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Typical emerging contaminants in sewage treatment plant effluent, and related watersheds in the Pearl River Basin: Ecological risks and source identification

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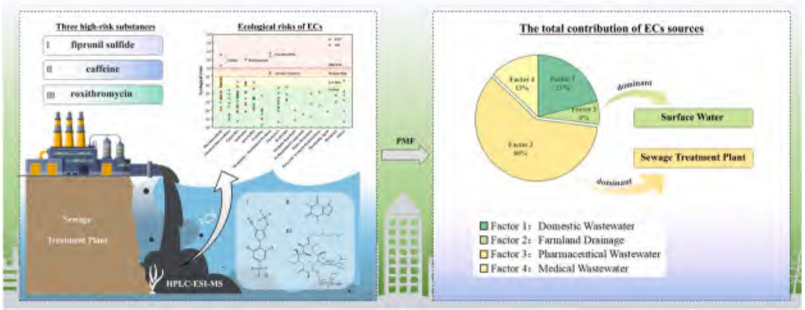
HIGHLIGHTS

- Analyzed ECs in sewage plants effluent and related watershed through HPLC-ESI-MS.
- Fipronil sulfide, caffeine, and roxithromycin were of high risk to aquatic organisms.
- Identified 4 sources: pharma, domestic sewage, medical effluent, & farmland drainage.
- Pharmaceutical wastewater was primary contributor to sewage treatment plant effluent.
- Agricultural drainage was the main source of contaminants in surface water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

Emerging contaminants pose a potential risk to aquatic ecosystems in the Pearl River Basin, China, owing to the high population density and active industry. This study investigated samples from eight sewage treatment plants, and five surface water bodies of related watersheds. To screen the risk of emerging contaminants (ECs), and clarify their sources, this study calculated the risk quotient of detected chemical and performed source identification/apportionment using the positive matrix factorization method. In total, 149 organic pollutants were identified. Pharmaceuticals showed significant concentrations in sewage treatment plant samples (120.87 ng/L), compared with surface water samples (1.13 ng/L). The ecological risk assessment identified three chemicals with a heightened risk to aquatic organisms: fipronil sulfide, caffeine, and roxithromycin. Four principal sources of contaminants were identified: pharmaceutical wastewater, domestic sewage, medical effluent, and agricultural runoff. Pharmaceutical wastewater was the primary contributor (60.4 %), to the cumulative EC concentration and to ECs in sewage treatment plant effluent. Agricultural drainage was the main source of ECs in surface water.

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This study provides a strategy to obtain comprehensive information on the aquatic risks and potential sources of EC species in areas affected by artificial activities, which is of substantial importance to pollutant management and control.

1. Introduction

Owing to the development of global manufacturing and urbanization, human requirements and demands are fulfilled by various commercial products and urban services. Long-term industrial activities have led to the massive consumption of chemicals and introduction of large amounts of waste into the ecosystem, creating millions of contaminated sites worldwide and posing potential threats to human health [1,2]. Emerging contaminants (ECs) are currently unregulated substances with no official emission standards, such as pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs), per- and polyfluoroalkyl substances (PFAS), surfactants, and industrial additives [3,4]. Due to the frequency of occurrence and potential risks of ECs, EC regulations are likely to be developed in the near future [5]. The impact of these pollutants does not depend on their persistence in the environment but on their high transformation and removal rates, which can be exacerbated by continuous entry into the environment [5].

The primary origin of ECs present in water bodies is sewage treatment plant discharge [4,6]. Most sewage treatment plants are designed to remove pathogenic biotics and biodegradable organic matter, leaving EC residues in treated sewage effluent [7,8]. PPCP, pesticides, persistent organic pollutants, and EDCs are frequently detected after sewage treatment, with removal efficiency for different chemicals varying from 20 % to 90 % [7,9,10]. During the dry season, when water flow rates are low, the ecological risk of the EC discharge into related watersheds may be higher than in other seasons, attributable to reduced dilution levels [9,11,12]. Because of the diverse nature of ECs across regions, conducting targeted and comprehensive investigations of ECs in sewage treatment plants and related watersheds in specific regions is crucial for effective management. Such information is essential for identifying and prioritizing chemicals that require additional management measures. Advanced analytical methods, such as high-resolution high-performance liquid chromatography-electrospray ionization-tandem mass spectroscopy (HPLC-ESI-MS), for targeted or non-targeted screening have substantially enhanced quantitative analysis and chemical species identification capabilities [13]. This technology has been applied to characterize and profile ECs in treated sewage and other water samples [14].

Many studies have characterized the occurrence, fate, and transport of ECs in sewage treatment plant effluents and surface waters [13,15,16]. Recently, the risks posed by some detected ECs have been assessed and confirmed in aquatic ecology studies [15,17,18]. Therefore, monitoring ECs has become a pressing concern for the scientific and industrial communities [6]. However, recent studies have mainly focused on a set of specific chemical derivatives at certain sites in watersheds [19,20]. In contrast, systematic studies on the profiling and ecological risk assessment of all identified ECs in sewage treatment plant effluents and related watersheds remain scarce. Information regarding risky ECs that are potentially transported from the effluent to the receiving water body is urgently necessary when screening chemicals of priority in monitoring and regulation.

Source identification and quantification of ECs are essential for preventing or reducing the risk of chemicals flowing into the environment. A series of statistical methods, such as cluster analysis, multivariable linear regression, and spatial autocorrelation, have been used for source apportionment [21–23]; among them, positive matrix factorization (PMF) is suitable for large datasets generated using mass spectrometry [24,25]. PMF is a multifactorial analysis tool that decomposes observed chemical composition data into a set of factors, each representing a potential pollution source contributing to the observed composition. These factors are characterized by their unique chemical profiles or typical pollutants, which are compared with known chemical signatures of potential pollution sources, such as industrial discharges, agricultural runoff, or urban wastewater. PMF can mitigate the issue of mixed sources and identify the sources of pollutants such as polycyclic aromatic hydrocarbons (PAHs), heavy metals, and volatile organic compounds [26]. Compared with other analytical tools, PMF is more reliable in terms of the accuracy of the sources, thereby enhancing the credibility of the analysis results. Therefore, PMF has become a commonly used tool for source apportionment.

The Pearl River Delta, adjacent to the west coast of the Pacific Ocean, is one of the most developed and prosperous regions in China. Owing to high levels of industrialization, urbanization, and population growth, water quality in this region has deteriorated significantly in recent years. For example, typical phenolic EDCs, such as nonylphenol and bisphenol A, are widely detected in different river matrices in the Pearl River Delta [27]. However, the presence of and risk posed by ECs from sewage treatment plants and related receiving watersheds in this region remain insufficient to attract public attention. Therefore, a comprehensive investigation of the ECs in the Pearl River Basin is necessary to improve the understanding of their distribution and potential risks. Additionally, concerning the resistance of certain ECs species during the sewage treatment process, sewage treatment plant effluents can serve as a source of ECs detected in nearby watersheds. Thus, understanding the potential sources of ECs, especially those posing high risks, is essential for determining whether certain chemicals should be regulated or monitored at their sources.

Therefore, this study aimed to investigate the composition and potential sources of ECs in the sewage treatment plant effluent, and related watersheds in the Pearl River Basin during the dry season, as well as their ecological implications. To achieve this, this study used high-resolution HPLC-ESI-MS to analyze water samples collected from representative sewage treatment plant effluents and related watersheds (Dongjiang and Beijiang Rivers), in the Pearl River Basin, employed the risk quotient (RQ), method to estimate the ecological risks of all ECs at their detected exposure levels, used a PMF model to perform source identification and apportionment, and compiled a list of ECs that require prioritization to support policy decisions. This study also presents a strategy to obtain comprehensive information on the aquatic risks, and potential sources of EC species in areas affected by artificial activities, which is of substantial importance for pollutant management and control.

2. Materials and methods

2.1. Sample collection

The Pearl River Basin is located in tropical and subtropical climate zones. The average annual temperature is 14–22 °C and the average humidity is 71–80 %. Of the total annual precipitation, 72–88 % occurs in April–September. The basin comprises three major tributaries: the Xijiang, Beijiang, and Dongjiang Rivers. The Beijiang River is the second-largest river system in the Pearl River (length, 468 km; basin area, 46,710 km^2). The Dongjiang River (length, ~520 km; basin area, 27,000 km^2), is an important surface water body for the Guangdong-Hong Kong-Macao Greater Bay Area and accounts for 6.6 % of the total area of the Pearl River Basin. The Xinfengjiang Reservoir (drainage area, 5813 km^2; total storage capacity, 13.9 billion m^3; average annual inflow, 6.1 billion m^3), the largest surface water body in Guangdong

Province, regulates the flow of the Dongjiang River. The water quality of the Xinfengjiang Reservoir critically affects the water quality of the Dongjiang River. The industrial park in the sampling area is primarily engaged in industries such as pharmaceuticals, electronic information, and light industry and it is equipped with a sewage treatment plant to ensure proper treatment of the wastewater generated during the production process.

A thorough investigation was conducted to comprehensively elucidate the potential presence of ECs in water bodies in industrial parks. A comprehensive scan of water samples was conducted at 13 strategically selected locations, encompassing critical sites such as sewage treatment plants, rivers, and reservoirs in the primary urban zones of Qingyuan and Heyuan, Guangdong Province, China. The sampling strategy incorporated the acquisition of eight representative effluent samples from sewage treatment plants, and five surface water samples from nearby waters. To simulate extreme adverse conditions, this study conducted sampling in the dry season, avoiding flood periods and high-water storage phases to prevent the potential dilution of pollutants. Detailed information on each sampling location is presented in Table 1 and Fig. 1.

Each sampling site collected water samples from a depth of 0.5 m below the water surface, totaling 1000 mL. All water samples were collected in amber glass bottles that had been washed with water and then rinsed with a 99 % ethanol solution. During transport, the samples were stored in foam boxes filled with plenty of ice packs. Upon arrival at the laboratory, the samples were immediately filtered through 1 μm glass fiber filters and 0.45 μm nylon membranes. The filtered water samples were stored in the dark at 4 °C until extraction.

2.2. Analytical methods

2.2.1. Reagents and instruments

The enrichment and concentration of pollutants are achieved through solid-phase extraction technology. An Oasis HLB cartridge was preconditioned with methanol and water; Oasis WAX cartridge with 0.5 % NH_4OH in methanol, methanol, and water; and Oasis WCX cartridge with 2 % HCOOH in methanol, methanol, and water. The activated Oasis HLB, Oasis WAX, and Oasis WCX columns were sequentially connected in series using polypropylene adapter fittings to enhance the overall recovery of unknown compounds. Elution was performed with 8 mL methanol for the Oasis HLB column, 8 mL 0.5 % NH_4OH in methanol for the Oasis WAX column, and 8 mL 2 % HCOOH in methanol for the Oasis WCX column. The eluent was concentrated to 1 mL under a gentle stream of nitrogen. The concentrate was centrifuged at 4000 rpm for 5 min and the supernatant was transferred into a polypropylene vial and stored at − 20 ℃ until analysis [28].

Organic pollutants, including ECs, were analyzed using a quadrupole time-of-flight tandem mass spectrometer (TripleTOF 5600, AB Sciex, Foster City, CA, USA), and BEH C18 chromatography column (Waters). In the positive ion mode, the mobile phase comprised MilliQ water containing 0.1 % formic acid, and methanol; in the negative ion mode, MilliQ water containing 2 mM ammonium acetate and methanol was used. The flow rate was maintained at 0.4 mL/min and a gradient elution program was implemented for effective organic compound separation [29,30]. The ion source, operating in electrospray mode, featured a nebulizer temperature of 550 °C, and nebulizing voltages of 5.5 kV (positive ion mode), and 4.5 kV (negative ion mode). Using the data-dependent acquisition mode, information from primary and secondary mass spectrometers was systematically collected. The primary mass spectrometry scans ranged from 50 to 1250 m/z and secondary mass spectrometry scans ranged from 30 to 1250 m/z. The collision energy for secondary mass spectrometry was set at 40 ± 20 eV (positive ion mode), and − 40 ± 20 eV (negative ion mode).

2.2.2. Quality assurance and quality control

To test whether there was contamination of target substances during the sample pretreatment and instrument testing processes, blank control samples ($n = 3$), were prepared under the same laboratory conditions as the onsite samples. Additionally, solvent blanks were analyzed every 10 injections. No residues of the target compounds or mass spectrometry marker targets were detected. Additionally, five replicate samples were prepared during the sampling process to test the repeatability of the entire process. The limit of detection (LOD), and limit of quantification (LOQ), of the method were determined using standard solutions prepared by continuous dilution until the signal-to-noise ratios of LOD and LOQ reached 3 and 10, respectively [7,28]. Table S1 summarizes the mass, retention time, LOD, and LOQ of individual analytes determined using LC-ESI-MS.

Table 1
Sampling location.

Serial Number	Region	Name
S1	Qingyuan	Inflow of Guangzhou (Qingyuan) Industrial Park Sewage Treatment Plant
S2		Outflow of Guangzhou (Qingyuan) Industrial Park Sewage Treatment Plant
S3		Outflow of Guangzhou Huadu (Qingxin) Industrial Transfer Park Sewage Treatment Plant
S4		Outflow of Guangdong Shunde Qingyuan (Yingde) Economic Cooperation Zone Sewage Treatment Plant
S5		Cross-section of Feilai Gorge Level I Surface Water Body Protection Area
S6		Water intake point of Qixinggang Level I Surface Water Body Protection Area
S7	Heyuan	Outflow of Shenzhen Futian (Heping) Industrial Park Sewage Treatment Plant
S8		Outflow of Shenzhen Dapeng (Heyuan Yuancheng) Industrial Park Sewage Treatment Plant
S9		Outflow of Shenzhen Yantian (Dongyuan) Industrial Park Sewage Treatment Plant
S10		Outflow of Shenzhen (Heyuan) Industrial Transfer Park Sewage Treatment Plant
S11		Fengshuba Cross-section
S12		Dongjiang Mujing Section (Xiantang Town Cross-section)
S13		Water intake of Xinfengjiang Reservoir Level I Surface Water Body Protection Area

2.3. Risk assessment

Aligned with the guidelines stipulated in the Technical Guidance Document on Risk Assessment [31], this study employed the RQ method to assess the potential ecological risks associated with ECs in the samples. The calculation formula was as follows:

$$RQs = \frac{MEC}{PNEC} \tag{1}$$

where MEC is the measured environmental concentration (ng/L) and PNEC is the predicted no-effect concentration (ng/L). Ecological risk levels were evaluated using the RQ classification method: $RQ < 0.01$, no risk; $0.01 \leq RQ < 0.1$, low risk; $0.1 \leq RQ < 1$, medium risk; and $RQ \geq 1$, high risk [32].

The derivation of the PNEC value primarily employed two methods: the statistical extrapolation method and assessment factor method. The statistical extrapolation method was used when the values of a minimum of eight no observed effect concentration values for distinct species were accessible, ideally surpassing 15. The assessment factor method calculates the PNEC values by dividing the assessment endpoint by a designated assessment factor. For scenarios involving multiple species and assessment endpoints, the PNEC is determined by dividing the lowest value by an assessment factor. The selection of the assessment factor depends on the availability of short- and long-term test data, with the

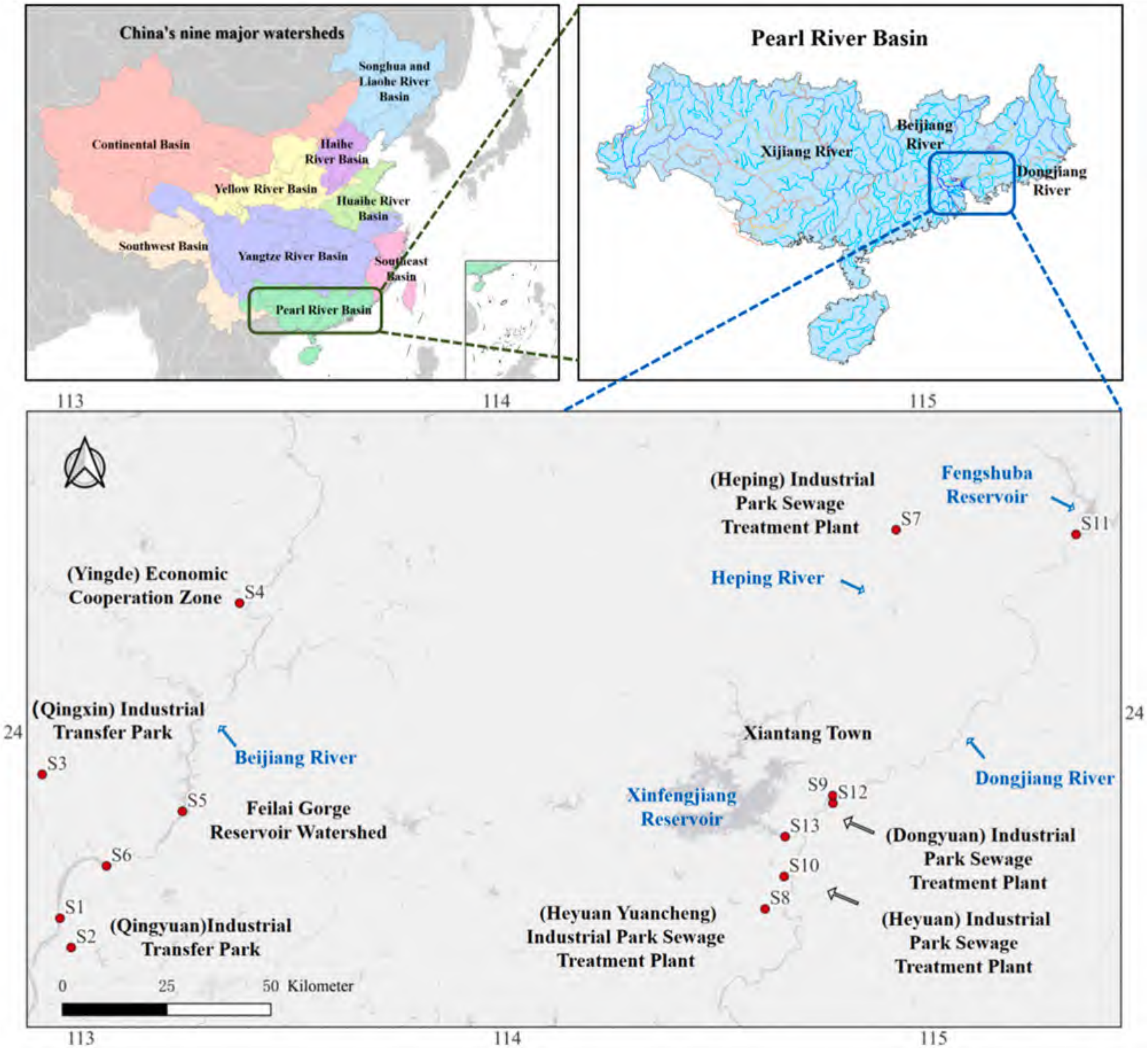

Fig. 1. Distribution map of sampling points in Qingyuan and Heyuan.

detailed factors delineated in Table 2.

$$PNEC = \frac{LC50}{AF} \text{ or } PNEC = \frac{EC50}{AF} \tag{2}$$

where LC50 is the lethal concentration of 50 % and EC50 is the half-maximal effective concentration, both measured in ng/L. AF is an assessment factor.

Table 2
Derivation of assessment factors for PNEC in water.

Available Test Data	Assessment Factors
For each of the three nutrient levels, at least one short-term L(E)C for each of the following: algae, crustaceans, and fish	1000
A NOEC for one long-term test for each of the 3 nutrient levels	100
Two long-term NOECs for two species at two nutrient levels	50
Two long-term NOECs for two species at two nutrient levels	10
Use of Species Sensitivity Distribution (SSD) method	adjusted as appropriate based on the actual circumstances

The PNEC values for various pollutants are listed in Table S2.

2.4. *Positive definite matrix factorization*

The PMF model was represented using Eq. (3).

$$x_{ij} = \sum\nolimits_{k=1}^{p} g_{ik} \times f_{ik} + e_{ij} \tag{3}$$

where x_{ij} is the concentration matrix X of the samples, that is, the concentration of the jth species in the ith sample; p is the number of pollution sources; g_{ik} is the contribution of the kth pollution source to the ith sample; f_{ik} is the concentration of the jth species in the kth pollution source; and e_{ij} represents the residuals.

The model imposes non-negativity constraints on G, and F matrices ($g_{ik}\geq 0$ and $f_{ik}\geq 0$). The factorization of the model was considered optimal when the weighted value of the square of the ratio of the residuals to the uncertainties Q was minimized. The PMF algorithm determined the G and F matrices by continuously minimizing Q. Q was defined using Eq. (4).

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{e_{ij}}{u_{ij}}\right)^2 \tag{4}$$

where n is the number of samples, m is the chemical components, and u_{ij} is the uncertainty of the pollutants in the samples. When the antibiotic concentration was less than or equal to the corresponding method detection limit, the uncertainty was represented by Eq. (5).

$$u_{ij} = \frac{5}{6} \times MDL \tag{5}$$

Otherwise, the uncertainty was calculated using Eq. (6).

$$u_{ij} = \sqrt{(\sigma_i \times x_{ij})^2 + (0.5 \times MDL)^2} \tag{6}$$

where σ_i is the error coefficient and generally ranges from 0.05 and 0.2.

3. Results and discussion

3.1. Chemical detection and classification

High-throughput screening analysis of eight effluent samples from the sewage treatment plant and five surface water samples in the investigated areas identified a total of 149 chemicals. Based on widely utilized chemical databases, including ChemicalBook, Molbase, and eChemPortal, these chemicals were classified into 25 categories, including pharmaceuticals, chemical intermediates, fungicides, antibiotics, insecticides, pesticides, surfactants, metabolites/transformed products, plasticizers, herbicides, mosquito repellents, perfluorinated compounds, flame retardants, PAHs, and hormones. Detailed results are presented in Table S3.

Pharmaceuticals, pesticides (including fungicides, insecticides, and herbicides), chemical intermediates, and antibiotics constituted 77 % of the total chemicals detected, at 34 %, 23 %, 13 %, and 7 %, respectively. The other major chemical categories were plasticizers, mosquito repellents, perfluorinated compounds, flame retardants, PAHs, plasticizers, and hormones. Details are illustrated in Fig. 2.

3.2. Characterization of organic pollutant distribution

The split violin plot in Fig. 3 highlights the disparities in the concentration and spatial distribution of ECs within effluents from sewage treatment plants and surface water samples. Specifically, the average detected concentrations of pharmaceuticals, antibiotics, flame retardants, chemical intermediates, and hormones were substantially higher in sewage treatment plant effluents, at 120.87, 96.99, 41.48, 23.61, and 11.98 ng/L, than in surface waters, at 1.13, 2.60, 3.41, 1.71, and 1.79 ng/L, respectively. Similarly, detection rates were predominantly higher in sewage treatment plant samples than in surface water samples. For instance, pharmaceuticals exhibited detection rates of 72 % and 26 % in sewage effluents and surface waters, respectively.

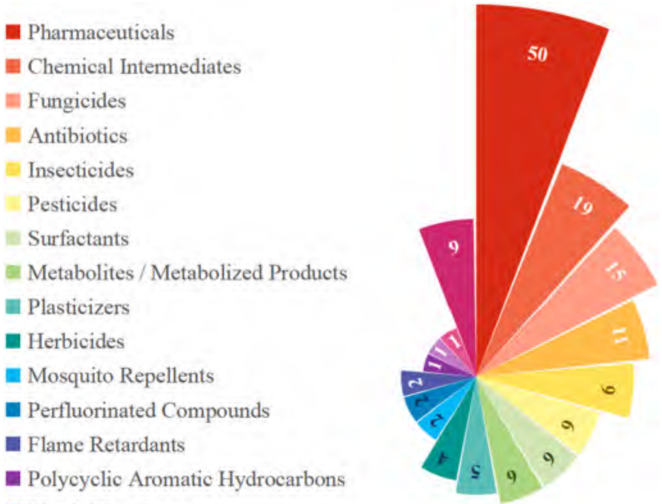

Fig. 2. Number of detected emerging contaminants in different categories.

This study identified ECs with significant concentration distribution differences, particularly those overlapping with PPCPs. PPCPs have garnered increasing attention from academia and the public due to their pervasive presence in various environmental matrices, such as sewage, surface water, groundwater, and soil, and their risks to ecological and human health. The global report on the concentrations of organic micropollutants in different types of water has highlighted sewage treatment plants as critical sources of PPCP contamination in surface waters [33,34], with concentrations typically elevated downstream of these facilities in the Pearl River Basin, corroborating our findings. Agricultural chemicals, such as fungicides, insecticides, pesticides, and herbicides, showed similar distribution patterns in sewage and surface water samples. ECs in natural surface waters typically remain at safe levels [35]. Nonetheless, effluents discharged from sewage treatment plants, such as surfactants, fungicides, and mosquito repellents, can escalate EC concentrations in surface waters. Conventional sewage treatment plants effectively remove standard pollutants, such as suspended particles, dissolved organics, nutrients, and pathogens, but are not specifically designed for EC elimination. Consequently, EC removal relies predominantly on biotransformation, biodegradation, and adsorption processes [3]. Because of the challenges of detecting and treating ECs, sewage treatment technologies have limitations in EC removal. Additionally, not every EC species poses a notable risk to aquatic ecology at the detected concentrations. Therefore, a comprehensive screening of ECs according to their potential risks in the Pearl River Basin is essential to determining priority chemicals.

3.3. Ecological risk assessment of typical organic pollutants

Based on the quantitative analysis of the ECs and lowest PNEC in the ECOTOX toxicology database, the RQ was calculated (Fig. 4). In effluent samples from the sewage treatment plant, RQ values for 56 ECs were below 0.1, indicating low risk. One EC, atrazine-2-hydroxy, a non-phytotoxic degradation product of atrazine [36], posed a medium risk, and three ECs exceeded an RQ of 1, indicating a high risk. Specifically, fipronil sulfide exhibited the highest RQ at 62.0, followed by caffeine at 41.2 and roxithromycin (ROX), at 11.8. In the effluent samples from the surface water, fipronil sulfide and caffeine exhibited high-risk values, 27.1 and 2.2, respectively; atrazine-2-hydroxy presented a medium risk; and the remaining 54 ECs exhibited a relatively low risk. Among the three ECs posing high risk, fipronil sulfide is the reduction product of fipronil, a phenylpyrazole insecticide used for controlling agricultural and non-agricultural pests. Despite its low concentration in aquatic environments, fipronil sulfide has higher toxicity with relatively lower PNEC values than fipronil. The calculated RQ values for fipronil sulfide were above 62.0, indicating that fipronil sulfide is a high-risk substance. Moreover, fipronil sulfide has a relatively long half-life and is more prone to accumulate in sediment and organisms than fipronil is [37,38].

ROX is a semi-synthetic macrolide antibiotic, the second most commonly used class of antibiotics, used in treating respiratory, urinary, and soft tissue infections [39]. In this study, ROX was only detected in samples from the sewage treatment plant, and its detection concentration was relatively higher than that of other ECs, at approximately 12 times the PNEC value. Long-term exposure to aquatic environments may also contribute to the emergence of antibiotic resistance genes [40]. ROX has been detected in aquatic environments worldwide, prompting countries such as Australia to set limits on ROX concentrations in water;

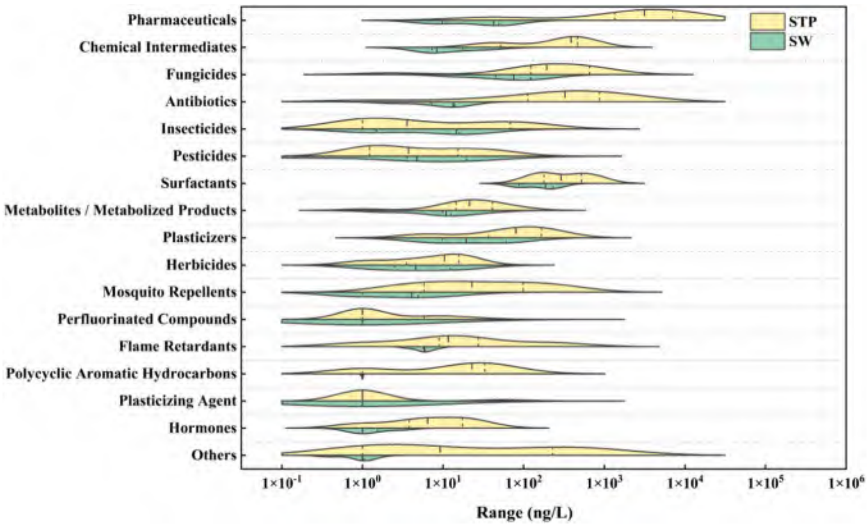

Fig. 3. Comparative diagram of ECs concentration classification in sewage treatment plant and surface water (STP: Sewage Treatment Plant, SW: Surface Water) .

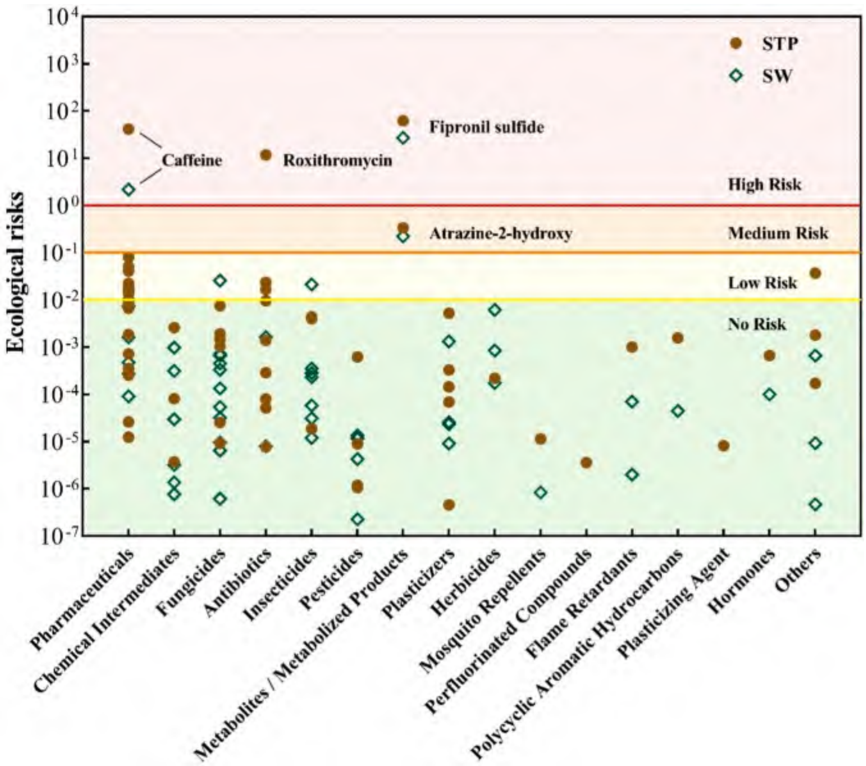

Fig. 4. Ecological risks of ECs in sewage treatment plant and surface water.

however, China has not yet regulated it [39].

Caffeine, an alkaloid xanthine, stimulates the central nervous system and is among the most widely used psychotropic drugs globally [41]. Often, conventional sewage treatment60plants do not adequately remove stable and highly soluble caffeine [42], resulting in its high detection rate and abundance in aquatic environments, posing significant environmental risks. In this study, the RQ of caffeine reached 41.2. Therefore, eliminating caffeine from aquatic ecosystems has become a focus of current research efforts [43].

3.4. Comparison of domestic and international priority chemical lists

The comparison of the 149 detected chemicals with 10 domestic and international priority chemical lists revealed 31 chemicals, constituting 21 % of all detected chemicals (Table 3). Among all samples, atrazine was detected 11 times, dibutyl phthalate and captan 10 times, and tebuconazole nine times. Nine chemicals were detected 5–8 times and 14 were detected 2–4 times. 2,4-dinitrotoluene, perfluorooctanesulfonic acid, quetiapine metabolites, and diethyl phthalate were detected once.

Notably, fipronil sulfide, caffeine, and ROX, which exhibited high-risk values, were not included in the domestic and international lists of concern. Fig. 5 illustrates detection rates of caffeine, fipronil sulfide, and ROX, at 69.2 %, 53.8 %, and 38.5 %, respectively. All three exhibited relatively high risk levels in the sewage treatment plant samples. Therefore, these compounds require special attention.

Table 3
31 Substances appearing on domestic and international lists and their detection frequencies.

Serial Number	Name	Molecular Formula	Detection Frequency	Key Chemical List*
1	Atrazine	$C_8H_{14}ClN_5$	11	[a,b]
2	Dibutyl phthalate	$C_{16}H_{22}O_4$	10	[a,b,c,d]
3	Carbendazim	$C_9H_9N_3O_2$	10	[b]
4	Tebuconazole	$C_{16}H_{22}ClN_3O$	9	[e]
5	4-Nitrophenol	$C_6H_5NO_3$	8	[b,f]
6	Erythromycin	$C_{37}H_{67}NO_{13}$	8	[e]
7	Nonylphenol	$C_{15}H_{24}O$	7	[b,d,e,g,h]
8	Fluorene	$C_{13}H_{10}$	6	[b,f]
9	2,4-Dimethylaniline	$C_8H_{11}N$	5	[d,g]
10	Bis(2-ethylhexyl phthalate (DEHP)	$C_{24}H_{38}O_4$	5	[b,f]
11	Benzoic acid (BA)	$C_7H_6O_2$	5	[b]
12	p-Cresidine	$C_8H_{11}O_1N_1$	5	[b]
13	Benzotriazole	$C_6H_5N_3$	5	[d]
14	Fusarenone-X	$C_{17}H_{22}O_8$	4	[g]
15	Propiconazole	$C_{15}H_{17}Cl_2N_3O_2$	4	[b]
16	1-Naphthylamine	$C_{10}H_9N$	3	[b,g]
17	Melamine	$C_3H_6N_6$	3	[g]
18	Quinoline	C_9H_7N	3	[e,g]
19	Bisphenol A	$C_{15}H_{16}O_2$	3	[a]
20	Diuron	$C_9H_{10}Cl_2N_2O$	3	[b,e]
21	Tebufenozide	$C_{22}H_{28}N_2O_2$	3	[e]
22	Diphenylamine	$C_{12}H_{11}N$	2	[b,g]
23	Nicotine	$C_{10}H_{14}N_2$	2	[b,g]
24	ortho-Anisidine	C_7H_9NO	2	[g]
25	Metolachlor	$C_{15}H_{22}ClNO_2$	2	[e]
26	Ametryn	$C_9H_{17}N_5S$	2	[b]
27	tris (2-chloroethyl) phosphate	$C_6H_{12}Cl_3O_4P$	2	[d]
28	2,4-Dinitrotoluene	$C_7H_6N_2O_4$	1	[b,c,f,e,i]
29	Perfluorooctane sulfonate (PFOS)	$C_8HF_{17}O_3S$	1	[b,d,g,h,j]
30	Quetiapine metabolite (+2 O, −2 H)	$C_{21}H_{23}N_3O_4S$	1	[g]
31	Diethyl phthalate	$C_{12}H_{14}O_4$	1	[a,d]

* The alphabet letters indicate the corresponding key chemical list:
[a] GB 5749–2022 Hygienic Standard for Drinking Water
[b] 2015 CERCLA Priority Pollutant List
[c] GB3838–2002 Environmental Quality Standards for Surface Water
[d] EU List of Substances of Very High Concern(168 items on the REACH-SVHC detection list)
[e] U.S. Drinking Water Alternative Pollutant Indicator List
[f] U.S. 129 Priority Control Pollutant Blacklist
[g] National Catalog of Hazardous Chemicals (2015 edition)
[h] Key Environmental Management Catalog of Hazardous Chemicals(2014 edition)
[i] China's Priority Control Pollutant Blacklist
[j] List of Toxic Chemicals Strictly Restricted in China (2018 edition)

3.5. *Source identification and apportionment through PMF*

PMF was employed to identify and allocate the main sources. Four factors were selected based on the optimal solutions according to the Qtrue/Qrobust values. PCA confirmed this result, explaining 80 % of the cumulative contribution rate. Thus, these four factors represent the main sources of ECs detected in the samples. Fig. 6 shows the EC profiles for each factor.

The first factor was closely associated with diethyltoluenamide (67.7 %), nonylphenol (50.9 %), and sulpiride (38.7 %), indicating an association with domestic wastewater. Diethyltoluenamide, the most widely used mosquito repellent globally, is a prevalent organic pollutant in various water matrices, including wastewater and surface water [44]. Research has suggested that households are the primary sources of mosquito repellents in the environment [45]. Nonylphenol is a typical environmental endocrine disruptor, mainly derived from the degradation of alkylphenol ethoxylates, widely used in household detergents [46]. It is frequently detected in domestic wastewater [47]. Sulpiride is an atypical antipsychotic drug commonly used for domestic purposes, especially as an antidepressant [48,49].

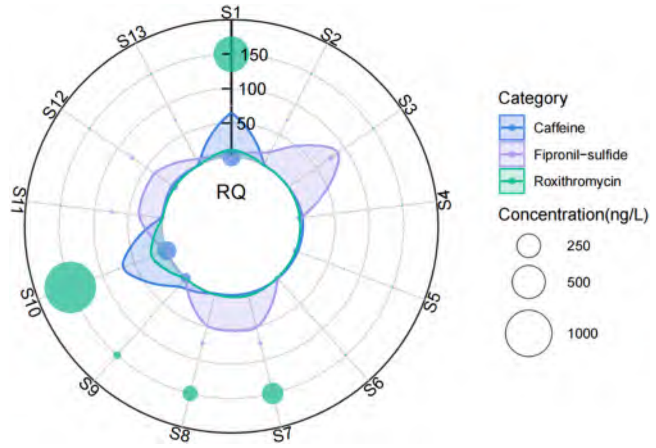

Fig. 5. A Bubble radar chart depicting concentrations and risk quotient values for three high-risk substances.

Regarding the second factor, carbendazim (64.3 %), tebuconazole (70.7 %), and atrazine (58.7 %) were notable contributors, indicating a likely connection with farmland drainage. Carbendazim, a fungicide widely used in agriculture, forestry, and veterinary medicine, is employed to combat fungal diseases [50]. Tebuconazole, a triazole fungicide, is one of the most crucial fungicides globally and is commonly used to manage a broad spectrum of fungal diseases in cereal, fruit, and vegetable crops [51–53]. Atrazine, the second most utilized herbicide worldwide, is employed in weed control in crops [54]. Consequently, factor 2 likely represented the influence of farmland drainage.

Factor 3 was characterized by the presence of various antibiotics and drugs; among them, cimetidine (71.9 %), amantadine (68.6 %), glyburide (climbazole, 65.0 %), sulpiride (61.0 %), tricyclazole (60.5 %), fipronil sulfide (58.1 %), and trimethoprim (53.1 %), significantly contributed to this factor. Cimetidine, classified as a highly toxic class I compound, is predominantly used to treat gastritis and gastric ulcers and is frequently detected in surface waters [55,56]. Amantadine, commonly used in neurological conditions such as Parkinson's disease [57], and gambutin, a common azole antifungal agent used as a depurative, also featured prominently in this context [58]. Sulpiride, an antipsychotic medication for schizophrenia, is frequently found in aquatic environments, raising concerns due to its significant presence and the formation of toxic transformation products through photodegradation [48]. Metribuzin is a broad-spectrum, highly effective, low-toxicity antimicrobial and fungicide that shares an antimicrobial spectrum with sulfonamides and is commonly used as a veterinary drug [59]. Therefore, factor 3 likely represents pharmaceutical wastewater.

Factor 4 consisted mainly of surfactants (ranging from 42.9 % to 64.7 %), and erythromycin (39.3 %). Hospitals and health centers significantly contribute to daily detergent discharge into wastewater streams [60]. Surfactants, known for their antimicrobial properties, can reduce the efficacy of the microorganisms involved in removing pollutants from sewage [61]. The presence of erythromycin, a broad-spectrum antibiotic used to treat human infections, helped identify this factor [62]. Therefore, factor 4 likely represented the influence of medical wastewater.

Fig. 7 shows that each factor had a relatively low contribution at the five surface water sites. Farmland drainage was the main source, while pharmaceutical wastewater had a minimal contribution. Conversely, samples from sewage treatment plant effluents highlighted the significant presence of medical and pharmaceutical wastewater compared with the surface water samples. This observation underscores the need

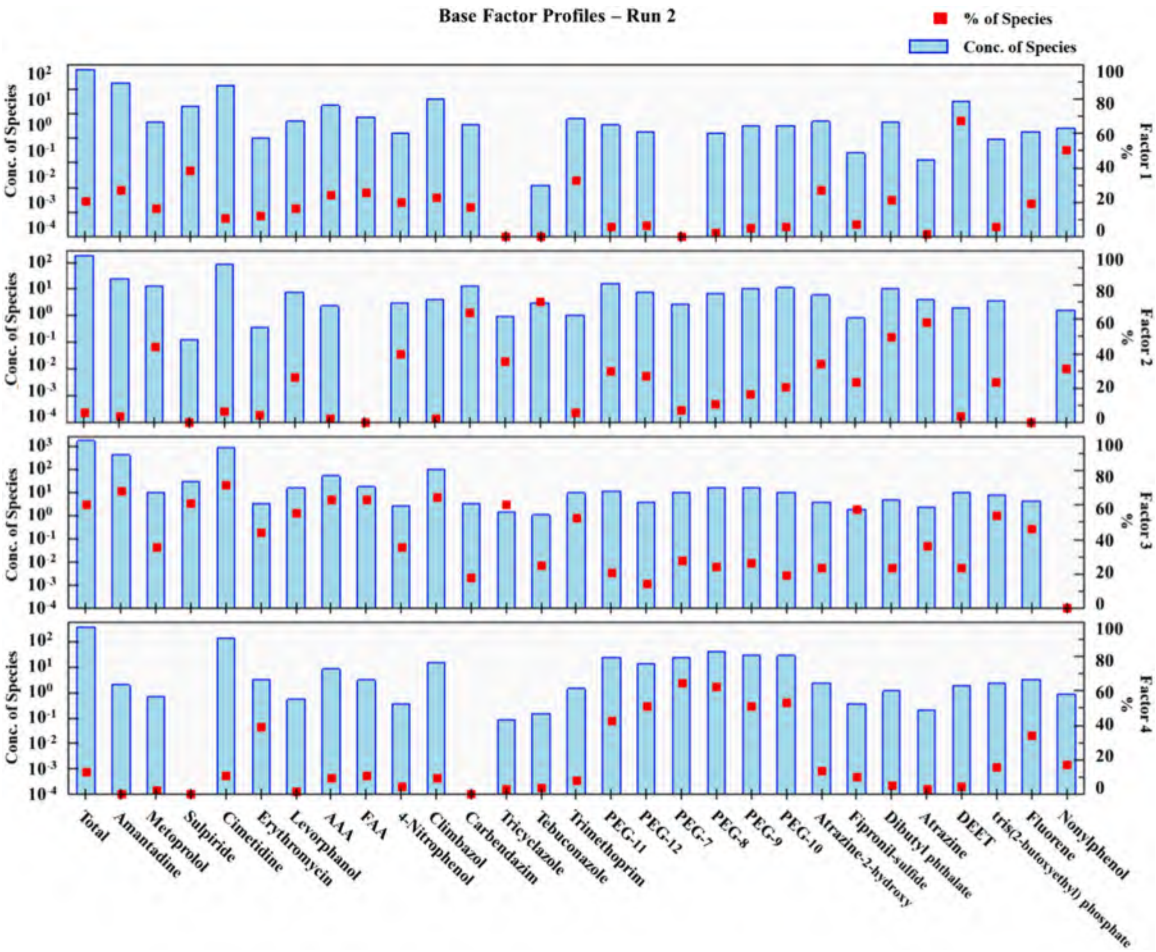

Fig. 6. Factor profiles and contributions to ECs.

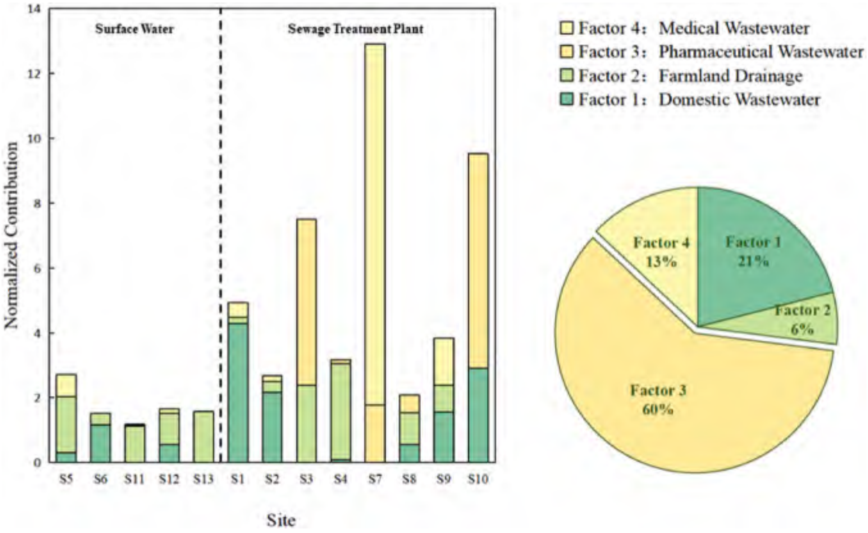

Fig. 7. Factor contributions of ECs at each sampling point and the total contribution of ecs sources in water samples.

for targeted measures during sewage treatment to counteract the effects of pharmaceutical and medical wastewater on water quality. However, drugs released into aquatic environments, whether unchanged or as metabolites, undergo natural attenuation processes, such as dilution, adsorption, photolysis, or biotransformation [63]. Due to the significant threat posed by agricultural pesticides to aquatic ecosystems, the impact of farmland drainage on surface water quality may be substantial. Therefore, implementing measures to reduce pesticide input into water bodies is necessary. Additionally, the contribution of domestic wastewater should be considered.

Fig. 7 illustrates the total contribution from the four sources. Pharmaceutical wastewater was the predominant source, accounting for

60.4 % of the total. This aligns with the local development strategy, with the biopharmaceutical and health industries being emerging strategic sectors in Qingyuan and Heyuan. The government prioritizes the pharmaceutical industry as a key sector within the "Four News" industries. The substantial discharge of chemicals from this industry significantly contributes to the detection of ECs.

Domestic wastewater was the second most significant source, accounting for 20.8 % of the total. Evolving lifestyles and consumption patterns, driven by improved living standards, have led to increased use of cosmetics, pharmaceuticals, and personal care products. However, financial constraints and outdated sewage systems have led to the direct discharge of domestic wastewater without adequate treatment, particularly in small towns and rural areas [64].

Medical wastewater discharge constituted 12.9 % of all sources, indicating the success of regulatory policies. In regions where medical wastewater had been identified as the main source, local ecological and environmental bureaus introduced substantial regulatory improvements, including the following measures: comprehensive oversight of medical waste disposal and the treatment of medical wastewater. Various preventive and control measures have been systematically implemented to ensure the proper treatment of medical wastewater. Farmland discharge represented the smallest proportion, comprising 5.9 %. Despite its modest contribution, farmland is a significant pollution source owing to the elevated aquatic risk associated with the agricultural chemicals detected among the identified ECs. The substantial presence of antibiotics and pharmaceuticals in pharmaceutical wastewater poses significant risks to aquatic ecosystems and remains one of the most challenging types of industrial wastewater [20]. Pollution challenges associated with ECs in industrial transfer zones demand attention from industry and the government.

4. Conclusions

Our analysis of water samples from eight representative sewage treatment plants and five surface waters in the Pearl River Basin identified 149 chemicals, mainly pharmaceuticals, pesticides, chemical intermediates, and antibiotics, exhibiting varying concentrations and detection frequencies. Our risk assessment of the detected chemicals indicates a generally lower level of risk for local aquatic organisms and that fipronil sulfide, caffeine, ROX, and atrazine-2-hydroxy require monitoring and further research due to their moderate- to high-risk values, largely originating from the pharmaceutical and agricultural sectors. Notably, 31 of the 149 detected chemicals were on the domestic and international priority list; the remaining 118 were not listed. Importantly, substances with high-risk values, such as fipronil sulfide, caffeine, and ROX, were absent from the priority lists, highlighting the need to update these lists. The primary sources of ECs comprised pharmaceutical wastewater, domestic sewage, medical effluent, and farmland drainage. Farmland drainage emerged as the main source of surface water contamination, and pharmaceutical wastewater significantly affected sewage treatment plants. Medical effluent was particularly dominant in certain specific locations. In addition, domestic wastewater played a pivotal role in influencing the EC concentrations across the studied sites. In summary, combining LC-ESI-MS high-throughput screening with PMF allows for effective source apportionment. This study successfully identified pharmaceutical wastewater as a significant source, which aligns with the predominant pharmaceutical industry in the research area, validating the reliability of this approach. Additionally, this study suggests collecting metadata alongside LC-ESI-MS data to assist with source apportionment.

Environmental implication

Our risk assessment pinpointed chemicals like fipronil sulfide, caffeine, roxithromycin, and atrazine-2-hydroxy as significant threats to aquatic ecosystems in the Pearl River Basin. Substances such as fipronil sulfide, caffeine, and roxithromycin are absent from national and global watchlists. These findings highlight the urgency for stricter monitoring, and potential inclusion of these chemicals in proactive monitoring lists. Additionally, pharmaceutical wastewater was the primary contributor to sewage treatment plant effluent, while agricultural drainage was the main source of ECs in surface water samples. Managing medical wastewater at treatment plant exits, and treating agricultural runoff are critical steps for reducing these risks.

CRediT authorship contribution statement

Xiaohui Zhu: Writing – original draft, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation. **Siyan Liu:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Xiaofeng Gao:** Writing – review & editing, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Yilu Gu:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Ying Yu:** Investigation, Data curation. **Min Li:** Investigation, Conceptualization. **Xiaowen Chen:** Investigation, Data curation. **Mengqi Fan:** Visualization, Software, Formal analysis. **Yujie Jia:** Visualization, Resources, Investigation, Data curation. **Liping Tian:** Visualization, Data curation. **Mingdeng Xiang:** Supervision, Resources. **Yunjiang Yu:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

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. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2024.135046.

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