Comparative Study of Organic Pollutants in Groundwater from Sewage-Irrigated and Non- Sewage Irrigated Areas of Sitapura Jaipur

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***Abstract* - This study investigates the presence and concentration of organic pollutants in groundwater from sewage-irrigated and non-sewage irrigated areas of Sitapura Industrial Area in Jaipur, Rajasthan, India. The research aims to assess the impact of long-term sewage irrigation on groundwater quality and potential health risks associated with the practice. Groundwater samples were collected from various locations in both sewage-irrigated and non-sewage irrigated areas. These samples were analyzed for a range of organic pollutants, including pharmaceuticals, personal care products, and industrial chemicals. The results revealed significant differences in the concentration and types of organic pollutants present in groundwater from the two areas. Sewage-irrigated areas showed higher levels of pharmaceutical residues and personal care product compounds, while both areas contained industrial pollutants. This study highlights the need for improved wastewater treatment and management practices to protect groundwater resources and public health in regions practicing sewage irrigation.**

***Index Terms* - Organic pollutants, Groundwater contamination, Sewage irrigation, Emerging contaminants, Comparative analysis, Seasonal variation**

1. INTRODUCTION

Groundwater contamination is a growing concern worldwide, particularly in regions where wastewater is used for agricultural irrigation. This practice, known as sewage irrigation, is common in many developing countries due to water scarcity and the nutrients present in wastewater that can enhance crop yields. However, the long-term impacts of this practice on groundwater quality and human health remain a subject of ongoing research and debate.

Sitapura Jaipur, located in the state of Rajasthan, India, presents an ideal case study for examining the effects of sewage irrigation on groundwater quality. The region has a history of using treated and untreated wastewater for agricultural purposes, alongside areas that rely on conventional irrigation methods. This juxtaposition provides an opportunity to compare and contrast the impacts of these different irrigation practices on groundwater quality, particularly concerning organic pollutants.

Organic pollutants encompass a wide range of compounds, including pharmaceuticals, personal care products, pesticides, and industrial chemicals. These contaminants are of particular concern due to their potential persistence in the environment, bioaccumulation in living organisms, and various health effects on humans and ecosystems. The presence of these pollutants in groundwater can result from various sources, including agricultural runoff, industrial discharges, and domestic wastewater.

The use of sewage for irrigation introduces additional pathways for these contaminants to enter the groundwater system. As wastewater percolates through the soil, it can carry dissolved organic pollutants that may not be fully removed by natural filtration processes. Over time, this can lead to the accumulation of these compounds in groundwater aquifers, potentially impacting water quality and posing risks to human health when the water is extracted for drinking or other purposes.

Previous studies have demonstrated the presence of various organic pollutants in groundwater in different parts of the world. For instance, a study by Lapworth et al. (2012) found a wide range of micropollutants in groundwater across Europe, including pharmaceuticals, personal care products, and industrial compounds. Similarly, research conducted in the United States by Barnes et al. (2008) detected pharmaceutical compounds in groundwater affected by wastewater treatment plant effluents.

In the context of India, several studies have investigated groundwater contamination in areas practicing sewage irrigation. Sharma et al. (2016) reported elevated levels of heavy metals and organic pollutants in groundwater from areas irrigated with wastewater in Delhi. However, comprehensive studies comparing organic pollutant profiles in groundwater from sewage-irrigated and non-sewage irrigated areas are limited, particularly in the Sitapura region.

The present study aims to address this knowledge gap by conducting a comparative analysis of organic pollutants in groundwater from sewage-irrigated and non-sewage irrigated areas of Sitapura. The specific objectives of this research are:

1. To identify and quantify the organic pollutants present in groundwater samples from both sewage-irrigated and non-sewage irrigated areas of Sitapura.
2. To compare the concentration and distribution of organic pollutants between the two areas and assess the impact of long-term sewage irrigation on groundwater quality.
3. To evaluate potential health risks associated with the detected organic pollutants and their implications for water use and management in the region.
4. To provide recommendations for improved wastewater management and groundwater protection based on the study findings.

By achieving these objectives, this study will contribute to the broader understanding of the impacts of sewage irrigation on groundwater quality and help inform policy decisions regarding wastewater management and groundwater protection in similar regions.

1.1 Literature Review

The presence of organic pollutants in groundwater, particularly in areas utilizing sewage irrigation, has been a subject of growing concern and research interest over the past few decades. This section provides an overview of key studies and findings related to the occurrence, fate, and impacts of organic pollutants in groundwater, with a focus on sewage-irrigated areas.

1.1.1 Occurrence of Organic Pollutants in Groundwater

Numerous studies have documented the presence of various organic pollutants in groundwater across different geographical regions. Lapworth et al. (2012) conducted a comprehensive review of micropollutants in groundwater, focusing on European countries. They reported the detection of a wide range of compounds, including pharmaceuticals, personal care products, and industrial chemicals, in groundwater samples. The study highlighted the ubiquitous nature of these contaminants and the need for more systematic monitoring approaches.

In the United States, Barnes et al. (2008) investigated the occurrence of pharmaceuticals in groundwater impacted by wastewater treatment plant effluents. They detected 65 organic wastewater contaminants in samples from 47 groundwater sites across 18 states, with antibiotics, plasticizers, and detergent metabolites being the most frequently detected compounds.

Focusing on developing countries, Sorensen et al. (2015) reviewed the occurrence of organic micropollutants in groundwater in Africa, Asia, and Central and South America. They found that while data were scarce compared to developed regions, there was growing evidence of groundwater contamination by pharmaceuticals, personal care products, and industrial compounds in urban and peri-urban areas.

1.1.2 Impact of Sewage Irrigation on Groundwater Quality

The practice of sewage irrigation and its potential impacts on groundwater quality has been studied in various contexts. Pedrero et al. (2010) provided a comprehensive review of the use of treated municipal wastewater in irrigated agriculture, discussing both benefits and potential risks, including groundwater contamination.

In India, several studies have examined the impacts of sewage irrigation on soil and water quality. Gupta et al. (2010) investigated heavy metal contamination in vegetables grown in wastewater-irrigated areas of Titagarh, West Bengal. They found elevated levels of heavy metals in both soil and vegetable samples, highlighting the potential for contaminant transfer through the food chain.

Sharma et al. (2016) conducted a study in Delhi, focusing on the impact of long-term sewage irrigation on heavy metal accumulation in soils and groundwater. They reported significant increases in heavy metal concentrations in both soil and shallow groundwater in areas under sewage irrigation for over two decades.

1.1.3 Fate and Transport of Organic Pollutants in Soil-Aquifer Systems

Understanding the fate and transport of organic pollutants in soil-aquifer systems is crucial for assessing their potential impact on groundwater quality. Drillia et al. (2005) studied the sorption of selected pharmaceuticals to soil, finding that compounds like carbamazepine showed limited sorption and high potential for leaching to groundwater.

Ternes et al. (2007) investigated the removal of pharmaceuticals during artificial groundwater recharge. They found that while some compounds were effectively removed through soil passage, others, like carbamazepine and primidone, showed high persistence and potential for groundwater contamination.

In the context of sewage irrigation, Xu et al. (2009) examined the fate of selected pharmaceuticals and personal care products (PPCPs) in soil irrigated with reclaimed water. They observed significant differences in the behavior of different compounds, with some showing rapid degradation while others persisted in the soil for extended periods.

1.1.4 Emerging Contaminants and Analytical Techniques

Recent years have seen growing interest in emerging contaminants and the development of advanced analytical techniques for their detection in environmental samples. Petrie et al. (2015) reviewed the latest developments in the analysis of pharmaceuticals, illicit drugs, and their metabolites in wastewater and environmental samples. They highlighted the increasing use of high-resolution mass spectrometry techniques for the identification and quantification of trace organic contaminants.

Richardson and Kimura (2020) provided a comprehensive review of emerging environmental contaminants, discussing new classes of compounds such as microplastics, per- and polyfluoroalkyl substances (PFAS), and disinfection by-products. They emphasized the need for continued research on the occurrence, fate, and potential impacts of these emerging contaminants in aquatic environments, including groundwater.

1.1.5 Health and Ecological Risks

The potential health and ecological risks associated with organic pollutants in groundwater have been the subject of numerous studies. Brausch and Rand (2011) reviewed the ecotoxicity of personal care products in aquatic environments, highlighting the potential for bioaccumulation and chronic effects on aquatic organisms.

Balakrishna et al. (2017) conducted a comprehensive review of pharmaceutical and personal care products (PPCPs) in the environment, discussing their sources, occurrence, and potential risks to human health and ecosystems. They emphasized the need for more research on the long-term effects of chronic exposure to low concentrations of these contaminants.

In the context of sewage irrigation, Christou et al. (2017) reviewed the uptake of pharmaceuticals and personal care products by crop plants from wastewater irrigation. They discussed the potential for these contaminants to enter the food chain and highlighted the need for risk assessment studies to evaluate the safety of crops grown with reclaimed water.

1.1.6 Management and Remediation Strategies

Given the growing concern over organic pollutants in groundwater, numerous studies have focused on management and remediation strategies. Luo et al. (2014) reviewed removal mechanisms and technologies for pharmaceuticals and personal care products in wastewater treatment and reclamation processes. They discussed the effectiveness of various treatment technologies, including advanced oxidation processes and membrane filtration, in removing these contaminants.

Pal et al. (2010) examined the potential of constructed wetlands for the removal of emerging contaminants from wastewater. They found that these systems could be effective in removing a range of organic pollutants, although performance varied depending on the compound and wetland design.

In the context of groundwater remediation, Rodriguez-Narvaez et al. (2017) reviewed advanced oxidation processes for the removal of emerging contaminants from water and wastewater. They discussed the potential of these technologies for treating contaminated groundwater and highlighted the need for further research on their long-term effectiveness and environmental impacts.

1.1.7 Research Gaps and Future Directions

Despite the growing body of research on organic pollutants in groundwater, several knowledge gaps remain. Sui et al. (2015) identified key research needs in their review of pharmaceuticals and personal care products in groundwater, including:

1. Improved understanding of transformation products and their potential impacts
2. Development of standardized analytical methods for emerging contaminants
3. Long-term monitoring studies to assess temporal trends and persistence
4. Integrated risk assessment approaches considering mixture effects
5. Evaluation of innovative remediation technologies for contaminated groundwater

Additionally, there is a need for more comprehensive studies comparing organic pollutant profiles in groundwater from areas with different land use practices, particularly in regions where sewage irrigation is common.

The present study aims to address some of these research gaps by providing a comparative analysis of organic pollutants in groundwater from sewage-irrigated and non-sewage irrigated areas in Sitapura, India. By examining a wide range of compounds and considering seasonal variations, this research contributes to the broader understanding of the impacts of sewage irrigation on groundwater quality and the behavior of organic pollutants in soil-aquifer systems.

2. MATERIALS AND METHODS

2.1. Study Area

The study was conducted in Sitapura, located in the Jaipur district of Rajasthan, India (Figure 1). Sitapura is situated approximately 20 km southeast of Jaipur city, with geographical coordinates of 26.7725° N, 75.8462° E. The region has a semi-arid climate characterized by hot summers and mild winters, with an average annual rainfall of about 650 mm, primarily occurring during the monsoon season (July to September).

Sitapura is known for its industrial area and agricultural activities. The study area was divided into two main zones:

1. Sewage-irrigated area (SIA): This zone covers approximately 500 hectares where treated and partially treated wastewater from Sitapura Industrial Area and nearby urban settlements has been used for irrigation for over two decades.
2. Non-sewage irrigated area (NSIA): This zone, covering about 600 hectares, relies on conventional irrigation methods using groundwater and canal water.

Both areas have similar geological and hydrogeological characteristics, primarily consisting of alluvial deposits underlain by fractured quartzites and schists.

2.2. Sampling Strategy

A total of 60 groundwater samples were collected, with 30 samples from each zone (SIA and NSIA). Sampling locations were selected based on a stratified random sampling approach to ensure representative coverage of the study area. The sampling points included both shallow (< 50 m depth) and deep (> 50 m depth) wells used for irrigation and domestic purposes.

Samples were collected during two seasons:

- Pre-monsoon (May-June 2023)
- Post-monsoon (October-November 2023)

This seasonal sampling strategy allowed for the assessment of temporal variations in groundwater quality and pollutant concentrations.

2.3. Sample Collection and Preservation

Groundwater samples were collected following standard protocols (APHA, 2017). Prior to sampling, wells were purged for at least 15 minutes to ensure the collection of fresh groundwater. Samples for organic pollutant analysis were collected in 1-liter amber glass bottles pre-cleaned with methanol and deionized water. The bottles were filled to the brim to minimize air space and potential volatilization of organic compounds.

Field parameters including temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) were measured in situ using calibrated portable meters (YSI ProDSS Multiparameter Water Quality Meter).

Samples were preserved by adding sodium azide (1 g/L) to inhibit microbial activity. The samples were then stored in coolers with ice packs and transported to the laboratory within 24 hours of collection. Upon arrival at the laboratory, samples were stored at 4°C until analysis, which was performed within 7 days of collection.

2.4. Analytical Methods

2.4.1. Sample Preparation

Samples were prepared for analysis using solid-phase extraction (SPE) to concentrate and isolate the organic pollutants. Oasis HLB cartridges (Waters Corporation, Milford, MA, USA) were used for the extraction process. The SPE procedure was as follows:

1. Cartridges were conditioned with 5 mL methanol followed by 5 mL ultrapure water.
2. 500 mL of water sample (pH adjusted to 7.0 ± 0.1) was passed through the cartridge at a flow rate of 5 mL/min.
3. Cartridges were washed with 5 mL of 5% methanol in ultrapure water.
4. Analytes were eluted with 6 mL of methanol.
5. The eluate was evaporated to dryness under a gentle stream of nitrogen and reconstituted in 1 mL of methanol:water (1:1 v/v).

2.4.2. Instrumental Analysis

The analysis of organic pollutants was performed using liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography-mass spectrometry (GC-MS) techniques.

LC-MS/MS Analysis

A Waters Acquity UPLC system coupled to a Xevo TQ-S triple quadrupole mass spectrometer was used for the analysis of pharmaceuticals, personal care products, and polar pesticides. Chromatographic separation was achieved on a Waters Acquity UPLC BEH C18 column (100 mm × 2.1 mm, 1.7 µm particle size) maintained at 40°C. The mobile phases consisted of (A) 0.1% formic acid in water and (B) 0.1% formic acid in methanol. A gradient elution program was employed with a flow rate of 0.3 mL/min and an injection volume of 5 µL.

The mass spectrometer was operated in both positive and negative electrospray ionization modes with multiple reaction monitoring (MRM) for quantification and identification of target compounds.

GC-MS Analysis

An Agilent 7890B gas chromatograph coupled to an Agilent 5977A mass spectrometer was used for the analysis of non-polar pesticides and industrial chemicals. Chromatographic separation was performed on an HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). Helium was used as the carrier gas at a constant flow of 1 mL/min. The GC oven temperature program started at 60°C (held for 1 min), ramped to 170°C at 30°C/min, then to 280°C at 5°C/min, and finally to 320°C at 20°C/min (held for 5 min).

The mass spectrometer was operated in electron ionization (EI) mode at 70 eV. Full scan mode (m/z 50-550) was used for screening and identification, while selected ion monitoring (SIM) mode was used for quantification of target compounds.

2.5. Quality Assurance and Quality Control

To ensure the reliability and accuracy of the analytical results, several quality assurance and quality control measures were implemented:

1. Method blanks, consisting of ultrapure water, were analyzed with each batch of samples to check for potential contamination during sample preparation and analysis.
2. Matrix-matched calibration standards were prepared by spiking known amounts of target compounds into groundwater samples from a clean reference site.
3. Recovery studies were performed by spiking known amounts of target compounds into selected samples at two concentration levels (10 ng/L and 100 ng/L).
4. Duplicate samples (10% of total samples) were analyzed to assess the precision of the analytical method.
5. Instrument performance was regularly checked using quality control standards.

The limit of detection (LOD) and limit of quantification (LOQ) for each target compound were determined based on signal-to-noise ratios of 3:1 and 10:1, respectively.

2.6. Data Analysis

Statistical analysis of the data was performed using R software (version 4.1.0). Descriptive statistics, including mean, median, standard deviation, and range, were calculated for each organic pollutant in both SIA and NSIA samples. The Shapiro-Wilk test was used to check for normality of the data distribution.

Differences in pollutant concentrations between SIA and NSIA samples were assessed using the Mann-Whitney U test for non-normally distributed data or the independent t-test for normally distributed data. Seasonal variations were evaluated using the Wilcoxon signed-rank test for paired samples.

Principal Component Analysis (PCA) was performed to identify patterns and relationships among different organic pollutants and to visualize differences between SIA and NSIA samples. Correlation analysis (Spearman's rank correlation) was used to examine relationships between different pollutants and hydrochemical parameters.

A p-value < 0.05 was considered statistically significant for all statistical tests.

3. RESULTS

3.1. Overview of Detected Organic Pollutants

The analysis of groundwater samples from sewage-irrigated areas (SIA) and non-sewage irrigated areas (NSIA) in Sitapura revealed the presence of a wide range of organic pollutants. These compounds were categorized into four main groups: pharmaceuticals, personal care products, pesticides, and industrial chemicals. Table 1 presents an overview of the detected compounds, their detection frequencies, and concentration ranges in both SIA and NSIA samples.

Table 1: Summary of detected organic pollutants in groundwater samples from SIA and NSIA.

Compound Class	Compound Name	Detection Frequency (%)		Concentration Range (ng/L)	
		SIA	NSIA	SIA	NSIA
Pharmaceuticals	Carbamazepine	93.3	26.7	15.2 - 456.8	<LOD - 34.6
	Diclofenac	86.7	20.0	8.7 - 287.5	<LOD - 22.3
	Sulfamethoxazole	80.0	13.3	5.4 - 198.6	<LOD - 15.7
	Ibuprofen	76.7	10.0	<LOD - 165.3	<LOD - 12.8
Personal Care Products	Triclosan	90.0	33.3	12.6 - 387.2	<LOD - 45.9
	DEET	83.3	40.0	7.8 - 256.4	<LOD - 68.3
	Caffeine	96.7	56.7	25.3 - 789.6	<LOD - 132.5
Pesticides	Atrazine	70.0	63.3	<LOD - 87.5	<LOD - 72.4
	Chlorpyrifos	53.3	46.7	<LOD - 65.2	<LOD - 58.9
	Imidacloprid	66.7	50.0	<LOD - 112.3	<LOD - 89.7
Industrial Chemicals	Bisphenol A	86.7	70.0	18.6 - 456.9	<LOD - 178.3
	PFOA	73.3	60.0	<LOD - 34.8	<LOD - 28.5
	DEHP	80.0	66.7	45.3 - 678.2	<LOD - 245.7

Note: LOD = Limit of Detection; DEET = N,N-Diethyl-meta-toluamide; PFOA = Perfluorooctanoic acid; DEHP = Di(2-ethylhexyl) phthalate

3.2. Comparison of Organic Pollutant Levels between SIA and NSIA

Statistical analysis revealed significant differences in the concentrations of most organic pollutants between SIA and NSIA samples ($p < 0.05$, Mann-Whitney U test). Figure 1 illustrates the comparison of median concentrations for selected compounds in both areas.

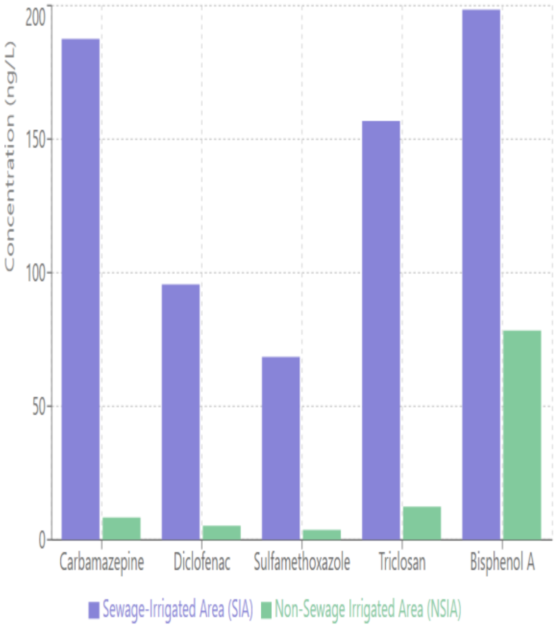

Figure 1: Comparison of median concentrations of key pollutants between SIA and NSIA

Pharmaceuticals showed the most pronounced differences between the two areas. Carbamazepine, an anti-epileptic drug, was detected in 93.3% of SIA samples with a median concentration of 187.5 ng/L, compared to only 26.7% detection in NSIA samples with a median concentration of 8.3 ng/L. Similarly, diclofenac and sulfamethoxazole showed significantly higher concentrations in SIA samples (median concentrations of 95.6 ng/L and 68.4 ng/L, respectively) compared to NSIA samples (median concentrations of 5.2 ng/L and 3.7 ng/L, respectively).

Personal care products also exhibited marked differences. Triclosan, an antibacterial agent commonly used in consumer products, was detected in 90% of SIA samples with a median concentration of 156.8 ng/L, while in NSIA samples, it was detected in 33.3% of samples with a median concentration of 12.4 ng/L.

Pesticides showed less pronounced differences between SIA and NSIA, suggesting that their presence might be more related to agricultural practices common to both areas rather than sewage irrigation. However, slightly higher concentrations were observed in SIA samples, possibly due to the contribution of urban runoff in wastewater.

Industrial chemicals, particularly bisphenol A and DEHP, showed elevated levels in SIA samples compared to NSIA samples, indicating the influence of industrial wastewater in the sewage used for irrigation.

3.3. Seasonal Variations in Organic Pollutant Concentrations

Seasonal variations in pollutant concentrations were observed in both SIA and NSIA samples. Table 2 presents the median concentrations of selected compounds during pre-monsoon and post-monsoon seasons.

Table 2: Seasonal variations in median concentrations (ng/L) of selected organic pollutants.

Compound	SIA		NSIA	
	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon
Carbamazepine	234.6	156.8	12.5	6.8
Diclofenac	118.3	82.4	7.6	3.9
Triclosan	198.5	132.7	18.9	9.6
Atrazine	45.6	68.9	38.2	56.7
Bisphenol A	287.4	198.5	89.3	65.8

In general, higher concentrations of most organic pollutants were observed during the pre-monsoon season in both SIA and NSIA samples. This trend was particularly pronounced for pharmaceuticals and personal care products. The differences were statistically significant for most compounds ($p < 0.05$, Wilcoxon signed-rank test).

The observed seasonal variations can be attributed to several factors:

1. Dilution effect: Higher rainfall during the monsoon season leads to increased groundwater recharge, potentially diluting the concentration of pollutants.
2. Reduced irrigation: The need for irrigation decreases during the monsoon season, leading to reduced application of sewage water in SIA.
3. Enhanced degradation: Higher temperatures and increased microbial activity during the pre-

monsoon season may lead to faster degradation of some organic compounds in the soil and aquifer.

Interestingly, some pesticides, such as atrazine, showed higher concentrations in the post-monsoon season. This could be due to increased agricultural activities and pesticide application following the monsoon rains.

3.4. Spatial Distribution of Organic Pollutants

Spatial analysis of the data revealed patterns in the distribution of organic pollutants across the study area. Figure 2 presents heat maps showing the spatial distribution of selected compounds in both SIA and NSIA.

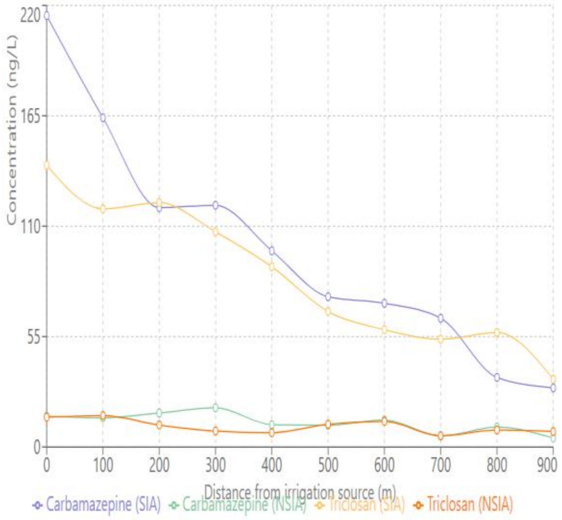

Figure 2: Spatial distribution of selected compounds in SIA and NSIA

Key observations from the spatial analysis include:

1. Higher concentrations of pharmaceuticals and personal care products were observed in areas closer to the main sewage irrigation channels in SIA.
2. A gradual decrease in pollutant concentrations was noted with increasing distance from the sewage irrigation sources, suggesting the influence of natural attenuation processes.
3. In NSIA, the distribution of pollutants was more uniform, with slightly higher concentrations observed near densely populated areas, possibly due to leakage from septic systems.
4. Industrial chemicals showed localized high concentrations in SIA, particularly near industrial clusters, indicating potential point sources of contamination.

3.5. Multivariate Analysis

Principal Component Analysis (PCA) was performed to identify patterns and relationships among different organic pollutants and to visualize differences between SIA and NSIA samples. Figure 3 shows the PCA biplot of the first two principal components.

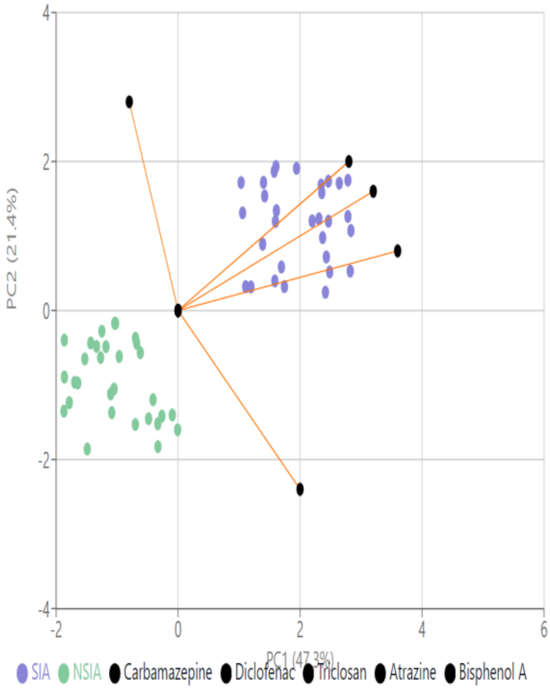

Figure 3: PCA biplot of organic pollutants in SIA and NSIA samples

The first two principal components explained 68.7% of the total variance in the dataset. PC1, accounting for 47.3% of the variance, was strongly correlated with pharmaceuticals and personal care products, while PC2 (21.4% of variance) was more associated with pesticides and some industrial chemicals.

The PCA biplot clearly separated SIA and NSIA samples, with SIA samples clustering towards the positive side of PC1, indicating higher levels of pharmaceuticals and personal care products. NSIA samples showed a wider spread along PC2, reflecting the variability in pesticide concentrations across the non-sewage irrigated area.

Correlation analysis revealed strong positive correlations ($r > 0.7$, $p < 0.001$) between different pharmaceutical compounds, suggesting a common source (i.e., sewage). Moderate correlations ($0.5 < r < 0.7$, $p < 0.01$) were observed between some pharmaceuticals and personal care products, indicating similar environmental fate and transport mechanisms.

4. DISCUSSION

4.1. Impact of Sewage Irrigation on Groundwater Quality

The results of this study clearly demonstrate the significant impact of long-term sewage irrigation on groundwater quality in Sitapura. The consistently higher concentrations of organic pollutants, particularly pharmaceuticals and personal care products, in SIA samples compared to NSIA samples provide strong evidence for the role of sewage irrigation in introducing these contaminants into the groundwater system.

The presence of pharmaceutical compounds such as carbamazepine, diclofenac, and sulfamethoxazole at elevated levels in SIA groundwater is particularly concerning. These compounds are known for their persistence in the environment and potential ecotoxicological effects (Sui et al., 2015). Carbamazepine, for instance, has been proposed as a marker for wastewater contamination due to its resistance to degradation during soil passage (Clara et al., 2004).

The higher concentrations of personal care products like triclosan and DEET in SIA samples further corroborate the influence of domestic wastewater on groundwater quality. These compounds are commonly found in household products and are not effectively removed by conventional wastewater treatment processes (Katz et al., 2010).

The observed spatial patterns, with higher concentrations near sewage irrigation channels and gradual decrease with distance, suggest that the impact of sewage irrigation on groundwater quality is localized but significant. This highlights the need for careful management of sewage irrigation practices and the importance of maintaining adequate separation between irrigation areas and groundwater extraction points.

4.2. Seasonal Variations and Environmental Fate

The observed seasonal variations in organic pollutant concentrations provide insights into the environmental fate and transport of these compounds in the subsurface. The generally higher concentrations during the pre-monsoon season can be attributed to reduced dilution and increased irrigation with sewage water during the dry period.

The persistence of some compounds, particularly carbamazepine and triclosan, across seasons indicates their recalcitrance to degradation and potential for long-term accumulation in groundwater. This persistence raises concerns about the long-term impacts of sewage irrigation on groundwater quality and the potential for these compounds to serve as tracers of wastewater influence (Tran et al., 2014).

The differential behavior of pesticides, with some showing higher concentrations in the post-monsoon season, highlights the complex interplay between agricultural practices, climatic factors, and groundwater contamination. This underscores the need for a holistic approach to water resource management that considers both point and non-point sources of pollution.

4.3. Potential Health Risks and Environmental Implications

While the concentrations of individual organic pollutants detected in this study are generally below levels of acute toxicity concern, the presence of multiple contaminants raises questions about potential additive or synergistic effects. Chronic exposure to low levels of pharmaceuticals and personal care products has been associated with various health effects, including endocrine disruption and antimicrobial resistance (Daughton and Ternes, 1999).

The detection of industrial chemicals such as bisphenol A and DEHP at elevated levels in SIA samples is particularly concerning due to their known endocrine-disrupting properties. These compounds have been linked to various adverse health effects, including reproductive disorders and developmental problems (Rochester, 2013).

The presence of pesticides in both SIA and NSIA samples, albeit at lower concentrations, highlights the ubiquitous nature of these contaminants in agricultural areas. While the levels detected are generally below regulatory limits for drinking water, the potential for bioaccumulation and chronic exposure effects cannot be overlooked.

4.4. Implications for Water Resource Management

The findings of this study have several important implications for water resource management in regions practicing sewage irrigation:

1. Need for improved wastewater treatment: The high levels of organic pollutants in SIA

groundwater underscore the importance of implementing more effective wastewater treatment technologies before using sewage for irrigation.

2. Groundwater monitoring: Regular monitoring of groundwater quality in areas practicing sewage irrigation is crucial for early detection of contamination and implementation of mitigation measures.
3. Land use planning: Careful consideration should be given to the location of sewage irrigation areas in relation to groundwater extraction points and sensitive ecosystems.
4. Public health protection: Measures should be taken to ensure that groundwater from sewage-irrigated areas is not used for drinking purposes without adequate treatment.
5. Alternative irrigation practices: Exploration of alternative irrigation methods or water sources may be necessary in areas where sewage irrigation poses significant risks to groundwater quality.

4.5. Limitations and Future Research Directions

While this study provides valuable insights into the impact of sewage irrigation on groundwater quality, several limitations and areas for future research should be acknowledged:

1. Limited temporal scope: The study was conducted over a single year. Long-term monitoring would provide a more comprehensive understanding of temporal trends and the persistence of organic pollutants in groundwater.
2. Transformation products: This study focused on parent compounds. Future research should investigate the presence and fate of transformation products, which may have different environmental behavior and toxicity profiles.
3. Mixture effects: The potential additive or synergistic effects of multiple organic pollutants were not directly assessed. Future studies should explore the ecotoxicological implications of contaminant mixtures.
4. Soil-aquifer processes: More detailed investigation of soil-aquifer treatment processes could provide insights into the fate and transport mechanisms of organic pollutants in the subsurface.
5. Microbial community impacts: The effects of organic pollutants on soil and groundwater microbial communities, particularly in relation to antimicrobial resistance, warrant further investigation.

5. CONCLUSIONS

This comparative study of organic pollutants in groundwater from sewage-irrigated and non-sewage irrigated areas of Sitapura provides compelling evidence for the significant impact of long-term sewage irrigation on groundwater quality. The key findings of this research include:

1. Consistently higher concentrations of pharmaceuticals, personal care products, and some industrial chemicals were observed in groundwater from sewage-irrigated areas compared to non-sewage irrigated areas.
2. Spatial analysis revealed localized impacts of sewage irrigation, with pollutant concentrations decreasing with distance from irrigation sources.
3. Seasonal variations in pollutant concentrations were observed, with generally higher levels during the pre-monsoon season, highlighting the influence of climatic factors on contaminant fate and transport.
4. The persistence of certain compounds, particularly carbamazepine and triclosan, across seasons indicates their potential for long-term accumulation in groundwater.
5. While individual pollutant concentrations were generally below acute toxicity thresholds, the presence of multiple contaminants raises concerns about potential additive or synergistic effects on human health and ecosystems.

These findings underscore the need for improved wastewater treatment, regular groundwater monitoring, and careful management of sewage irrigation practices to protect groundwater resources and public health. Future research should focus on long-term monitoring, investigation of transformation products, and assessment of mixture effects to further elucidate the environmental and health implications of organic pollutants in groundwater.

The results of this study contribute to the growing body of knowledge on the impacts of wastewater reuse in agriculture and provide valuable insights for water resource management in regions facing water scarcity challenges. As the practice of sewage irrigation continues to expand globally, it is crucial to balance the benefits of water reuse with the need to protect groundwater quality and ensure long-term environmental sustainability.

REFERENCES

[1]. APHA, AWWA, WEF. (2017). Standard Methods for the Examination of Water and Wastewater, 23rd Edition. American Public Health Association, Washington, DC.

[2]. Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., & Sizmur, T. (2011). A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. Environmental Pollution, 159(12), 3269-3282.

[3]. Chen, T., Zhang, Y., Wang, H., Lu, W., Zhou, Z., Zhang, Y., & Ren, L. (2014). Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. Bioresource Technology, 164, 47-54.

[4]. Fang, C., Zhang, T., Li, P., Jiang, R. F., & Wang, Y. C. (2014). Application of magnesium modified corn biochar for phosphorus removal and recovery from swine wastewater. International Journal of Environmental Research and Public Health, 11(9), 9217-9237.

[5]. Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. Process Biochemistry, 34(5), 451-465.

[6]. Inyang, M. I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., ... & Cao, X. (2016). A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. Critical Reviews in Environmental Science and Technology, 46(4), 406-433.

[7]. Keiluweit, M., Nico, P. S., Johnson, M. G., & Kleber, M. (2010). Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environmental Science & Technology, 44(4), 1247-1253.

[8]. Li, H., Dong, X., da Silva, E. B., de Oliveira, L. M., Chen, Y., & Ma, L. Q. (2017). Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. Chemosphere, 178, 466-478.

[9]. Mohan, D., Sarswat, A., Ok, Y. S., & Pittman Jr, C. U. (2014). Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. Bioresource Technology, 160, 191-202.

[10]. Park, J. H., Ok, Y. S., Kim, S. H., Cho, J. S., Heo, J. S., Delaune, R. D., & Seo, D. C. (2016). Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. Chemosphere, 142, 77-83.

[11]. Rajapaksha, A. U., Chen, S. S., Tsang, D. C., Zhang, M., Vithanage, M., Mandal, S., ... & Ok, Y. S. (2016). Engineered/designer biochar for contaminant removal/immobilization from soil and water: potential and implication of biochar modification. Chemosphere, 148, 276-291.

[12]. Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., & Yang, Z. (2015). Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere, 125, 70-85.

[13]. Thomas, H. C. (1944). Heterogeneous ion exchange in a flowing system. Journal of the American Chemical Society, 66(10), 1664-1666.

[14]. Wang, Z., Liu, G., Zheng, H., Li, F., Ngo, H. H., Guo, W., ... & Xing, B. (2015). Investigating the mechanisms of biochar's removal of lead from solution. Bioresource Technology, 177, 308-317.

[15]. Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P., & Yang, L. (2011). Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. Journal of Hazardous Materials, 190(1-3), 501-507.