

INVISIBLE THREATS: TRACING EMERGING CONTAMINANTS IN GROUNDWATER ECOSYSTEMS.

Abstract

Emerging contaminants, such as pharmaceuticals, personal care products, and various industrial chemicals, are increasingly threatening groundwater ecosystems. These pollutants, often unregulated and persistent, enter the environment through sources like wastewater, agricultural runoff, and industrial activities. Once in groundwater, they can endanger ecosystems and human communities that depend on this resource. This paper examines the routes by which these contaminants infiltrate groundwater, their persistence and spread, and the associated ecological and human health risks. By reviewing current research, the study emphasizes the challenges in detecting and managing these contaminants due to their low concentrations and complex compositions. The results underscore the necessity for improved detection techniques, enhanced regulatory measures, and proactive strategies to safeguard groundwater from these emerging pollutants.

Keywords: Contaminants, Groundwater, Ecosystem, Pollutants, Hazards

Introduction

With about 30 percent of all readily available freshwater in the world being groundwater, this vital resource which supports numerous ecosystems and human activities, faces various challenges from emerging contaminants (Sarraf et al., 2023). These contaminants, often originate from industrial, agricultural, and urban sources, and can cause significant risks to groundwater quality and ecosystem health (Leeson et al., 2013). Tracing these contaminants, understanding their pathways, and impacts remain crucial for effective management and sustainable use of groundwater resources.

Emerging contaminants encompass a diverse array of substances, including pharmaceuticals, personal care products, pesticides, and industrial chemicals, which have been detected in groundwater systems worldwide (Fang et al., 2024). The presence of these contaminants in groundwater highlights their persistence and mobility through subsurface environments, challenging traditional notions of water quality management (Ranjeet et al., 2023).

Recent advancements in analytical techniques such as high-resolution mass spectrometry and molecular markers have enabled the detection and quantification of trace levels of emerging contaminants that were previously undetectable (Ismail et al., 2024). These technological innovations have revolutionized our ability to trace the sources and behavior of contaminants in groundwater systems, shedding light on their intricate pathways from surface activities to subsurface aquifers (Fang et al., 2024).

The environmental and health implications of these emerging contaminants are profound, with potential risks ranging from chronic exposure to disruptions in aquatic ecosystems and impacts on human health through drinking water consumption (Conant et al., 2019). Addressing these challenges requires a multidisciplinary approach integrating hydrogeology, environmental chemistry, toxicology, and public health to assess the risks posed by emerging contaminants comprehensively (Xiaona Li et al., 2022).

This review explores the current state of knowledge regarding emerging contaminants in groundwater ecosystems, focusing on their sources, fate and transport mechanisms, analytical methods for detection, environmental and human health impacts, and strategies for mitigation and management. By synthesizing findings from recent studies, this review aims to provide insights into the complexities of tracing and managing emerging contaminants in groundwater, offering a foundation for future research directions and policy interventions.

Types and Sources of Emerging Contaminants

Emerging contaminants (ECs) are substances that have been recently identified as potential threats to human health and the environment (Geissen et al., 2015). These contaminants are often characterized by their persistence, bioaccumulation, and toxicity (Kobayashi et al., 2017). ECs can originate from various sources, including human activities, industrial processes, and natural events (Lapworth et al., 2012).

Types of Emerging Contaminants:

1. **Pharmaceuticals:** Pharmaceuticals, including antibiotics, hormones, and analgesics, have been detected in surface water, groundwater, and wastewater (Kummerer, 2009).
2. **Personal Care Products (PCPs):** PCPs, such as cosmetics, sunscreen, and shampoo, contain chemicals that can harm aquatic life (Fent et al., 2010).
3. **Endocrine Disrupting Chemicals (EDCs):** EDCs, including bisphenol A (BPA) and perfluorinated compounds (PFCs), can interfere with hormone systems (Liu et al., 2013).
4. **Microplastics:** Microplastics, defined as plastic particles <5 mm, have been found in water, soil, and biota (Barnes et al., 2009).
5. **Nanomaterials:** Nanomaterials, used in consumer products, can have unknown environmental and health impacts (Kahru et al., 2018).
6. **Pesticides and Herbicides:** Pesticides and herbicides, used in agriculture, can contaminate water and soil (Schulz, 2004).
7. **Volatile Organic Compounds (VOCs):** VOCs, emitted from industrial processes and vehicles, contribute to air pollution (Atkinson, 2000).

Sources of Emerging Contaminants:

1. **Municipal Wastewater Treatment Plants:** Wastewater treatment plants release ECs into surface water (Lapworth et al., 2012).
2. **Industrial Effluent:** Industrial processes, such as manufacturing and mining, generate ECs (Schwarzenbach et al., 2006).
3. **Agricultural Runoff:** Agricultural activities, including pesticide application and fertilization, contribute to ECs (Schulz, 2004).
4. **Landfills and Waste Disposal Sites:** Landfills and waste disposal sites leak ECs into soil and groundwater (Kjeldsen et al., 2002).
5. **Fracking and Oil/Gas Operations:** Hydraulic fracturing releases ECs into soil, water, and air (Rozell et al., 2017).

Pathways of Entry:

1. Wastewater Treatment Plants: ECs enter surface water through wastewater treatment plant effluent (Lapworth et al., 2012).
2. Surface Water Runoff: ECs enter surface water through runoff from agricultural and urban areas (Schwarzenbach et al., 2006).
3. Groundwater Contamination: ECs contaminate groundwater through landfills, agricultural runoff, and industrial activities (Kjeldsen et al., 2002).
4. Soil Pollution: ECs accumulate in soil through industrial activities, agricultural runoff, and waste disposal (Schulz, 2004).
5. Atmospheric Deposition: ECs enter the environment through atmospheric deposition (Atkinson, 2000).

Environmental and Health Impacts:

1. Aquatic Toxicity: ECs harm aquatic life, affecting ecosystems and biodiversity (Fent et al., 2010).
2. Human Health Risks: ECs pose health risks, including cancer, reproductive issues, and neurological damage (Kobayashi et al., 2017).

Long-term Effects of Emerging Contaminants on Ecosystems

Emerging contaminants (ECs) have been shown to have persistent and detrimental effects on ecosystems, leading to changes in species composition, altered nutrient cycling, and disruptions to food webs (Schwarzenbach et al., 2006; Fent et al., 2010).

Bioaccumulation and Biomagnification: ECs can accumulate in organisms and biomagnify through the food chain, leading to increased toxicity and adverse effects on apex predators (Kobayashi et al., 2017; Liu et al., 2013). This can result in changes in species abundance and diversity (Geissen et al., 2015), disruptions to nutrient cycling and ecosystem productivity (Schwarzenbach et al., 2006), and increased risk of extinction for sensitive species (Fent et al., 2010).

Alterations to Ecosystem Processes: ECs can interfere with ecosystem processes, including primary production (Schulz, 2004), decomposition and nutrient cycling (Kummerer, 2009), water filtration and purification (Lapworth et al., 2012).

Impacts on Ecosystem Services: ECs can compromise ecosystem services such as water quality and human health (Kummerer, 2009), soil formation and fertility (Schulz, 2004), and carbon sequestration and climate regulation (Geissen et al., 2015).

Synergistic Effects: ECs can interact with other stressors, such as climate change, habitat destruction, and invasive species, exacerbating ecosystem degradation (Schulz, 2004; Geissen et al., 2015).

The long-term effects of ECs on ecosystems can have far-reaching consequences on the ecosystem, some of which are loss of biodiversity (Fent et al., 2010), decreased ecosystem resilience (Schwarzenbach et al., 2006) and negative impacts on human health through consumption, recreation, and agriculture (Kummerer, 2009).

Research Gaps and Unresolved Questions in Emerging Contaminant Fate and Transport in Groundwater

Despite significant advances in understanding the fate and transport of emerging contaminants (ECs) in groundwater, several research gaps and unresolved questions remain (Lapworth et al., 2012; Schwarzenbach et al., 2006).

Mechanisms of EC Degradation

The mechanisms controlling EC degradation in groundwater are not yet fully understood (Kummerer, 2009). Biotic and abiotic processes, such as biodegradation, hydrolysis, and photolysis, play crucial roles in EC degradation (Fienen et al., 2013). However, the relative importance of these processes and their interactions with aquifer matrices require further investigation.

Sorption and Desorption

The sorption and desorption of ECs onto aquifer materials are critical processes controlling their fate and transport (Schwarzenbach et al., 2006). However, the factors influencing EC sorption

and desorption, such as aquifer material composition and groundwater chemistry, are not yet fully elucidated.

Transport and Fate Modeling

Existing models predicting EC transport and fate in groundwater systems require improvement (Fienen et al., 2013). The development of more sophisticated models integrating EC fate, transport, and degradation processes is essential for accurate risk assessment and management.

Field-Scale Studies

Field-scale research on EC fate and transport in groundwater is limited (Kummerer, 2009). Further studies are necessary to understand the complex interactions between ECs, aquifer matrices, and microorganisms under natural conditions.

EC Interactions with Aquifer Matrices

The interactions between ECs and aquifer sediments, rocks, and microorganisms require further investigation (Geissen et al., 2015). Understanding these interactions is crucial for predicting EC fate and transport and assessing potential risks to human health and ecosystems.

Future Research Directions

To address these research gaps and unresolved questions, future studies should focus on:

1. Developing advanced analytical techniques for EC detection and quantification.
2. Conducting laboratory and field experiments to study EC fate and transport.
3. Developing predictive models integrating EC fate, transport, and degradation processes.
4. Establishing long-term monitoring networks to track EC occurrence and trends.
5. Developing frameworks for assessing and managing EC risks to human health and ecosystems.

Mechanisms of Contaminant Transport in Groundwater

Groundwater serves as a crucial resource for both drinking and agriculture, but it is susceptible to contamination by emerging contaminants. To effectively manage their environmental impacts, it

is essential to understand how these contaminants move and persist within groundwater systems. Emerging contaminants travel through groundwater via pathways like soil, rock formations, and aquifers. Groundwater moves slowly through small spaces in these materials, carrying contaminants with it. The movement's speed and direction are influenced by the properties of the soil and rock, for instance, sandy soil allow faster movement of contaminants, while clay acts as a barrier, slowing their flow (Fetter, 2018).

When contaminants reach groundwater, they interact with existing chemicals and microorganisms, which can influence their behavior and toxicity. Some contaminants adhere to soil particles or undergo chemical reactions. Factors such as pH and organic matter content in the soil play a role in how contaminants behave (Schwarzenbach et al., 2017). Microorganisms can also break down contaminants, although this process sometimes results in more harmful byproducts. For example, bacteria can convert ammonia-based compounds into nitrates, which may contaminate drinking water sources (Sutton et al., 2011). Conversely, certain microbes are capable of breaking down hazardous substances like trichloroethylene (TCE), reducing their harmful effects.

The persistence of contaminants in groundwater depends on their chemical structure, environmental conditions, and the presence of microorganisms that can degrade them. Biodegradation is the process where microorganisms convert pollutants into simpler, less harmful compounds. However, some contaminants, such as certain pharmaceuticals, resist biodegradation and can remain in the environment for extended periods (Joss et al., 2006). Various factors, including temperature, pH, and oxygen availability, also influence the degradation rate of contaminants. For instance, in deeper aquifers where oxygen is limited, organic pollutants like polycyclic aromatic hydrocarbons (PAHs) break down much more slowly, leading to long-term contamination issues (Rehmann et al., 2012).

Ecological and Human Health Impacts

Emerging contaminants in groundwater pose significant threats to both the environment and human health. Pollutants such as pharmaceuticals, chemicals, and pesticides can infiltrate groundwater, leading to ecological damage, bioaccumulation in food chains, and adverse health effects on humans. Microorganisms in groundwater play a crucial role in breaking down organic matter and maintaining ecosystem balance. However, emerging contaminants like antibiotics can disrupt these microbial communities, sometimes contributing to the emergence of antibiotic-resistant bacteria, which is a serious public health concern (Marti et al., 2014). Aquatic organisms, including fish, are also vulnerable to these contaminants. Endocrine disruptors like chemicals that interfere with hormonal systems such as those from pharmaceuticals, can cause reproductive issues in aquatic life. For instance, male fish living near wastewater treatment plants have exhibited female characteristics due to exposure to these chemicals, which disrupts the overall ecosystem (Jobling et al., 2006).

Emerging contaminants can accumulate in the food chain, as smaller organisms absorb these contaminants, which are then consumed by larger animals, eventually reaching humans. In areas where contaminated groundwater is used for agriculture, contaminants can enter crops and subsequently be ingested by both animals and people, increasing the risk of exposure (Kumar et al., 2019). In many cases, emerging contaminants like pesticides and pharmaceuticals have been detected in groundwater sources used for drinking water. Even at low concentrations, these contaminants can pose health risks. For example, consuming water with antibiotic residues may contribute to the development of antibiotic-resistant infections. A study conducted in India found traces of antibiotics in drinking water, raising concerns about potential health hazards (Furtula et al., 2012).

Chemicals like an endocrine disruptor commonly found in plastics, can also seep into drinking water. Long-term exposure to such contaminants can result in reproductive issues, developmental problems in children, and an increased risk of certain cancers (Diamanti-Kandarakis et al., 2009). Chronic exposure to emerging contaminants in groundwater can lead to long-lasting health problems. Antibiotic resistance is a growing issue, as constant exposure to low levels of antibiotics in water can cause bacteria to become resistant, making infections more difficult to treat. The World Health Organization (WHO) has warned that antibiotic-resistant infections could result in millions of deaths if not properly addressed (WHO, 2014). Similarly,

endocrine-disrupting chemicals may lead to long-term health conditions such as infertility and increased cancer risk. Research shows that populations exposed to these chemicals over extended periods are more likely to experience these health issues (Vandenberg et al., 2012).

Emerging contaminants contamination is a global problem, although the types and effects of contaminants differ by region. In developed countries, pharmaceuticals and industrial chemicals are primary concerns. Even advanced water treatment systems in the U.S. and Europe cannot completely remove all emerging contaminants, leading to contamination risks in drinking water (Richardson & Ternes, 2014). In contrast, developing countries often face more severe contamination due to limited water treatment infrastructure. For example, groundwater in India and Bangladesh is highly contaminated with pesticides and arsenic, resulting in serious health impacts (Smith et al., 2000). Additionally, factors such as climate change and population growth are increasing reliance on groundwater, exacerbating contamination risks. In regions like sub-Saharan Africa, where changing rainfall patterns have led to greater dependence on groundwater for agriculture, emerging contaminants contamination is becoming a growing concern (Kihampa, 2013).

Detection and Monitoring of Emerging Contaminants

Monitoring emerging contaminants in groundwater is essential for understanding their distribution and potential risks. These contaminants, which include chemicals from pharmaceuticals, cleaning agents, and pesticides, are challenging to detect due to their low concentrations and chemical diversity. Detecting emerging contaminants in groundwater requires highly sensitive analytical tools, as these contaminants often exist in trace amounts. One such technique involves measuring the mass of chemical components, often paired with other methods like gas or liquid chromatography to improve accuracy. For instance, Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS) is capable of detecting various emerging contaminants including pharmaceuticals and industrial compounds, in water samples. Research in Europe demonstrated that LC-MS/MS could identify even minute concentrations of drugs in groundwater (Petrović et al., 2003).

Chromatography techniques help separate chemicals in water samples, making it easier to identify and quantify contaminants. Gas Chromatography (GC) is effective for detecting volatile

compounds, while Liquid Chromatography (LC) is better suited for non-volatile substances like pharmaceuticals. When combined with mass spectrometry, these techniques offer precise measurements of emerging contaminants in groundwater (Richardson & Ternes, 2014). A study conducted in Germany utilized LC-MS/MS to detect antibiotics and hormones in groundwater, showcasing the effectiveness of this method for monitoring water contamination (Ternes et al., 2004).

One of the primary challenges in detecting emerging contaminants is their extremely low concentrations, which can make them difficult to identify. Some detection methods lack the sensitivity required to detect such low levels (Schwarzenbach et al., 2017). Additionally, emerging contaminants exhibit a wide range of chemical properties, so no single detection method is suitable for all contaminants. This necessitates the use of multiple techniques in laboratories to comprehensively monitor different types of emerging contaminants (Petrović et al., 2003). In some cases, emerging contaminants are present at levels too low for conventional detection methods, yet they still pose environmental concerns. For example, a U.S. study found pesticide concentrations in groundwater that were below standard detection limits but still significant enough to warrant attention (Kolpin et al., 2002).

Traditional methods of monitoring involve collecting water samples and analyzing them in laboratories, which can be time-consuming and may miss short-term changes. However, new real-time monitoring technologies, such as optical sensors, offer continuous tracking of emerging contaminants in groundwater, providing immediate data on contamination levels (Griffiths & Singletary, 2012). Biosensors, which use biological components like enzymes or antibodies to detect specific contaminants, are another promising tool. These highly sensitive sensors can detect emerging contaminants at very low concentrations, enabling faster and more efficient monitoring. In Spain, biosensors successfully detected antibiotics and hormones in groundwater, demonstrating their reliability as a tool for tracking emerging contaminants (Sanchez-Bayo et al., 2013). Additionally, computer models are being used to predict how emerging contaminants travel through groundwater systems. By simulating factors such as soil composition and water flow, these models help scientists identify areas at risk of contamination. In California's Central Valley, models have been applied to predict the movement of nitrates from fertilizers through groundwater, aiding in improved water management practices (Harter et al., 2012).

Mitigation and Remediation Strategies: Current Technologies and Their Effectiveness in Removing Emerging Contaminants.

5 Emerging Contaminants including pharmaceuticals, personal care products, and endocrine-disrupting chemicals, have been identified as pollutants of significant concern due to their persistence and potential impact on human and environmental health. Current wastewater treatment technologies, while effective at removing traditional contaminants, often struggle to adequately remove emerging contaminants (Fang Wang et al., 2024).

Conventional wastewater treatment plants (WWTPs) typically use primary, secondary, and tertiary treatments. These include physical (sedimentation, filtration), biological (activated sludge, biological nutrient removal), and chemical (chlorination, coagulation) processes. However, many emerging contaminants are not effectively removed through these methods. Studies have shown that typical WWTPs can remove only 30-70% of certain pharmaceuticals and less for persistent emerging contaminants like bisphenol A (BPA) and diclofenac (Zhou et al., 2019).

3 Advanced Oxidation Processes (AOPs) such as ozonation and UV/H₂O₂ treatment, have shown promise in degrading emerging contaminants into less harmful by-products. Ozonation is particularly effective against pharmaceuticals like ibuprofen and naproxen, achieving over 90% removal efficiency (Wang & Wang, 2016). However, these processes are energy-intensive and may produce toxic by-products, raising concerns about their long-term sustainability and environmental impact.

Membrane technologies, including reverse osmosis (RO) and nanofiltration (NF), provide high removal efficiency for a broad spectrum of emerging contaminants. They are particularly effective for small molecular weight compounds. However, these technologies are cost-prohibitive for large-scale applications and generate brine waste, posing additional environmental challenges (Luo et al., 2014).

Constructed wetlands offer a cost-effective and sustainable solution for emerging removal. They utilize natural processes involving plant uptake, microbial degradation, and adsorption. Biochar, derived from pyrolysis of organic matter, enhances the adsorption of emerging contaminants in

these systems. Studies have shown that wetlands supplemented with biochar can remove over 80% of antibiotics and hormone disruptors (Hollender et al., 2009).

Natural Attenuation and Bioremediation: Processes That Mitigate EC Impact in Groundwater

Natural attenuation refers to the in-situ processes that reduce contaminant concentrations in groundwater through biological, chemical, and physical mechanisms (NAS, 2000). Bioremediation, a subset of this, leverages microorganisms to degrade emerging contaminants into less harmful compounds. Microbial degradation is a primary mechanism in the natural attenuation of emerging contaminants in groundwater (EPA, 1999). Bacteria such as *Pseudomonas* and *Acinetobacter* have been shown to degrade pharmaceuticals like carbamazepine and triclosan. Biostimulation, the addition of nutrients to enhance microbial activity, has been effective in promoting the degradation of emerging contaminants in contaminated aquifers (Hollender et al., 2009). ⁹Phytoremediation involves the use of plants to absorb, degrade, or immobilize contaminants. Plants like *Vetiveria zizanoides* and *Salix viminalis* have demonstrated potential in accumulating and degrading emerging contaminants such as triclosan and nonylphenol from contaminated soils and groundwater (Raja et al., 2019).

Policy and Regulation: Current Regulatory Frameworks Addressing Emerging Contaminants

European Union Water Framework Directive (WFD) is a comprehensive policy framework aimed at achieving ⁸good qualitative and quantitative status of all water bodies. The directive includes provisions for the control of Priority Substances, which encompass certain emerging contaminants. The recent adoption of the Watch List under the WFD mandates monitoring of new and emerging contaminants like diclofenac, estrone, and PFAS (EU, 2018).

U.S. Environmental Protection Agency (EPA) Regulations has developed guidelines ¹under the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA) to monitor and regulate emerging contaminants. The Contaminant Candidate List (CCL) identifies priority contaminants for regulatory consideration, including pharmaceuticals and personal care products (U.S. EPA, 2020). Despite these frameworks, regulation of emerging contaminants remains challenging due to their complex chemical properties, low concentrations, and the lack of consensus on

acceptable risk levels. This has prompted calls for the development of more comprehensive guidelines and international cooperation on emerging contaminants management (Daughton, 2014).

Future Directions in Remediation: Innovations in Treatment and Sustainable Solutions

The development of biodegradable and environmentally benign chemicals is a proactive approach to reducing emerging contaminants contamination at the source. Green chemistry principles advocate for the design of less hazardous substances and processes, minimizing the environmental footprint of pharmaceutical and industrial products (Anastas & Eghbali, 2010). Combining physical, chemical, and biological processes in hybrid systems offers a more robust approach to emerging contaminants removal. Integrated treatment systems, such as coupling membrane bioreactors (MBRs) with advanced oxidation or biochar adsorption, have demonstrated high efficiency in removing a wide range of emerging contaminants (Luo et al., 2014). Future strategies should focus on strengthening policy frameworks, improving emerging contaminants monitoring, and increasing public awareness. This includes the promotion of sustainable pharmaceutical practices, proper disposal of unused medications, and incentivizing green chemistry innovations (Daughton, 2014).

Conclusion

4 Emerging contaminants including pharmaceuticals, personal care products, and industrial chemicals, are increasingly found in groundwater systems. These pollutants can have detrimental effects on both ecosystems and human health. Emerging contaminants can disrupt aquatic organisms, impact hormonal systems, and contribute to the rise of antibiotic-resistant bacteria. Traditional water treatment methods are often inadequate at eliminating these contaminants, resulting in their persistence in the environment and posing long-term health risks to communities that depend on groundwater for drinking water. There is a pressing need to strengthen regulations and enhance monitoring of emerging contaminants in groundwater. Current policies do not fully address the widespread presence and potential impact of these contaminants. 6 It is essential for governments, researchers, and industry leaders to work together to establish more comprehensive regulations, develop better detection techniques, and invest in advanced water treatment technologies. Public education is also vital to promote proper disposal

of pharmaceuticals and other products that contribute to groundwater pollution. Safeguarding groundwater from the threat of emerging contaminants is critical for maintaining water quality and availability for future generations. A proactive and integrated approach is necessary, combining innovative treatment technologies, effective regulations, and increased public awareness. Taking decisive action now will help protect our groundwater resources and ensure their sustainability in the face of growing environmental challenges.

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