Pharmaceuticals and Agro-Chemicals in Groundwater of Hyderabad, India

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Abstract. Organic micropollutants continue to worsen groundwater pollution, especially in many areas of the world where water resources are becoming scarce. India uses groundwater more than any other nation. The main objective of this study is to evaluate the groundwater quality of Hyderabad, India by comprehensively analyzing organic micropollutants. Samples were collected from groundwater borewells in eight different sites (Begumpet, Bharatnagar, Dundigal, Jubilee Hills, Kukatpally, Sanath nagar, Tarnaka, and Tirumalagiri). The non-targeted screening analysis was performed using liquid chromatography-quadrupole time-of-flight (LC-QTOF). About 250 different compounds were detected in total from all the samples. This includes pharmaceuticals, herbicides, fungicides, pesticides, hormones, steroids, cosmetics, plasticizers, cyanotoxins, and metabolites. In all samples, pharmaceuticals accounted for approximately 50% of the detected compounds. The Sanath nagar groundwater sample had been detected with more than 130 compounds and the least number of compounds were detected in Taranaka, Jubilee Hills, and Kukatpally areas. Apramycin (veterinary drug) and Bis(2-ethylhexyl) phthalate (plasticizer) had been found in all eight samples. The high abundance values were observed for 17αβ - Dihydroequilin, Avobenzone, Butachlor, Clarithromycin-N-oxide, Dibutyl phthalate, Doxepin, Estriol, Napropamide, and Nefazodone. Estriol and 17αβ - Dihydroequilin are the largest endocrine disruptors. The presence of various pharmaceuticals and agrochemicals in groundwater reveals pollution either directly or indirectly, by the discharge of domestic and industrial wastewater.

Keyword. Cyanatoxin, EDC, Non-target screening, LC-QTOF, PCA, PFAS

1 Introduction

The Telangana region has few surface water sources due to its hard-rocky terrain, and as rains become shorter, more intense, and irregular, groundwater serves as the main source of surface water for the local population. As a result, groundwater usage is rising, particularly in urbanizing cities. Unfortunately, human activity in urban areas is the primary driver of pollution that impacts adjacent cities and watershed aquifers. Among the many different kinds of micropollutants, people frequently use hormones, insecticides, personal care products (PPCPs), and pharmaceuticals. These hazardous compounds may endanger aquatic life after being released into the environment, mostly through sewage discharge [1]. According to several research investigations, micropollutants and their metabolites are extensively distributed in urban aquatic habitats, which has raised global concerns [2-6]. Humans as well as livestock are often treated with pharmaceuticals and hormones; nevertheless, these drugs have the potential to contaminate groundwater. Even at low concentrations, these bioactive compounds may have negative effects on human health such as endocrine disruption and propagate antibiotic resistance genes within the human microbiome [7].

Agrochemicals are any substances that are used to prevent, decrease, control, or repel pests from crops. In modern agriculture, pesticides are frequently employed to increase crop productivity to meet the food demand of the increased population. There are several different types of pesticides, including termiticides, algaecides, fungicides, germicides, herbicides, insecticides, miticides, molluskicides, and rodenticides. They are substances used by human civilization to ward off or subdue pests including germs, nematodes, insects, mites, birds, rodents, and other organisms that are harmful to human health or food production. They could be chemical, biological, or a combination of the two. In India, the most common pesticides used are insecticides (51%), followed by herbicides (16%) and fungicides + bactericides (33%) [8]. An average of only 0.1 percent of pesticides are known to reach the intended species; the remainder infiltrates different parts of the ecosystem.

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The level of contamination risk depends on the relative rates of infiltration and degradation within the soil profile. Several factors, including climate, soil properties, chemical composition, application rate, depth of the aquifer, and agricultural practices, influence these processes.

India is one of the largest manufacturers of medicines in the global market. Hyderabad is the country's primary pharmaceutical manufacturing hub. There are over 800 biotech and pharmaceutical companies in the Hyderabad area. The groundwater sample from Patancheru, Hyderabad, consisted of a total of 12 pharmaceuticals, with cetirizine, ciprofloxacin, enoxacin, and metoprolol being the most prevalent [9]. Sewage in the Patancheru-Bollaram industrial region had high levels of voriconazole, fluconazole, and moxifloxacin [10]. In many parts of Hyderabad, groundwater concentrations of dichlorodiphenyltrichloroethane, endosulfan, and lindane exceeded their corresponding acceptable daily intake values established for human consumption [11]. This study aims to detect micropollutants and evaluate the magnitude of groundwater pollution resulting from human activities in different areas of Hyderabad.

2 Materials and methodology

2.1. Sample collection

Samples were collected from groundwater borewells in eight different sites (Begumpet, Bharatnagar, Dundigal, Jubilee Hills, Kukatpally, Sanath nagar, Tarnaka, and Tirumalagiri) which are densely populated urban areas in Hyderabad, Telangana. The map with sampling sites is given in Figure 1.

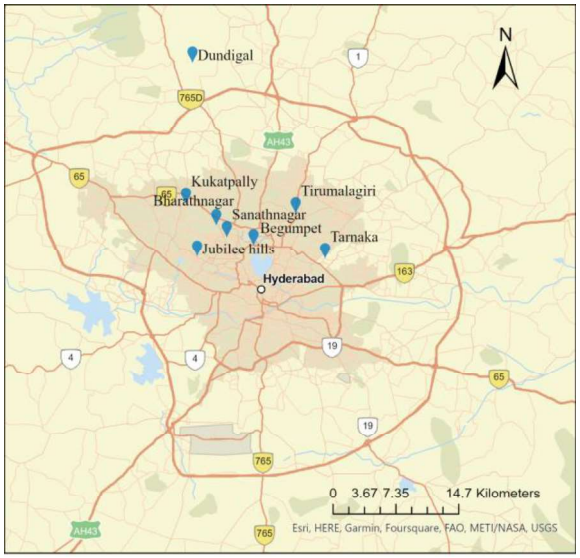

Fig. 1. Selected sampling sites.

Samples were collected in March and April of 2023. Collected samples were passed through a 0.22 µm filter and filtered samples were stored at 4 ºC until analysis.

2.2 Analysis of Micropollutants

The filtered samples were transferred to 2 mL amber LC vials and injected into the instrument via an auto-sampler for the identification of micropollutants. Screening of the samples was conducted using an Agilent 6545 Liquid Chromatography-Quadrapole Time of Flight (LC-QTOF) system. The system was equipped with a 1260 Infinity II pump, and a 10 µL portion of the sample was injected for screening. Gradient flow was employed for the separation and identification of target compounds. For this study, a mobile phase consisting of an aqueous solution of 5 mM ammonium acetate and 0.1% acetic acid (mobile phase A), and 0.1% acetic acid in MeOH (mobile phase B) was used. All chemicals and solvents used were of MS grade.

The mobile phase A was initially set at 95% for 0.5 minutes and then gradually increased to 100% B over the next 10.5 minutes. The system maintained 100% B for 2 minutes, followed by a ramp back to 95% A over 5 minutes. Subsequently, 95% A was held for 2 minutes. The total run time for each sample was 20 minutes. A 1-minute post-run was performed after each sample to eliminate any residual interference from the previous sample before the next injection. A Zorbax Eclipse plus C18 (Narrow Bore RR) column with dimensions of 2.1 x 100 mm and a diameter of 3.5 microns was used, maintaining a mobile phase flow rate of 0.22 mL/min. The maximum allowable column pressure was set at 450, and the column temperature was held steady at 40±0.4 ºC.

Mass spectrometry was conducted using an Agilent Jet Stream Electrospray Ionization source operating in both positive and negative modes. The mass range was set from m/z 100 to 1200 with a data acquisition rate of 3 spectra/s. Specific parameters were maintained during the measurement, including a gas temperature of 150 ºC, drying gas (N2) flow rate of 10 L/min, nebulizer gas pressure of 35 psi, sheath gas temperature of 375 ºC, sheath gas flow of 11 L/min, 3500 V capillary voltage, and 125 V fragmentor voltage. Additionally, a reference compound solution with m/z values of 121.0509, 922.0098 (positive ionization mode), and m/z 112.9856, 966.0007 (negative ionization mode) was injected for mass drift correction.

The spectra files were processed using Agilent MassHunter Qualitative Workflows B.08.00 software for target/suspect screening. Data files were screened using the Agilent MassHunter Personal Compound Database and Library (PCDL)-water library to identify compounds, along with their respective abundance and Q-Score.

2.3 Statistical analysis

The principal component analysis (PCA) for each compound's abundance values detected at different sampling sites was carried out using the Microsoft Excel XLSTAT statistical program. PCA is a multivariate statistical technique for data visualization and dimensionality reduction. The popular statistics software XLSTAT has a PCA analysis tool. The PCA analysis equations in XLSTAT involve several mathematical operations. Each variable is standardized by subtracting the mean from each variable and dividing by the standard deviation, to have a mean of zero and a standard deviation of one. The covariance matrix is derived from the standardized data. The eigenvalues and eigenvectors of the covariance matrix are calculated. The eigenvectors are used to represent the principal components, which are orthogonal (uncorrelated) linear combinations of the starting variables. The eigenvalues are variances of each basic component. For calculating the main component scores, the eigenvector matrix is multiplied by the standardized data matrix. The data points for the new main component space are based on these findings. The variance that each major component contributes was determined by simply dividing each eigenvalue by the sum of all eigenvalues. This demonstrates the proportion of the total variability of the data that each basic component was able to record. The two main components and the relationship between each original variable and the loading scores are presented. These findings show which variables have the most effects on each key parameter. PCA assists in better understanding the underlying structure and patterns in the data by using these equations.

2.4 Geospatial analysis

The spatial mapping of the compounds that are identified in at least seven sampling sites was shown using the "inverse distance weighted (IDW)" interpolation method in the ArcGIS pro application. ArcGIS Pro is a well-known geographic information system application that has reliable capabilities for creating interpolation maps. It provides an extensive range of interpolation methods suitable for various data types and geographic patterns one sort of interpolation that is regularly used is IDW. This method makes use of weights that are based on the distance between nearby sample sites in order to estimate values in unsampled areas. To project values at locations that weren't sampled, ArcGIS's IDW interpolation technique employs the equation below:

$$Z(x) = \frac{\sum_{i=1}^{n}\left(\frac{Z_i}{d(x,x_i)^p}\right)}{\sum_{i=1}^{n}\left(\frac{1}{d(x,x_i)^p}\right)} \quad (1)$$

In this equation, $z(x)$ represents the estimated value at the desired location x, Z_i is the measured value at the sampling location i, $d(x,x_i)$ designates the distance between the target location x and the sampling location i, p is the power parameter that calculates each sample point's effect based on its location. The weighted average of the observed values at the sample sites is calculated using the IDW interpolation method, where the weight given to each point is inversely proportional to the distance raised to the power p. IDW interpolation uses a power value of two by default, which is also a typical number.

3 Results and discussion

The number of compounds detected in the groundwater samples is given in Figure 2. The Sanath nagar groundwater sample had been detected with more than 130 compounds and the least number of compounds were detected in Taranaka, Jubilee Hills, and Kukatpally areas.

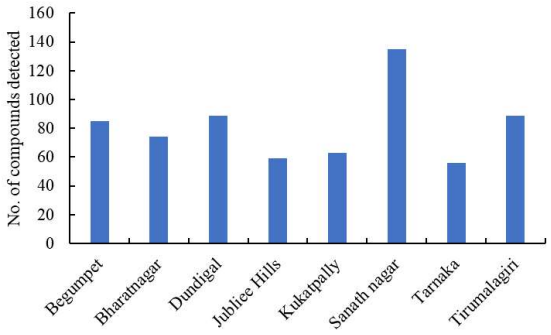

Fig. 2. Total number of compounds detected in the sampling sites.

These detected compounds were categorized as pharmaceuticals, metabolites, herbicides, fungicides, insecticides, pesticides, hormones and steroids, plasticizers, cyanotoxins, cosmetics (primarily UV filters), and miscellaneous. The average composition of the detected compounds at all locations is represented as a pie chart in Figure 3. In all the samples the pharmaceuticals accounted for more than 50% of the detected compounds. Agrochemical compounds (insecticides, herbicides, fungicides, and other pesticides) varied between 10 - 20% of the total detected compounds. Overall, more than 70% of the detected compounds belong to pharmaceuticals and agrochemicals. The Sanath nagar sample had 63% of pharmaceutical compounds and 20% of agrochemical compounds in the total detected compounds. Tarnaka and Jubilee Hills samples had the least number of pharmaceuticals (30% of the total) and 12% of agrochemicals.

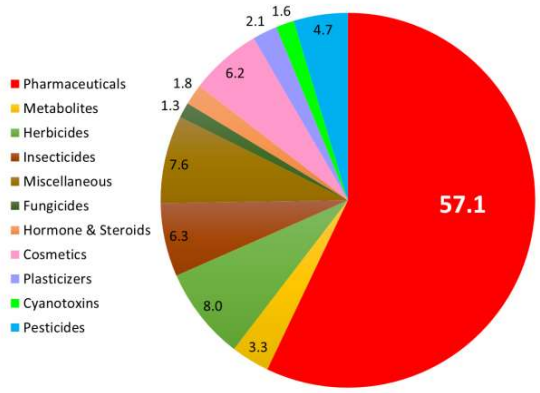

Fig. 3. Composition of the detected compounds.

The principal component analysis (PCA) results of all the identified compounds across all samples and sampling sites is shown in Figure 4. The eigenvalues are depicted as red segments, which represent sampling sites that have the greatest influence on each principal component. Results of the PCA showed a separation of the parameters related to herbicides, hormones, personal care products, pharmaceuticals, and plasticizers on the two independent axes. The first component (PC1), accounts for 51.1% of the variance and the second component (PC2), explains 22.7% variance. PC2 effectively separated the selected sampling sites into two sets. The sampling sites Sanath Nagar, Dundigal, Begumpet, and Tirumalgiri were situated in the positive direction of PC2. Within this cluster of groundwater samples, over 85 compounds were detected. The sampling sites with fewer than 85 detected compounds formed the second cluster of sample sites. The second set of sampling sites, including Tarnaka, Jubilee Hills, Kukatpally, and Bharat Nagar, were distributed in the negative direction of PC2. The micropollutant cluster with positive loading in both PC1 and high PC2 values consists of six pollutants, namely Avobenzene, Estriol, 17α-Dihydroequilin, Butachlor, Sibutramine and Bis(2-ethylhexyl) phthalate. These pollutants were detected in high abundance in the sampling sites of Sanath Nagar, Dundigal, Begumpet, and Tirumalgiri. On the other hand, the other cluster consists of five compounds, namely Clarithromycin-N-oxide, Dibutyl phthalate, Doxepin, Nefazodone, and Napropamide, which were abundantly detected in Tarnaka, Jubilee Hills, Kukatpally, and Bharat Nagar. The remaining compounds (~225) were mainly located on PC1 component axis with low PC2 values (both negative and positive). The compounds Nefazadone, Napropamide, Microcystin-LR, N-Methylpyrrolidone, and Apramycin had been detected in at least seven sample sites. Apramycin and Bis(2-ethylhexyl) phthalate had been found in all eight samples. The compounds Dextilidine, Erythromycin, and Narasin are majorly detected in Begumpet, Dundigal, Sanath nagar, and Tirumalagiri groundwater samples. The remaining (~200) compounds were identified in at least one sampling site. The compounds like Simetryn, Methadone-d3, N-Methylacetanilide, Naftidrofuryl, Pindolol, Nuarimol, Reserpine, and Codeine-d6 which are primarily on PC2 are mainly detected in Sanath nagar samples.

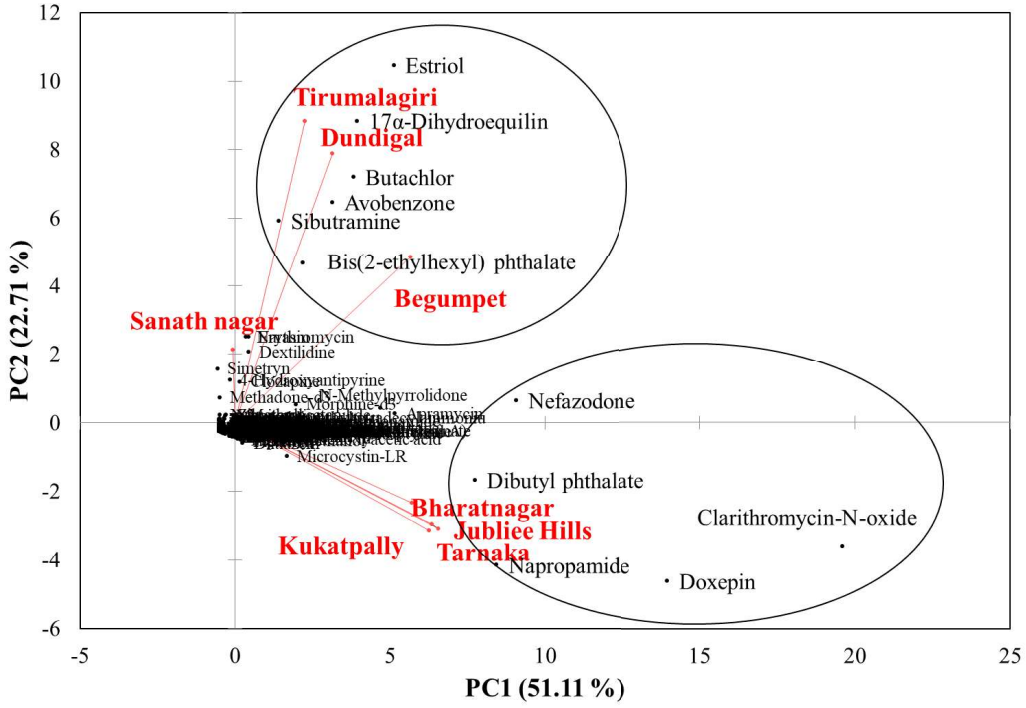

Fig. 4. Principal component analysis of all compounds detected in all the samples at all sampling sites.

Clozapine is an antipsychotic drug used to treat symptoms of schizophrenia: hallucinations and delusions was also detected in five sampling sites in low abundance (<30,000). The groundwater samples contained perfluorooctanoic acid (PFOA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), and perfluorotetradecanoic acid (PFTDA). These chemicals belong to the class of poly- and perfluoroalkyl substances (PFASs), which are highly stable fluorinated aliphatic compounds. PFASs are commonly utilized in various applications such as cosmetics, firefighting foams, nonstick cookware, water- and oil-resistant garments, and carpets. PFOA had been detected mainly in the Bharat nagar groundwater sample. PFHxA was detected in Jubilee Hills. Exposure to PFAS can lead to health effects such as kidney cancer, increased liver weight, elevated cholesterol, decreased fertility, obesity, thyroid issues, and immunosuppression [12,13].

The compounds that are detected at high abundance greater than 30,000 were given in Table 1. Thirty compounds showed high abundance values greater than 30,000 among them 16 belong to pharmaceuticals and 5 compounds are agrochemicals. Clarithromycin N-oxide is a urinary metabolite of Clarithromycin, an antibiotic that was detected in almost all the samples indicating the pollution of groundwater with domestic wastewater. The pharmaceutical compounds Apramycin, Doxepin, and Nefazodone were detected in almost all the samples. Apramycin is an aminoglycoside veterinary antibiotic used to treat infections in animals. Doxepin and Nefazodone are medications belonging to the antidepressant class of drugs used to treat major depressive disorder, anxiety disorders, chronic hives, and insomnia. These are detected in seven groundwater samples. Sibutramine an anti-obesity drug was found in high abundance in Dundigal and Tirumalgiri groundwater samples. 4-Hydroxyantipyrine is a major human metabolite of antipyrine which is used for ear infections. Codeine is commonly prescribed as a pain reliever that is converted to its metabolite, morphine, in the liver by an enzyme known as cytochrome P450 isoenzyme 2D6 (CYP2D6). Morphine has been detected as a urinary metabolite of codeine [14] and excessive levels of morphine in the breast milk of codeine-prescribed mothers have been associated with infant mortality [15]. Codeine had been detected in only two sampling locations (Bharat nagar and Sanath nagar) whereas Morphine had been identified in seven groundwater samples indicating the discharge of domestic wastewater. Erythromycin an antibiotic had been detected in five locations with high abundance in the Tirumalgiri sample. Exposure to Erythromycin at 0.1 μg/L concentration in aquatic environments delayed hatching and decreased the survival rate of zebrafish [16,17]. Pindolol a beta blocker used to treat high blood pressure is detected in Sanath nagar groundwater. Fish exposed to these substances may experience cardiovascular dysfunction, which might decrease their growth rate [18].

Butachlor is a common herbicide, used for stopping weeds from developing new plant tissues, highest abundance values were detected in Begumpet and Dundigal groundwater samples. The majority of butachlor enters the environment through various agricultural, horticultural, and forestry practices, which include improper water management, rainfall, and runoff from agricultural areas to watersheds and aquatic habitats [19]. Butachlor ingestion is not highly toxic. However, there have been some rare instances of serious neurological and cardiovascular effects, particularly after oral consumption [20]. Butachlor is not permitted in Hokkaido, Japan, during the rice-planting season due to the herbicide's potential to contaminate aquatic environments. Butachlor-containing formulations for "Machete" also include inert ingredients such as xylenes and N-butyl alcohol. Either of these chemicals has the potential to affect the liver and kidneys. Memory, attention, and hearing issues can develop in the brain as a result of prolonged exposure to xylenes. Other consequences include decreased bone marrow production and low blood cell count. Napropamide is a herbicide that is widely utilized. Although it exhibits low toxicity to mammals, it can cause irritation to the skin and eyes. It possesses moderate solubility in water and displays persistence in soil systems. Available data suggests that, under specific conditions, it may also persist in water. Significant quantities of Napropamide were found in Jubilee Hills, Kukatpally, and Tarnaka. On the other hand, the insecticide Picaridin, commonly used as an insect repellent, was detected in samples from Bharat Nagar and Sanath Nagar. The most commonly reported side effects following exposure to insect repellents were nausea, vomiting, red eyes/conjunctivitis, and mouth irritation.

Dibutyl phthalate is a synthetic compound that is incorporated into plastics and various other chemicals. In the context of plastics, it serves as a plasticizer, contributing to their softness. It is also utilized in elastomers, lacquers, explosives, printing inks, solvents for resin and perfume oils, paper coatings, adhesives, and nail polish. The highest abundance values were observed in Begumpet, Bharat nager, and Jubilee Hills samples. Prolonged exposure to butyl phthalate may be harmful to the liver, kidneys, developing fetus, and male testes. Bis(2-ethylhexyl) phthalate (DEHP) is detected in all the samples with high abundance in Dundigal groundwater. The U.S. Environmental Protection Agency has determined that DEHP is a probable human carcinogen that can cause cancer, birth defects, development of the fetus, and male reproductive damage [21].

The compound Avobenzone is a UVA blocker used as an active ingredient in sunscreens. The highest concentration of Avobenzone is detected in Tirumalgiri and Begumpet groundwater samples. In early pregnancy, avobenzone can trigger mitochondrial dysfunction-mediated apoptosis, which results in abnormal placentation [22]. Estriol and 17αβ - Dihydroequilin had high abundance values in Begumpet, Dundigal, and Tirumalgiri. These compounds are estrogens which are classified as the greatest endocrine disruptors among many micropollutants. The concentration of these hormones, which play a role in the development of

feminine features in a variety of living creatures, has increased recently in aquatic environments [23]. Humans as well as animals regularly produce the natural estrogens estriol and 17-Dihydroequilin [24]. Microcystin-LR a cyanotoxin that is generated by cyanobacteria during eutrophication, was also identified at seven sample locations with the highest abundance in the Kukatpally sample indicating the contamination of water with high nutrients or algae.

Table 1. Micropollutants identified in different groundwater samples of Hyderabad.

	Names	Begumpet	Bharat nagar	Dundigal	Jubliee Hills	Kukatpally	Sanath nagar	Tarnaka	Tirumalagiri
Cosmetic	Avobenzone	**163403**	4158	25187	N.D.	N.D.	21113	N.D.	**169373**
Cyanotoxins	Microcystin-LR	2237	N.D.	7555	2286	**105749**	671	3375	3966
Fungicide	Nuarimol	N.D.	415	N.D.	N.D.	N.D.	**39050**	N.D.	N.D.
Insecticide	Picaridin	N.D.	**48966**	N.D.	N.D.	N.D.	1913	N.D.	N.D.
Herbicide	Butachlor	**163403**	N.D.	**216699**	N.D.	N.D.	19692	N.D.	26746
	Napropamide	7938	16300	7604	**124720**	**149439**	2113	**122073**	N.D.
	Simetryn	N.D.	N.D.	N.D.	N.D.	N.D.	**223937**	N.D.	N.D.
Hormones and Steroids	17α-Dihydroequilin	**146019**	11487	**100076**	N.D.	N.D.	6193	N.D.	**217578**
	Estriol	**175638**	27280	**169976**	N.D.	N.D.	15518	N.D.	**208464**
Metabolite	Clarithromycin-N-oxide	**219218**	**204354**	62738	**200859**	**236678**	N.D.	**182870**	11689
Miscellaneous	N-Methylpyrrolidone	44707	51350	44699	38276	**59370**	N.D.	48541	42282
	N-Methylacetanilide	869	N.D.	N.D.	N.D.	N.D.	**52625**	N.D.	1608
	4-Nonylpenoxyacetic acid	N.D.	38727	N.D.	N.D.	N.D.	853	N.D.	N.D.
Pharmaceuticals	4-Hydroxyantipyrine	N.D.	N.D.	18057	N.D.	N.D.	**42877**	N.D.	31784
	Apramycin	28237	**73373**	47297	50564	57976	2523	50579	51914
	Codeine-d6	N.D.	572	N.D.	N.D.	N.D.	37347	N.D.	N.D.
	Dextilidine	26272	N.D.	18939	N.D.	N.D.	721	N.D.	**66004**
	Doxepin	**112908**	**255076**	4776	**129622**	**174821**	N.D.	**117224**	1629
	Erythromycin	5360	838	53874	N.D.	N.D.	1564	N.D.	**63655**
	Lovastatin	1245	30989	625	N.D.	N.D.	2484	N.D.	N.D.
	Methadone-d3	N.D.	822	N.D.	603	607	**123497**	564	N.D.
	Morphine-d3	26408	25221	33572	25274	N.D.	20335	31313	15143
	Naftidrofuryl	N.D.	N.D.	N.D.	N.D.	N.D.	43395	N.D.	N.D.
	Narasin	1922	N.D.	51583	N.D.	N.D.	14217	N.D.	**62789**
	Nefazodone	**103249**	N.D.	88061	**102249**	**126016**	3778	**101246**	46716
	Pindolol	1196	N.D.	N.D.	N.D.	N.D.	**39216**	N.D.	N.D.
	Reserpine	N.D.	N.D.	983	N.D.	N.D.	**38177**	N.D.	957
	Sibutramine	2385	N.D.	**103655**	N.D.	N.D.	N.D.	N.D.	**164261**
Plasticizer	Bis(2-ethylhexyl) phthalate	9982	20789	**210045**	8258	4903	29380	3365	14598
	Dibutyl phthalate	**109689**	**223355**	5684	**129622**	12070	N.D.	6469	1507

N.D. = not detected.

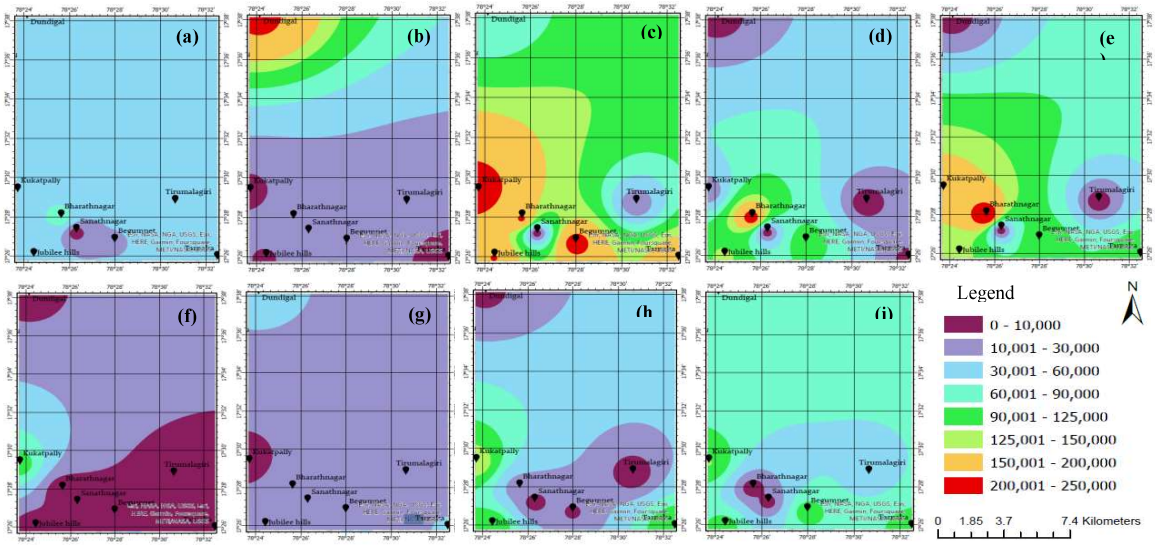

Fig. 5. Spatial mapping of micropollutants abundance values detected in at least seven groundwater samples (a) Apramycin, (b) Bis(2-ethylhexyl) phthalate, (c) Clarithromycin-N-oxide, (d) Dibutyl phthalate, (e) Doxepin, (f) Microcystin-LR, (g) Morphine-d3, (h) Napropamide, (i) Nefazodone

The Spatial mapping of micropollutants (Apramycin, Bis(2-ethylhexyl) phthalate, Clarithromycin-N-oxide, Dibutyl phthalate, Doxepin, Microcystin-LR, Morphine-d3, Napropamide, Nefazodone) detected in at least seven groundwater samples is shown in Figure 5. The spatial mapping of the Apramycin shows that the most prevalent abundance value range between 30,000 to 60,000. The highest abundance value of the compound is detected in Bharat nagar. The veterinary hospitals and poultry farms are majorly located in Begumpet, Kukatpally, Tarnaka, Sanath nagar, Jubilee hills, and Tirumalgiri areas. The spatial distribution of DEHP shows that most of the contamination of plasticizer is in Dundigal areas (Figure 5(b)). The spatial mapping of Clarithromycin-N-oxide metabolite indicates the groundwater contamination with domestic wastewater near Kukatpally, Begumpet, Bharat nagar, Jubilee hills, and Tirumalgiri areas. The spatial distribution of Dibutyl phthalate suggests that the higher abundance is near Bharat nagar areas. The presence of Dibutyl phthalate could be due to domestic wastewater discharge as it is also used in perfumes and nail polish. The mapping of Doxepin shows that regions near Kukatpally and Bharat nagar have a higher abundance of antidepressant. The prevalent abundance values of Microcystin-LR and Morphine-d3 ranged between 0 to 30,000. The highest abundance values of Napropamide and Nefazodone were detected mainly in Kukatpally, Jubilee Hills, and Tirumalgiri areas. The spatial mapping indicated that the Kukatpally, Bharat nagar, and Jubilee hills had high abundance value of the detected compounds even though the number of compounds detected are less than 80 indicating the intensity of pollution.

Based on the internet search about 200 pharmaceutical companies were located in the premises of the sample collected areas. The approximate number of pharmaceutical companies in Begumpet, Bharat nagar, Dundigal, Jubilee Hills, Kukatpally, Sanath nagar, Tarnaka, and Tirumalagiri were 14, 4, 5, 4, 12, 10, 6, and 14 respectively. Approximately 40 pharma companies are located near the premises of Sanath nagar and Begumpet areas. Although the number of companies in the region was less, the discharge from these surrounding companies could be one of the reasons for the high number of pharmaceutical compounds detected in groundwater samples from Sanath nagar and Begumpet. The next highest number of pharmaceuticals were detected in Dundigal area which had around 14 pharma companies nearby. Among the top 30 compounds, 13 pharmaceuticals were detected in Sanath nagar, 11 in Dundigal, and 10 in Begumpet and Tirumalgiri areas. The number of agrotech companies were also densely located near Jubilee Hills, Sanath nagar, and Begumpet areas where there is a possibility of discharge of the compounds through these industries. The urinary metabolites detected in the groundwater indicate the discharge of domestic wastewater or sewage mostly into the soil which would have contaminated the groundwater. Most of Hyderabad's residential communities have decentralized wastewater treatment plants where part of the treatment takes place and the treated water is recycled for daily needs such as gardening and toilet flushing. In most cases, the partially treated wastewater is sent to a centralized wastewater treatment facility. The inefficiencies of these treatment plants, leakage of wastewater during transportation, or infiltration of solid waste leachate could be the reasons for contamination. Almost all the sampling sites have at least one dumping yard.

The absence of monitoring micropollutants in these plants can be attributed to the lack of strict regulations and guidelines addressing these pollutants. Historically, the focus of wastewater treatment plants has been on conventional pollutants (like chemical oxygen demand, biological oxygen demand, and nutrients) than micropollutants. Furthermore, it is difficult for many treatment facilities to maintain the sophisticated

equipment needed for micropollutant analysis in order to monitor micropollutants. To address these concerns, it is crucial to establish stricter regulations and guidelines specifically addressing micropollutants in wastewater treatment. Efforts should also be made to improve treatment plant efficiency, minimize wastewater leakage, and prevent solid waste leachate infiltration. Proper waste management practices and the implementation of monitoring systems can help identify and mitigate potential sources of contamination. Additionally, public awareness should be increased regarding the risks associated with micropollutants, and advanced treatment processes should be promoted in wastewater treatment plants. Regulatory agencies should work towards establishing guidelines and regulations for monitoring and controlling micropollutants, ensuring the protection of water resources and public health.

Source control measures should be implemented to prevent the introduction of micropollutants into groundwater. This can include stricter regulations and best management practices for industrial, agricultural, and residential activities. By reducing the use of harmful substances or implementing proper containment and disposal methods, the potential for micropollutant contamination can be minimized. Upgrading wastewater treatment plants, implementing constructed wetlands, managing aquifer recharge, and monitoring groundwater quality are among the recommended measures. Advanced treatment technologies such as activated carbon adsorption, ozonation, UV irradiation, and membrane filtration have shown promise in removing a wide range of micropollutants. Education and awareness campaigns are also important in promoting the responsible use and disposal of chemicals and fostering sustainable behaviors and practices. It is essential to customize the approach to each specific situation and micropollutant, as effectiveness may vary based on local conditions and characteristics. A comprehensive and site-specific strategy is necessary to effectively address emerging micropollutants in groundwater.

4 Conclusion

The groundwater samples of Hyderabad had been contaminated with many different classes of micropollutants with the majority belonging to pharmaceuticals and agrochemicals. The detected pharmaceuticals consist of veterinary medications, narcotic pharmaceuticals, pain killers, anti-psychotic, anti-depressant, and anti-obesity drugs. Sanath nagar and Begumpet areas which are surrounded by more pharmaceutical and agrochemical companies had shown more pharma and pesticide compounds in groundwater indicating the discharge of the industrial wastewater. The presence of urinary metabolites Clarithromycin N-oxide, 4-Hydroxyantipyrine, and Morphine indicates the discharge of domestic wastewater into the aquifers. The majority of the compounds identified have concerning effects on human health. The presence of micropollutants in groundwater, despite the short duration of this investigation, suggests that appropriate wastewater and solid waste treatment procedures should be implemented. Since a lot of new pollutants are consistently entering the market, continuous tracking measures and emission controls must be executed.

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