (SPE) was conducted with an automated extraction system using Waters Oasis HLB SPE cartridges, pre-conditioned with 6 mL of methanol followed by 6 mL of ultra-high purity water. A 500 mL water sample was loaded onto the cartridge at a flow rate of 10 mL min^{-1}. An isotopically labelled internal standard (Carbutamide-d9) was added to each pre-conditioned SPE cartridge to assess instrument performance. After loading, the cartridge was washed with 6 mL of ultra-high purity water and the sorbent dried fully with high purity nitrogen, followed by elution with 6 mL of 0.1% formic acid in methanol:acetonitrile (1:1) then 6 mL of dichloromethane. The eluted fractions were collected separately, with the dichloromethane eluate evaporated to incipient dryness under a gentle nitrogen stream. The corresponding methanol:acetonitrile eluate was transferred to dry dichloromethane vials and evaporated to 100 μL. Ultra-high purity water (900 μL) was added to each vial to a total volume of 1000 μL. The sample was vortex mixed, filtered (Whatman-Spartan 13/0.2 RC) and transferred to a salinized screw top vial for analysis. Ultra-high Performance Liquid Chromatography/Quadrupole-Time-of-Flight Mass Spectrometry (LC/Q-TOF-MS) analysis was performed using a semi-quantitative method on an Agilent Q-TOF (model 6545). This broad screening approach allows for semi-quantitation of >750 compounds. Additional analytical and QA/QC details are provided in Supplementary Information.

2.4. Data processing and analysis tools

EOC data was compiled using a customized C# application. Statistical analysis was conducted using OriginPro 2017. Regression statistics were calculated via simple linear regression models and are reported, on the basis of slope, as "*t(degrees of freedom) = t statistic; p = p value*" at 95% confidence. Maps were created using QGIS (version 3.12.2 București) with open access layers from OpenStreetMap (www.openstreetmap.org) and Natural Earth (https://www.naturalearthdata.com/). Population density data was from LandScan 2018™ High Resolution Global Population Data Set, and is used under a License for Educational Use and Academic Research (Rose et al., 2019); please see license/usage details (https://landscan.ornl.gov/license). Extraction of population density data was conducted using ArcMap (ESRI, 2016) with a 200 m buffer zone at each site. The PubChem database at the National Institutes of Health was used to screen primary compound usage; this was verified for medical compounds where possible (American Society of Health-System Pharmacists, 1959–2020; Hochadel, 2009–2020).

3. Results and discussion

3.1. Occurrence of emerging organic compounds

A total of 73 EOCs were detected within the 51 groundwater samples (Table S1). Concentrations of individual compounds ranged from below the limit of identification (typically 0.001–0.1 μg.L^{-1}, Table S1) to a maximum of 1.2 μg.L^{-1} (sucralose). The detection frequency in groundwater (F_{GW}) ranged from 2% to 41%, with the highest frequency compounds sucralose, fluconazole, diuron and carbamazepine (Figure S2 and Table S1). Within a single sample, a wide range of compounds were detected (ranging from 0 to 24 compounds), typically reflecting mixed contributions from medical/veterinary, agrochemical, industrial and lifestyle chemicals (Fig. 2). The maximum concentration (C_{max}) of the sum of EOCs was 2.3 μg.L^{-1}, with lifestyle components usually by far the largest contributor to total concentration. Sub-categories of dominant usage are described individually.

Importantly, seventeen detected EOCs have been flagged for priority monitoring and/or regulatory importance (see Table S1 for summary statistics and Table S2 for sample specific concentrations). Compounds on the *EC Priority Substance list* (European Commission, 2019) include diuron and atrazine. Compounds on the *EC 2018 surface water Watch list* (European Commission, 2018) include imidacloprid, thiamethoxam, clothianidin and acetamiprid, all of which are in the neonicotinoids insecticides class. Perfluorooctane sulfonate (PFOS) was detected, along with four other related compounds (perfluorobutane sulfonate, perfluorohexane sulfonate, perfluorooctanoic acid and perfluoropentane sulfonate), all in the broader category of perfluoroalkylated substances; perfluorooctane sulfonic acid and its derivatives are *EC Priority Hazardous Substances* in EC Directive 2013/39/EU (Environment Agency, 2019; European Commission, 2013). A further compound which was on the first 2015 EC *surface water Watch List* (Carvalho et al., 2015), but which has been removed upon update, is the pharmaceutical diclofenac. Compounds on the *WHO Highly Important Antimicrobial list* (World Health Organization, 2018) include sulfanilamide, sulfamethoxazole, dapson and sulfathiazole. Compounds on the *World Organisation for Animal Health Veterinary Critically Important Antimicrobial Agents list* (World Organisation for Animal Health (OIE), 2018) include sulfanilamide (also on WHO list) and sulfamethazine. Clopidol is included on the recently proposed *voluntary groundwater watch list* (CIS Working Group Groundwater, 2019; Lapworth et al., 2019).

The overall profile of EOCs detected has mixed consistency with what has been previously reported in northern India. The EOC profile is generally similar to what has been previously reported in Varanasi (Lapworth et al., 2018). The relatively high frequency of carbamazepine here is consistent with carbamazepine in Hooghly River sediment (Chakraborty et al., 2019). Concentrations of PFOS here are very similar to previous groundwater studies in the Gangetic basin including near Patna (Sharma et al., 2016). Other detected compounds (*e.g.* atenolol, carbamazepine, cetirizine, diclofenac, fluconazole, sucralose, sulfamethoxazole and triclosan) are consistent with a recent review (Philip et al., 2018 and references within). Some notable differences include previously reported compounds in India that were not detected here (*e.g.* amoxicillin, caffeine, ciprofloxacin and ibuprofen; not exhaustive). Caffeine in particular has been widely reported (Ben et al., 2018; Deblonde et al., 2011; Sharma et al., 2019; Tran et al., 2018; Williams et al., 2019), although not detected here, noting that caffeine is easily biodegraded (Tran et al., 2018) and the impact of storage time prior to analysis cannot be precluded. In addition to variable and location-specific inputs, previous studies have varied in terms of extraction and analytical procedures (*c.f.* Philip et al., 2018).

3.1.1. Medical and veterinary compounds

The dominant usage of ~45% (n = 33) of the detected compounds is for medical and veterinary purposes; see Table S1. The four antibiotics, sulfamethoxazole, sulfanilamide, sulfamethazine and sulfathiazole, are all sulfonamides. Dapson is an antimicrobial and anti-inflammatory drug. The veterinary drugs sulfanilamide and sulfamethazine are used in a wide range of animal species

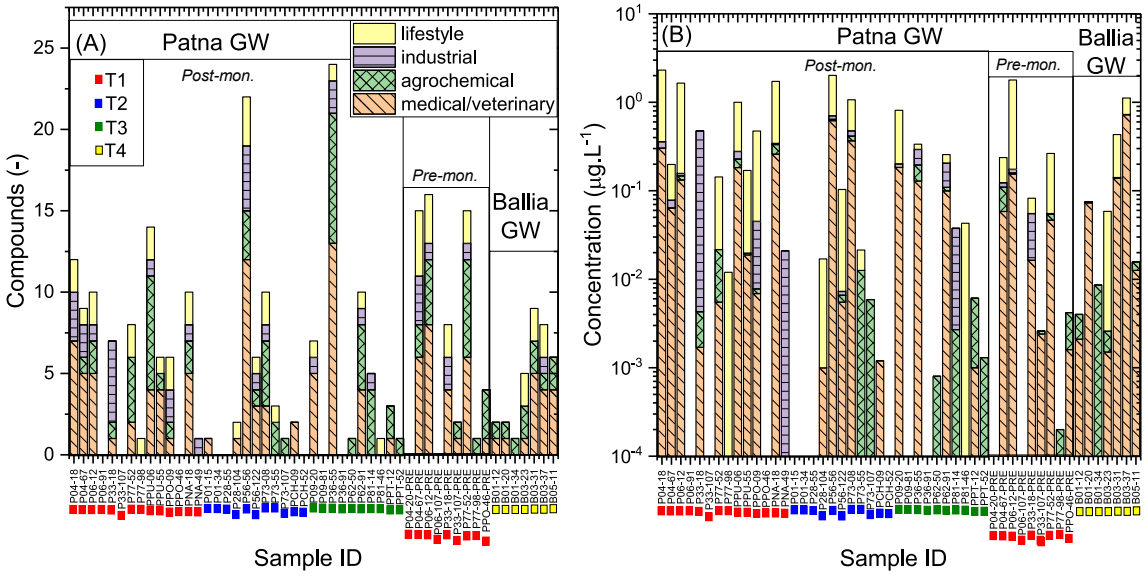

Fig. 2. Main category/usage sub-groups of all samples (n = 51 samples) showing (A) number of compounds detected (in total 73 compounds) and (B) total EOC concentration (log-scale) per sample ID. Individual samples are represented by a single stack column, sub-divided for Patna (post-monsoon and pre-monsoon) and Ballia groundwater (GW). Sample IDs are ordered by (1) transect as indicated by color tag; (2) increasing distance from River Ganges; and (3) increasing depth at a particular site; see corresponding site map (Fig. 1) and sampling depth profile (Figure S1). No compounds were detected in 10 samples; for P01-15 concentration is not available (aspirin reported as presence/absence only). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(World Organisation for Animal Health (OIE), 2018). Compounds at low frequency tend to be spread across multiple sites rather than converging on the same or similar locations.

3.1.2. Agrochemicals

The detected agrochemicals (n = 27) represent a wide range of herbicides, insecticides, fungacides and pesticides. Herbicides (diuron, atrazine, 2,6-dichlorobenzamide, fenuron, monuron, bentazone, atrazine-desethyl, bromoxynil, cycluron, haloxyfop-methyl and pendimethalin) are the most frequently detected agrochemicals, noting many detected compounds are components of registered herbicides in India (Choudhury et al., 2016). Insecticides include imidacloprid, thiamethoxam, clothianidin, acetamiprid, buprofezin (noting a proposed ban in India has gained substantial public commentary (AgroPages, 2020)); flubendiamide; triazophos and fipronil. Fungicides include carbendazim, tricyclazole (proposed to be banned with buprofezin (AgroPages, 2020)), metalaxyl, hexaconazole, azoxystrobin, carboxin and cyprodinial.

3.1.3. Industrial compounds

The industrial compounds (n = 9) are used for a variety of purposes. Surfactants include perfluorobutane sulfonate, perfluorohexane sulfonate, perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluoropentane sulfonate, belonging to the group of anthropogenic chemicals known as perfluoroalkyl and polyfluoroalkyl substances (PFAS) (Environment Agency, 2019; Organisation for Economic Co-operation and Development (OECD), 2007). Other compounds include flame retardants melamine and triphenyl phosphate, and compounds used in plastics (*e.g.* bisphenol S) and dyes (*e.g.* acridine).

3.1.4. Lifestyle compounds

Lifestyle compounds (n = 4) typically dominate the total EOC concentration in groundwater, even though the number of compounds detected is less than the other sub-categories. The lifestyle compounds are comprised mostly of artificial sweeteners (sucralose, acesulfame and saccharin) and the tobacco biomarker cotinine.

3.2. EOC comparison to predicted No-Effect concentration (PNEC) and health advisory values

Although the purpose of this study is not to provide a formal nor comprehensive risk assessment, measured EOC concentrations are compared to selected published PNEC (Tran et al., 2018) or health advisory (US EPA, 2016) values (Figure S3). The two compounds with resistance-based PNECs (sulfamethoxazole and sulfamethazine) are well below resistance PNEC values for all samples, suggesting likely low risk of bacteria resistance selection. However, one compound, carbamazepine, is in exceedance of its ecotoxicity-based PNEC (25 $ng.L^{-1}$) (Tran et al., 2014b) in two samples (P04–18 and B03-37). Previous studies have identified moderate risks for aquatic organisms from sulfamethoxazole and triclosan, amongst other compounds, in the River Ganges (Sharma et al., 2019). The total concentration of PFAS was in exceedance of the U.S. Environmental Protection Agency drinking water health advisory level of 70 $ng.L^{-1}$ (Cordner et al., 2019; US EPA, 2016) in one sample (P33-18). It is noteworthy that our results show that even groundwater EOCs, albeit for a limited number of samples and compounds, can be near or in exceedance of PNEC or health advisory values, particularly as most of the water samples are known to be used for drinking water and for other domestic purposes. Other compounds with ecotoxicity-based PNECs for aquatic organisms were far below PNEC values (*e.g.* sulfamethoxazole, atenolol, diclofenac and triclosan).

3.3. Distribution of EOCs in groundwater

The spatial distribution of EOCs (Fig. 3) shows that composition and concentration varies widely. Groundwater EOCs in Patna (Fig. 3A) and Ballia (Fig. 3B) districts are widely distributed and include compounds, at varying proportions, from each of the identified sub-categories. In Patna District, concentrations and diversity of compounds are typically highest near the urban center (which is located in relatively close proximity to the River Ganges) as well as in relatively large villages (whilst noting substantial localized influences in some areas); in contrast concentrations are generally lower and dominated by agrochemicals in rural areas in the southeast part of the sampling frame. Approximately half of the samples where no EOCs were detected are located very close to river banks, with the others distributed throughout the study area and typically deriving from deeper samples. In the Ballia samples, concentrations and categories are broadly similar to what is seen in the more rural, southern areas of Patna District. Whilst total number of compounds is highly correlated with total EOC concentration ($t(49) = 6.2$; $p < 0.01$; Figure S4) in general, it is important to note that there are exceptions to this; for example P36-55 has the highest number of compounds (n = 24), yet the total concentration is comparatively low (~0.3 $\mu g.L^{-1}$). The important implication here is that observations based on concentration versus compounds may be different in some cases.

Depth profiles of EOCs in groundwater indicate that a wide range of EOCs are detected even to depths of >100 m (Fig. 4). The peak total number of compounds detected occurs ~60 m in depth and is dominated by medical/veterinary compounds as well as contributions from agrochemicals (Fig. 4A). There are >10 EOCs detected for most depths, which is fairly widely distributed across the depth range, and there is no statistically significant correlation between total compounds and depth. The significantly correlated relationship between total EOC concentration and depth reveals that total EOC concentrations are highest at shallow depths, especially < ~20 m, ($t(49) = -2.7$; $p < 0.05$) (Fig. 4B), and is broadly consistent with previous observations in Varanasi (Lapworth et al., 2018). Total concentrations throughout the depth profile are heavily dominated by contributions from lifestyle compounds. Sucralose, a wastewater indicator, and depth are also significantly correlated ($t(49) = -2.2$; $p < 0.05$), with the highest sucralose concentrations (up to ~ 1.2 $\mu g.L^{-1}$) clearly occurring at shallow depths although still present at high concentrations (~0.9 $\mu g.L^{-1}$) even at depths of ~60 m in a localized area (Fig. 4C). Notably, the total number of EOCs, EOC concentrations and sucralose were all substantially lower and restricted to a narrower depth range in Ballia as compared to Patna. Importantly this reveals that groundwaters in rapidly developing urban areas, such as in Patna, are vulnerable to the influence of surface-derived organic contamination, particularly at shallow depths as well as in deeper aquifers in localized areas. Such localized influences could plausibly be attributed to geological high-permeability windows in the sub-surface and/or from poorly constructed boreholes, contributing to rapid downward transport of surface-derived contamination.

The relationship between groundwater EOCs and approximate perpendicular distance to the Ganges River (Fig. 5) is more heterogeneous than the depth-dependency. The number of EOCs, EOC concentration and sucralose concentration all peak within approximately 10 km of the river, consistent with urban inputs expected particularly from Patna. Interestingly, the number of compounds (Fig. 5A) peaks farther away from the river (*e.g.* ~ 5–10 km) where the urban center of Patna is located, whereas the EOC and sucralose concentrations are highest even closer to the river (*e.g.* ~ 0–5 km) (Fig. 5B and C). Importantly, however, localized elevated EOC compounds and concentrations

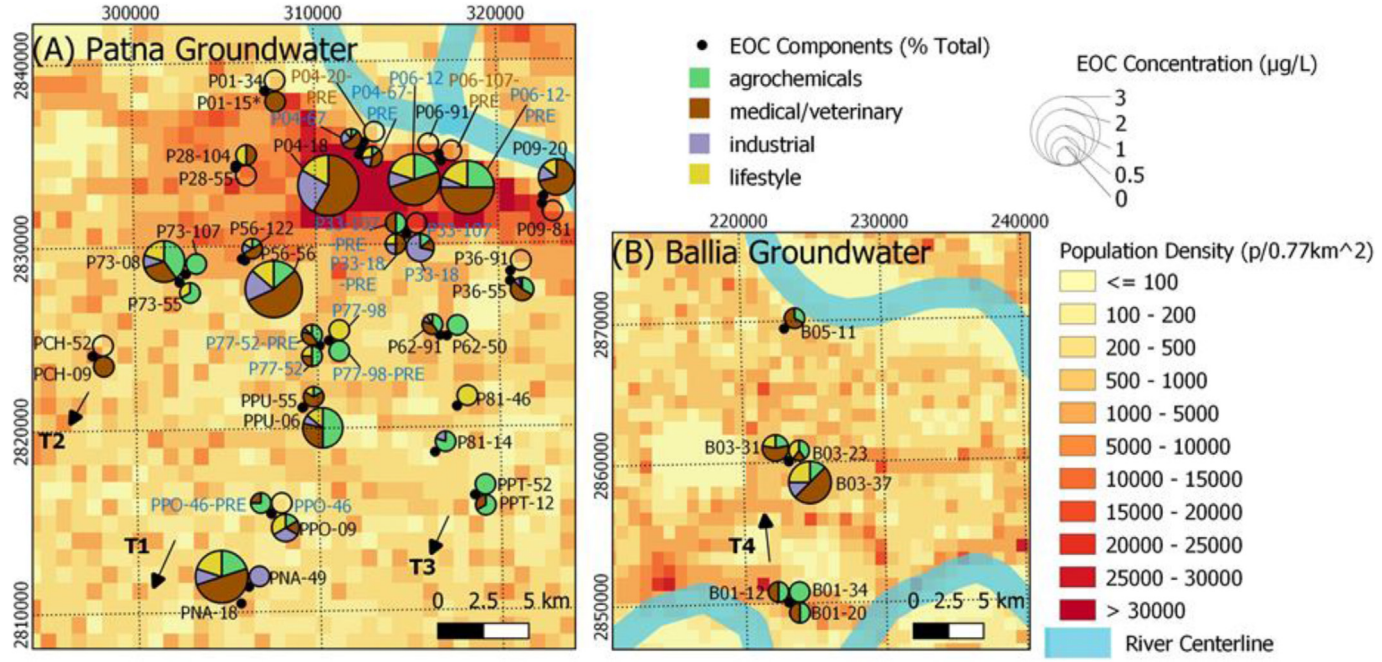

Fig. 3. Distribution of EOCs with symbol colors representing pie charts of the composition of EOCs on the basis of relative proportions of sub-categories of dominant usage (agrochemicals, medical/veterinary, industrial and lifestyle) of detected compounds and symbol size representing total EOC concentration in groundwater in (A) Patna and (B) Ballia. Pie charts have been offset from sampling points (black dots) in some cases to avoid data overlap. Black sample ID = post-monsoon sampling; blue ID = paired post- and pre-monsoon sampling of identical well; brown ID = pre-monsoon sampling only; *P01-15 concentration quantitation not possible as compound detected (aspirin) is presence/absence only. Underlying layer shows population density data from LandScan 2018™ High Resolution Global Population Data Set, used under a License for Educational Use and Academic Research (Rose et al., 2019); see website (https://landscan.ornl.gov/license). River centerlines have been exaggerated and do not represent river width. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

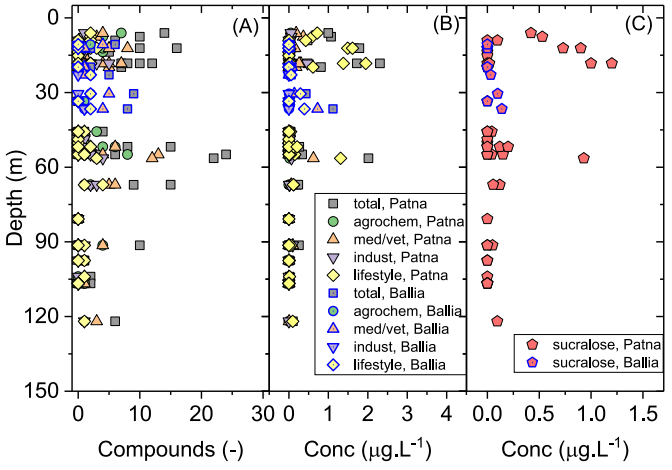

Fig. 4. Well depth versus (A) number of EOC compounds and (B) concentration of EOCs, total and subcategorized by dominant usage (agrochemicals, medical/veterinary, industrial and lifestyle), and (C) sucralose in pre- and post-monsoon groundwater. Non-detected sucralose concentrations are plotted as 0 µg.L^{-1}. Symbols with blue edge and center mark are from Ballia; others from Patna. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

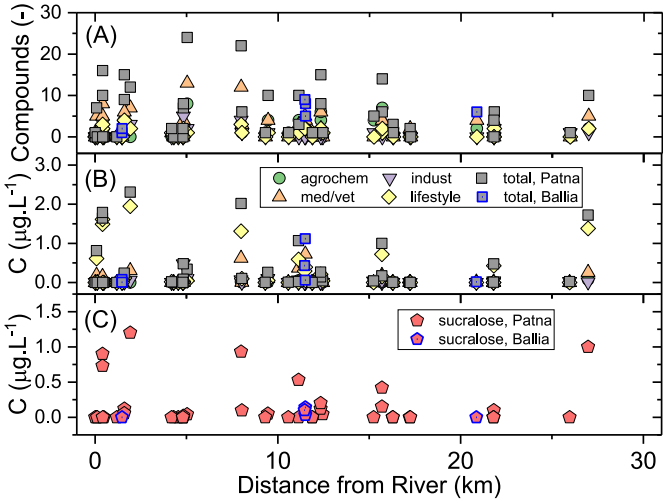

Fig. 5. (A) Number of EOC compounds and (B) concentration of EOCs, total and sub-categorized by dominant usage (agrochemicals, medical/veterinary, industrial and lifestyle), and (C) sucralose in pre- and post-monsoon groundwater against perpendicular distance from the Ganges River. Non-detected sucralose concentrations are plotted as 0 µg.L^{-1}. Symbols with blue edge and center mark are from Ballia; all others are from Patna. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

are also found much farther from the Ganges, particularly in a shallow sample at the farthest site ~27 km away (sample PNA-18, T1). Especially due to this apparent heterogeneity, there is no statistically significant relationship (at the $p < 0.05$ level) between Ganges river distance and EOC compounds or concentration, either for the Patna or Ballia sub-sets. This suggests that the dominant flow control is vertical rather than horizontal, and that localized surface influences can impact groundwater regardless of immediate proximity to the main river corridor. Horizontal groundwater gradients are typically very low in the Gangetic floodplain, with vertical flow dominating overall (Lapworth et al., 2015b). In the case of Ballia, wedged between the Ganges and Ghagara Rivers, there appears to be a peak in EOCs at the middle site (~12 km along

T4) which suggests that surface-derived EOC inputs farther from the rivers are likely greater than those deriving from groundwater-surface water interactions, and thus that the River Ganges is likely to be a receptor rather than a source of groundwater EOCs.

Given the heterogeneous trends, the distribution of EOCs is further unpicked by a transect-specific depth-distance-EOC bubble representation (Figure S5). Here the highest EOC compounds and concentrations are again observed, particularly in shallow samples within the 0–10 km distance range, within the overall set (Figure S5A) and for specific Patna transects T1, T2 and T3 (Figure S5B, C, D, respectively). In Ballia (T4, Figure S5E) the highest concentrations are instead observed in the middle sample in the older alluvial sediments between the Ganges and Ghagara rivers, noting that both compounds and concentrations are generally lower than in Patna. Several localized "hot spot" areas (*e.g.* P56, P36, P04, P06, PPU, PNA) are distributed across the study area, although with generally higher prevalence near Patna. Observed trends in sucralose (Figure S5F) are consistent with the overall EOC observations.

3.4. Relationship between groundwater EOCs and population density

The relationship between groundwater EOCs and population density (in a 200 m buffer zone around the well location) shows a mixed relationship (Fig. 6). The highest number of EOC compounds occur in areas of relatively low population density; this is particularly observed in Ballia ($t(5) = -4.8$; $p < 0.01$) where there are less urban inputs and fewer competing processes likely to impact local hydrogeochemical conditions (Fig. 6A). This may be counter-intuitive, however in such rural areas open defecation is highly prevalent and a common habit, and in addition treatment facilities are very limited or non-existent, leading to potential direct inputs of compounds associated with un-treated domestic waste, as well as agrochemicals which are widely applied in agricultural areas. In Patna, this overall relationship between EOC compounds and population density trends towards a positive correlation but is not statistically significant ($t(42) = 1.6$; $p = 0.1$), noting the highest number of components is still observed in areas of lower population density. In Patna, a positive correlation could be explained by higher populations contributing to higher people-based and urban inputs. Conversely, the inverse relationship of high inputs at low population densities in Patna could plausibly be attributed to inputs from hospitals or factories where apparent population density may be lower but inputs might be disproportionally higher, more advanced wastewater treatment particularly in urban centers, transport of waste into peripheral zones, or the same processes described for Ballia (noting that the Patna sampling covered both urban and rural areas). Similar mixed trends in total EOC and sucralose concentration (Fig. 6B and C) support that high levels of EOCs can occur in areas of varying population density. The notable elevated point at the highest population density of ~55,000 p. km^{-2} is located in a shallow sample (P04-18) in a very busy part of the city in very close proximity to high capacity housing where relatively high domestic inputs (including lifestyle compounds) might be reasonably expected.

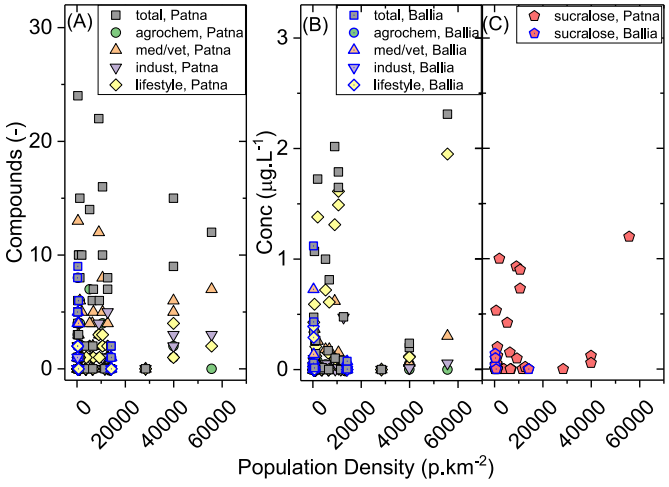

Fig. 6. (A) Number of EOC compounds and (B) concentration of EOCs, total and sub-categorized by dominant usage (agrochemicals, medical/veterinary, industrial and lifestyle), and (C) sucralose in groundwater against estimated population density. Non-detected sucralose concentrations are plotted as 0 µg.L^{-1}. Symbols with blue edge and center mark are from Ballia; others from Patna. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.5. Seasonal variation of groundwater EOCs

The composition of EOCs in groundwater are strongly correlated between the pre-monsoon and post-monsoon 2019 season (Figure S6), indicating that seasonal differences (at least on the basis of a single sample year) are generally less prevalent than site-based controls. Total EOC compounds are highly correlated seasonally (Figure S6A; $t(5) = 6.6$; $p < 0.01$), with the number of compounds (especially agrochemicals and medical/veterinary compounds) generally higher in the dry pre-monsoon season (slope = 1.4); this suggests that some dilution or flushing may occur during or after the monsoon season due to higher ingress of monsoon-based recharge and/or changing groundwater flow gradients. In West Bengal, seasonally variable groundwater flow patterns are impacted by both aquifer structure and pumping (Mukherjee et al., 2007); this could also be reasonably expected in Bihar. Usage of some compounds (*e.g.* agrochemicals) may be higher pre-monsoon. However, as seasonal concentrations are also highly correlated but with a slope much closer to 1 (*e.g.* slope = 1.05; $t(5) = 7.9$; $p < 0.01$; Figure S6B), the increase in number of pre-monsoon components only leads to a small change in overall concentration. There is a notable exception to this (site P33-60), where additional industrial components (*e.g.* melamine, acridine and perfluoropentane sulfonate) and concentrations increase post-monsoon; this is likely indicative of local industrial inputs or could be due to a nearby drainage channel contributing to ingress of surface-derived EOCs.

3.6. EOC parent and transformation compounds

A very limited number of parent compounds and associated transformation products (TPs) included in the LCMS screen have been identified. Parent compound atrazine was found in one sample (P77-52-PRE) at lower concentrations than TP atrazine-desethyl detected at another site (PPT-12). The observation that both parent and TPs were observed indicates a variability in the timing and relative processing of inputs, noting the adsorption coefficient of atrazine is higher than that of atrazine-desethyl (Brouwer et al., 1990). Atrazine was not detected in the corresponding post-monsoon sample of the same well. The parent compound carbamazepine was found in many samples (n = 16), however the corresponding TP acridine was only detected in one sample. This indicates that carbamazepine has not undergone significant degradation, consistent with carbamazepine's relatively high environmental persistence and high dissipation half-life (median ~ 300 days, estimated from recirculating plume experiments (Jaeger et al., 2019; Posselt et al., 2020)). Interestingly, of two identical wells sampled pre- and post-monsoon where

carbamazepine was detected in both seasons, the shallow well (P06-12) had identical carbamazepine concentrations across seasons, whereas the deeper well (P77-170) had much higher concentrations of carbamazepine post-monsoon (73 ng.L^{-1}) than pre-monsoon (27 ng.L^{-1}), indicating an additional input during the monsoon. The detection of selected TPs suggests the presence of an active microbial community, although, particularly given limited sample numbers, it remains unclear if transformation processes are likely to be occurring in shallow soil/sediments or in groundwater itself.

In addition, the parent compound fipronil was identified without detection of known TPs included in the LCMS screen (*e.g.* fipronil sulfide; fipronil sulfon). Notably, fipronil has a relatively low half-life in water on the order of 10s of days (Chopra and Kumari, 2009), indicating relatively fast dissipation. The detection of parent compounds in the absence of TPs suggests a relatively low degree of environmental processing of those compounds. Bacterial diversity is a major control on the transformation of wastewater-derived organic compounds, and may particularly impact the transformation of specific compounds (Posselt et al., 2020). Conversely, one TP, chlorothiazide, was quantified, although the corresponding and relatively persistent parent compound hydrochlorothiazide was not, noting that biodiversity significantly impacts hydrochlorothiazide transformation (Posselt et al., 2020). Importantly chlorothizide is also used as a diuretic; the origin here is unknown. In additional to microbial processes, other processes are also expected to impact environmental dissipation, including sorption, particularly for compounds with relatively high log K_{OW} (such as carbamazepine) (Jaeger et al., 2019), and photolysis (Baena-Nogueras et al., 2017). In addition, degradation and transport processes are challenging to disentangle, particularly as parent compounds and TPs have different transport rates, and, for diuron, solid phase concentrations are generally higher than porewater concentrations (Gooddy et al., 2002).

4. Conclusions

We have used a broad screening approach to identify and characterize groundwater EOCs in northern India in and around an exemplar rapidly developing urban center in Patna District (Bihar) as well as a comparatively rural area in Ballia District (Uttar Pradesh) with low urban growth. A total of 73 EOCs were detected within the 51 samples, typically at ng.L^{-1} to low μg.L^{-1} level concentrations, and were broadly categorized by dominant usage (*e.g.* medical and veterinary, agrochemicals, industrial and lifestyle). The lifestyle compound sucralose was most frequently detected and at highest concentration. Seventeen groundwater EOCs are flagged for priority monitoring and/or regulatory importance (herbicides: diuron, atrazine; insecticides: imidacloprid, thiamethoxam, clothianidin and acetamiprid; surfactants: perfluorooctane sulfonate, perfluorobutane sulfonate, perfluorohexane sulfonate, perfluorooctanoic acid and perfluoropentane sulfonate; medical/veterinary compounds: diclofenac, sulfanilamide, sulfamethoxazole, dapson, sulfathiazole and sulfamethazine) (Carvalho et al., 2015; European Commission, 2013, 2018; 2019; World Health Organization, 2018). In addition, clopidol is included on the recently proposed *voluntary groundwater watch list.* Concentrations of carbamazepine, although not a flagged substance, exceeded the published PNEC value for ecotoxicity in some samples, and total PFAS exceeded health advisory levels in one sample.

The spatial distribution of groundwater EOCs varies widely. Total EOC concentration and depth are significantly and inversely correlated, with highest concentrations in shallow groundwaters although localized elevated concentrations at greater depths are observed. This suggests that groundwater, especially in the Patna district, is vulnerable to the influence of surface-derived organic contamination, particularly at shallow depths as well as in deeper aquifers in localized areas. Localized influences could plausibly be related to well construction, aquifer heterogeneity or surface-derived draw down associated with high levels of groundwater abstraction. The relationship between groundwater EOCs and distance to the River Ganges is heterogeneous, with EOCs generally reaching a peak within ~10 km of the river, consistent with urban inputs expected from Patna, although elevated EOCs are also found much farther from the Ganges in some samples. These relationships suggest that the dominant flow control is vertical rather than horizontal, and is consistent with the model of ingress of surface-derived organics, as derived from rapidly developing cities, into groundwater. Evaluation of trends across specific sampling transects indicate localized EOC “hot spots”, generally with higher prevalence near the river and urban center of Patna (although these can also occur in more peri-urban or rural areas). The mixed relationship between groundwater EOCs and population density may reflect confounding factors such as varying types and amounts of inputs, and differences in groundwater withdrawal rates and wastewater treatment infrastructure. Pre- and post-monsoon EOCs are strongly correlated, indicating that both depth and localized influences are more important controls than seasonality. The detection of several parent compounds, with or without known associated TPs, likely reflects the relative degree of biodegradation of such compounds, noting that biogeochemical transformation processes are complex and impacted by microbial diversity and other processes such as sorption and photolysis. This current study provides important baseline characterization and information on the key controls on groundwater EOC distribution in the context of Patna, Bihar as an exemplar of a rapidly developing urban area in northern India. Further systematic monitoring of EOCs is recommended, particularly for the flagged compounds identified, and may contribute to understanding groundwater vulnerability in northern India and similar environments. Ongoing work is focusing on the processes associated with the ingress of organic matter into shallow aquifers and groundwater-surface water interaction.

Credit author statement

LAR: Formal analysis; Investigation; Data curation; Visualization; Supervision; Project administration; Methodology; Funding acquisition; Writing - original draft. RK: Investigation; Writing - review & editing. DW: Methodology; Writing - review & editing. NK: Investigation; Writing - review & editing. AK: Investigation; Writing - review & editing. AG: Conceptualization, Funding acquisition; Writing - review & editing; S Kumar: Investigation; Writing - review & editing. BC: Supervision; Writing - review & editing. CL: Software; Writing - review & editing. WC: Investigation; Writing - review & editing. DJL: Conceptualization; Methodology; Funding acquisition; Writing - review & editing. S Krause: Conceptualization; Methodology; Funding acquisition; Writing - review & editing. DAP: Conceptualization; Methodology: Resources; Supervision; Project administration; Funding acquisition; Writing - review & editing. DCG: Conceptualization; Methodology; Resources; Supervision; Project administration; Funding acquisition; Writing - review & 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.

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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.2020.115765.

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