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# Impacts, Chemistry, and Mechanisms of Contaminants and Pollutants on Surface and Groundwater Around Polluted Sites

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**Abstract:** The contamination of surface and groundwater by chemical pollutants poses a major global challenge, threatening ecological balance, human health, and sustainable water resources. Pollutants, including heavy metals, organic compounds, nutrients, pharmaceuticals, per- and polyfluoroalkyl substances (PFAS), and microplastics, infiltrate aquatic systems through industrial discharges, mining, agriculture, and urban runoff. Their persistence, transformation, and mobility are governed by complex chemical and biological mechanisms, such as adsorption, precipitation, complexation, redox reactions, and microbial biodegradation. For instance, arsenic undergoes redox cycling between As(III) and As(V), mercury is transformed into toxic methylmercury, while lead forms insoluble hydroxides or carbonates depending on pH and carbonate concentrations. Similarly, organic pollutants undergo hydrolysis, photolysis, and microbial degradation, though many yield toxic intermediates. Emerging contaminants like PFAS resist degradation due to strong C–F bonds, while microplastics act as carriers for hydrophobic organics and metals. Mechanistic insights are vital for understanding toxicity, such as cadmium-induced oxidative stress, lead interference with neurotransmission, and endocrine disruption by

organics. This review synthesizes recent advances in the chemistry and mechanisms governing contaminant behavior in surface and groundwater. It highlights the mechanistic underpinnings of pollutant fate, health effects, and remediation technologies, emphasizing the need for integrated, interdisciplinary approaches to safeguard water quality and ecosystem health.

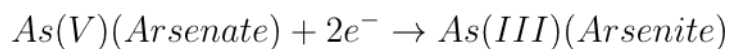
**Keywords:** Surface water; Groundwater contamination; Heavy metals; Emerging pollutants; Mechanisms.

## **1.0 Introduction**

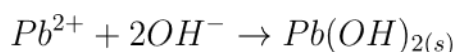
Water is an indispensable natural resource, vital for sustaining life, agricultural productivity, industrial processes, and ecological integrity. However, the contamination of freshwater resources—both surface and groundwater—has emerged as one of the most pressing environmental concerns of the 21st century. The growing release of contaminants and pollutants into aquatic systems has been driven by rapid industrialization, urbanization, agricultural intensification, and population growth (Ihenetu et al., 2024; Lapworth et al., 2023; Ubuoh et al., 2023). Polluted sites, whether associated with mining, industrial effluents, landfills, or agricultural hotspots, serve as point and non-point sources of diverse contaminants that compromise water quality and threaten human and ecosystem health (Kalmakhanova et al., 2025; Okoro et al., 2023).

Groundwater, often regarded as naturally protected, is increasingly vulnerable to contamination due to the infiltration and percolation of pollutants from surface activities. Surface water bodies such as rivers, lakes, and wetlands, meanwhile, receive direct discharges of untreated or poorly treated effluents. Collectively, these processes result in the accumulation of contaminants including heavy metals (lead, cadmium, mercury, arsenic), nutrients (nitrate, phosphate), organic pollutants (pesticides, industrial solvents, hydrocarbons), and emerging pollutants such as pharmaceuticals, microplastics, and PFAS (Alvarado-Zambrano et al., 2023; Ubuoh et al., 2023). A critical dimension of understanding the impacts of contaminants lies in the chemistry and mechanisms underlying their

environmental behavior. For example, arsenic mobility in groundwater is strongly influenced by redox transformations:



This reduction increases toxicity and solubility, exacerbating risks to human health (Gao et al., 2020; Han et al., 2019; Li, Bundschuh, et al., 2022; Zhang, Xie, et al., 2023). Similarly, the precipitation of lead as insoluble hydroxide can be expressed as:



Such geochemical processes determine whether pollutants persist in soluble forms or are immobilized in sediments. Organic contaminants exhibit complex transformation pathways, undergoing hydrolysis, photolysis, and oxidation, often forming intermediate metabolites that can be equally or more toxic than their parent compounds (Mitra et al., 2024a; Shi et al., 2023; Yang et al., 2025). Pharmaceuticals, for instance, degrade through hydroxyl radical attack in advanced oxidation processes:



Yet incomplete mineralization results in persistent byproducts (Hama Aziz et al., 2025; Kanakaraju et al., 2025; Zhang, Guo, et al., 2023). Emerging pollutants introduce additional challenges. PFAS resist degradation due to strong carbon-fluorine (C-F) bonds, making them virtually non-biodegradable (Wackett, 2024; Zhang et al., 2022). Microplastics serve as both pollutants and vectors, adsorbing hydrophobic organic contaminants and heavy metals onto their surfaces, thus facilitating co-transport into aquatic systems (Adeleye et al., 2024; Pal et al., 2024).

The mechanistic toxicology of these contaminants reveals profound health impacts. Lead disrupts neurotransmission by mimicking calcium and interfering with synaptic signaling (de Souza et al., 2019; Liu et al., 2021). Cadmium generates oxidative stress by producing reactive oxygen species (ROS) that damage proteins and DNA (Branca et al., 2020; Saladeen et al., 2025). Mercury undergoes microbial methylation to form methylmercury, which bioaccumulates and biomagnifies in food chains, posing neurological risks (Kang et

al., 2024; Lavoie et al., 2013). Similarly, nitrates in drinking water are reduced in the human body to nitrites, which can form carcinogenic N-nitrosamines under acidic gastric conditions (Picetti et al., 2022; Ward et al., 2005). Beyond health, contaminants profoundly affect aquatic ecosystems. Excessive nutrient inputs trigger eutrophication, resulting in harmful algal blooms, oxygen depletion, and fish mortality (San Diego-McGlone et al., 2024). Persistent organic pollutants disrupt endocrine systems in aquatic organisms, leading to reproductive and developmental abnormalities (Ibor et al., 2023; Peskova & Bladhova, 2025).

The significance of reviewing the chemistry and mechanisms of contaminants in polluted sites cannot be overstated. Mechanistic knowledge informs risk assessment, enhances predictive models of contaminant transport, and underpins the development of effective remediation technologies (Burgess et al., 2023; Khalifa et al., 2024; Samborska-Goik & Pogrzeba, 2024). This review synthesizes recent advances (2020–2025) in contaminant chemistry, transport mechanisms, toxicology, and remediation, with a focus on both surface and groundwater systems. By bridging geochemistry, environmental chemistry, and mechanistic toxicology, this work aims to provide a comprehensive perspective on the threats posed by contaminants and the scientific basis for sustainable water protection.

## **2.0 METHODOLOGY**

This review was developed through a systematic and integrative literature synthesis approach. Peer-reviewed journal articles, conference proceedings, and authoritative reports published between 2020 and 2025 were prioritized to ensure currency and relevance. Databases including Scopus, Web of Science, ScienceDirect, and PubMed were queried using combinations of keywords such as surface water contamination, groundwater pollution, pollutant chemistry, mechanistic toxicology, and remediation technologies.

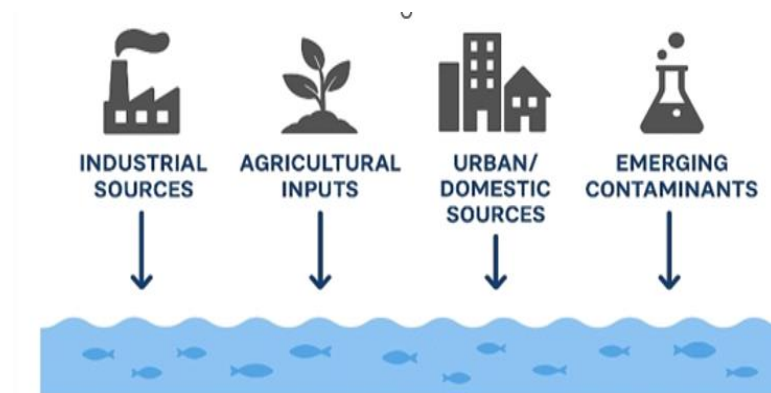
The inclusion criteria were: (i) studies addressing the occurrence, chemistry, mechanisms, or impacts of pollutants in surface or groundwater; (ii) mechanistic studies describing transformation pathways (e.g., redox, adsorption, microbial degradation); and

(iii) studies reporting environmental or health implications of pollutants. Exclusion criteria included studies without a mechanistic focus or those limited to modeling without chemical/biochemical interpretation.

The final pool of literature was critically analyzed, synthesized, and organized thematically into major contaminant classes and mechanisms. Emphasis was placed on chemical equations, mechanistic pathways, and toxicological processes in explanatory contexts. This ensured a balanced perspective that integrates fundamental chemistry, environmental processes, toxicological endpoints, and remediation strategies.

### 3.0 SOURCES AND CLASSES OF CONTAMINANTS

Contaminants entering aquatic systems originate from both natural and anthropogenic activities. Natural processes such as weathering of rocks, volcanic eruptions, and biogeochemical cycling contribute arsenic, fluoride, and other trace metals to groundwater (Bianchini et al., 2020; Chandrajith et al., 2020; Mustafa et al., 2023; Raju, 2022). However, anthropogenic activities are the dominant drivers of pollution in modern systems, as shown in Figure 1.



**Figure 1** Sources of contaminants in aquatic systems

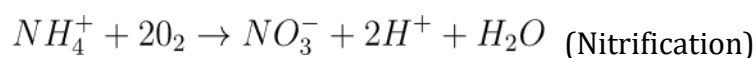
#### 3.1 Industrial sources

Effluents from textile, tannery, pharmaceutical, chemical, and mining industries release heavy metals (e.g.,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ), solvents, hydrocarbons, and complex organics (Christian et al., 2023; Matebese et al., 2024; Okoro et al., 2023; Oladimeji et al., 2024;

Saravanakumar et al., 2022; Zhao et al., 2022). Industrial activities are major contributors to the release of a wide range of emerging contaminants (ECs) into environmental media, particularly aquatic systems. These contaminants include pharmaceuticals and personal care products, per- and polyfluoroalkyl substances (PFAS), industrial solvents, flame retardants, and endocrine-disrupting chemicals that are not always effectively removed by conventional wastewater treatment systems. Chemical manufacturing processes and the pharmaceutical industry discharge active pharmaceutical ingredients (APIs), synthesis by-products, and transformation products into wastewater, which can persist in the environment due to their chemical stability and resistance to degradation (Li et al., 2025). Similarly, textile and dyeing industries contribute synthetic dyes and surfactants, while electronics and fluorochemical manufacturing plants release PFAS and specialty metal-organic compounds, which can accumulate in water bodies and sediments (Yusuf et al., 2021). In many cases, industrial effluents contain complex mixtures of contaminants that are not captured in regulatory monitoring programs and therefore continue to pose ecological and human health risks (Samal et al., 2022). This pervasive industrial input underscores the need for improved regulatory frameworks and advanced treatment technologies designed to monitor and mitigate industrial EC sources.

### 3.2 Agricultural inputs

Excessive fertilizer and pesticide use introduce nitrates, phosphates, and organophosphates into groundwater and surface water. The classic pathway of nitrate contamination occurs via:



Nitrates leach into aquifers, elevating risks of methemoglobinemia and carcinogenic nitrosamine formation (Hagage et al., 2025; Rotiroti et al., 2023).

Modern agricultural systems are significant contributors to the release of emerging contaminants (ECs) into the environment. These contaminants include veterinary pharmaceuticals, antibiotics, pesticides, hormones, microplastics, and other organic pollutants that are not fully regulated or routinely monitored but have been increasingly

detected in soils, water bodies, and food crops. Veterinary medicines and antibiotics administered to livestock can enter agricultural soils directly through grazing or indirectly when manure and slurry from intensive animal production are applied as fertilisers, leading to residues in soil and runoff into surface and groundwater bodies (Tillitt & Buxton, 2012). Pesticides and herbicides, widely used to control pests and weeds, can persist in the environment, migrate via runoff and leaching, and adversely affect non-target organisms and ecosystem health (Nwankwo et al., 2025). The use of biosolids and treated wastewater for irrigation also introduces pharmaceuticals, hormones, and personal care products into farmlands, resulting in the accumulation of these compounds in soil and uptake by plants (Sardar et al., 2025). Additionally, microplastics and nanomaterials derived from agricultural plastics, mulching films, and soil amendments are increasingly recognised as emerging pollutants that alter soil properties and potentially facilitate transport of other contaminants. Collectively, these agricultural sources contribute to a complex mixture of ECs in agroecosystems, posing ecological risks and potential human health concerns through food chain transfer, contamination of water resources, and disruption of soil microbial communities.

### **3.3 Urban and domestic sources**

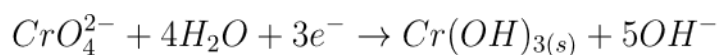
Sewage, landfill leachates, and stormwater runoff discharge pharmaceuticals, microplastics, surfactants, and endocrine-disrupting compounds (EDCs) (Peter et al., 2024; Werbowski et al., 2021; Wilkinson et al., 2022). Urban and domestic activities are major contributors to the release of emerging contaminants (ECs) into aquatic environments through multiple pathways. A significant source is municipal and household wastewater, which carries pharmaceuticals and personal care products (PPCPs) such as analgesics, antibiotics, fragrances, and sunscreen agents that enter sewer systems through human use and improper disposal (AL Falahi et al., 2022). These contaminants often bypass or are partially removed by conventional wastewater treatment plants (WWTPs), ultimately being discharged into rivers, lakes, and coastal waters, where they persist due to their chemical stability and resistance to degradation (Yuan et al., 2025). Domestic sewage and greywater from residential areas also contribute household chemicals and surfactants into the urban

water cycle, including detergents, disinfectants, and endocrine-active compounds (Zillien et al., 2022). Additionally, urban stormwater runoff transports ECs from impervious surfaces such as roads, roofs, and parking lots into water bodies; these include pesticides, vehicle-derived hydrocarbons, microplastics, and PPCPs from everyday human activities (Mutzner et al., 2023). The combination of dense population, extensive wastewater networks, and inadequate removal of trace organic contaminants makes urban and domestic sources key drivers of EC presence in the environment, posing ecological and human health risks due to long-term exposure even at trace concentrations.

### 3.4 Emerging contaminants

PFAS, pharmaceuticals, personal care products, and nanomaterials represent new classes of pollutants with poorly understood long-term mechanisms (Lyu et al., 2022; Peter et al., 2024; Wilkinson et al., 2022).

Pollutants may exist as dissolved ions, complexes, particulates, or sorbed phases, and their distribution depends on environmental conditions such as pH, redox potential (Eh), ionic strength, and organic matter content. Understanding their chemical speciation is critical because toxicity, mobility, and persistence are governed by these forms. For example, hexavalent chromium (Cr(VI)) is highly mobile and toxic, while trivalent chromium (Cr(III)) tends to precipitate or adsorb to surfaces (Arp & Hale, 2022; Dvoynenko et al., 2021; Rapljenović et al., 2024; Zulfiqar et al., 2023):



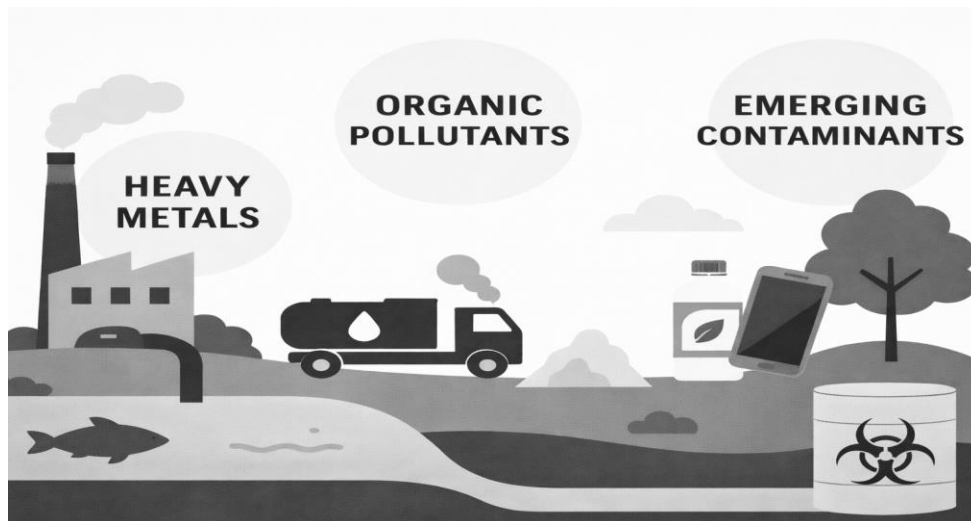
Thus, the classification of contaminants not only reflects their origin but also their chemical mechanisms of persistence, transformation, and impact.

## 4.0 CHEMISTRY OF VARIOUS POLLUTANTS IN AQUATIC SYSTEMS

Environmental pollution spans several chemical classes, each with distinct sources, environmental behaviour, and toxicological relevance. The most commonly discussed groups are heavy metals, organic pollutants, and emerging contaminants, as illustrated in Figure 2 below. From a research perspective, especially in integrated water-sediment-biota



studies, heavy metals, organic pollutants, and emerging contaminants are often prioritized due to their persistence, complex speciation and strong interactions with environmental matrices. The chemistry of different pollutants in aquatic systems is summarized in Table 1



**Figure 2** Common pollutants in the environment

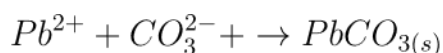
#### 4.1 Heavy metals

Metals with a specific gravity exceeding  $5.0 \text{ g/cm}^3$  are generally classified as heavy metals, encompassing high-atomic-weight elements and transition metals mainly from Groups III and IV of the periodic table (Salaudeen, 2020). These metals are environmentally persistent and can accumulate in living organisms through contaminated food chains and drinking water, rendering them hazardous and non-biodegradable even at trace concentrations (Salaudeen et al., 2022; Salaudeen et al., 2025). Heavy metals represent some of the most studied pollutants due to their toxicity, persistence, and lack of biodegradability. The chemistry of metals in water is controlled by speciation, redox state, complexation, and precipitation.

##### 4.1.1 Lead (Pb)

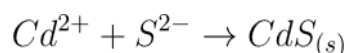
Lead enters aquatic systems as dissolved  $\text{Pb}^{2+}$ , inorganic complexes, and particulate-bound forms; its partitioning between dissolved and particulate phases is controlled by pH, ionic strength, and adsorption to suspended particles and organic matter. In oxygenated

surface waters Pb forms stable hydroxo- and carbonate complexes, but in estuaries and sediments, ion-exchange and sorption onto iron/manganese oxides and organic colloids dominate its fate, producing a strong association with particulates and sediments. Bioavailability depends on speciation and particle association; dissolved labile Pb is most bioavailable and readily accumulated by phytoplankton, invertebrates and fish, causing oxidative stress and neurological effects. Recent global syntheses quantify spatial patterns and anthropogenic drivers of inland-water Pb (Wei et al., 2023). In aqueous systems,  $Pb^{2+}$  readily forms complexes with carbonate, sulfate, and chloride ions. Under neutral to alkaline conditions, insoluble hydroxides and carbonates precipitate (Fitzgerald et al., 2023; Li et al., 2021; Madlangbayan et al., 2024; Wahman et al., 2021):



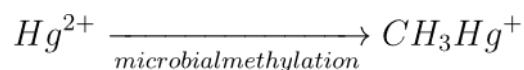
#### 4.1.2 Cadmium (Cd)

Cadmium is a soft, silvery-white metal with chemical properties similar to those of mercury and zinc. It is highly toxic and can cause severe damage to multiple organs in the body (Salaudeen et al., 2025). Cadmium typically occurs in aquatic systems as the free ion  $Cd^{2+}$  and as complexes with chloride, sulfate, and dissolved organic matter; speciation shifts with salinity and dissolved organic carbon.  $Cd^{2+}$  is highly soluble, weakly adsorbed relative to other divalent metals, and thus can remain mobile in freshwaters; in estuarine and marine waters, chloride complexation increases Cd solubility while promoting different bioavailability. In organisms, Cd competes with  $Ca^{2+}$  and  $Zn^{2+}$  at uptake sites, disrupting ionoregulation and causing oxidative damage, kidney and gill pathologies in fish. Microbial and phytoremediation approaches target Cd removal from water/sediment; detoxification in biota often involves metallothionein induction and sequestration into inert compartments (Farias et al., 2024).  $Cd^{2+}$  is highly mobile under acidic conditions but precipitates as  $CdCO_3$  or  $Cd(OH)_2$  under alkaline conditions. Its interactions with sulfides are particularly relevant in reducing sediments (Ekubatsion et al., 2021; Hyun et al., 2021; Song et al., 2022):



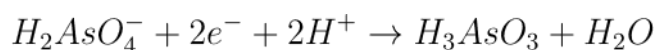
#### 4.1.3 Mercury (Hg)

Mercury cycles between inorganic Hg(II), elemental Hg(0), and methylated forms ( $\text{CH}_3\text{Hg}^+$ ); the most toxic form in aquatic food webs is methylmercury (MeHg), which is produced mainly by microbial methylation in anoxic sediments and microenvironments. Factors controlling Hg methylation include availability of inorganic Hg, organic matter, redox gradients, sulfate and iron cycling, and microbial community composition (hgcAB-carrying microbes). MeHg strongly bioaccumulates and biomagnifies through trophic levels due to slow depuration and high lipid affinity; even low environmental MeHg concentrations lead to elevated fish tissue burdens and neurotoxic risk to predators and humans. Recent work highlights methylation also occurring in surprising oxic microenvironments and under changing climatic conditions (Rodríguez, 2023). Microbial methylation of  $\text{Hg}^{2+}$  under anaerobic conditions yields methylmercury, a potent neurotoxin that bioaccumulates (Lu et al., 2017; Tepper et al., 2025; Tian et al., 2021):



#### 4.1.4 Arsenic (As)

Arsenic in aquatic systems occurs chiefly as inorganic arsenate (As(V)) under oxic conditions and arsenite (As(III)) under reducing conditions, with organic As species less abundant except in some marine organisms. Speciation controls toxicity and mobility: As(III) is more mobile and toxic than As(V), while adsorption to iron oxides and association with particulate matter removes As from the dissolved phase in oxic waters. Reductive dissolution of iron minerals under anoxic conditions can release adsorbed As to porewaters, elevating dissolved As concentrations and enabling uptake by aquatic biota. Biotransformations (methylation, thiolation) and trophic transfer influence exposure and ecological risk across freshwater and marine systems (Wang et al., 2022). The interconversion between arsenite (As(III)) and arsenate (As(V)) is governed by redox conditions (Castillejos Sepúlveda et al., 2022; Mishra et al., 2021; Su & Wilkin, 2020):



As(III) is more toxic, mobile, and poorly adsorbed compared to As(V).

The geochemistry of heavy metals thus dictates their mobility and toxicity. Sediments and aquifer matrices act as sinks through adsorption and co-precipitation processes, but changing conditions (e.g., acidification, reducing environments) can remobilize metals (Baran & Tarnawski, 2015; Gao et al., 2023; Mali et al., 2024).

## 4.2 Organic Pollutants and Transformation Mechanisms

Organic contaminants are a broad class of pollutants, including pesticides, hydrocarbons, industrial solvents, dyes, and pharmaceuticals. Their behavior in aquatic systems is governed by solubility, partitioning between aqueous and solid phases, and degradation mechanisms (Bu & Ma, 2025; Mitra et al., 2024; Selwe et al., 2022). Fate processes include volatilization, photolysis, biodegradation (often slow), sorption to particulate organic carbon, and trophic transfer via lipid accumulation. Partition coefficients ( $K_{ow}$ ,  $K_{oc}$ ) predict bioaccumulation potential: high- $K_{ow}$  compounds concentrate in fatty tissues and biomagnify. Temperature, dissolved organic carbon, and sediment characteristics mediate transport and remobilization. Recent global assessments document continued widespread occurrence and climate-linked redistribution of many POPs despite regulatory controls (Aravind Kumar et al., 2022).

### 4.2.1 Hydrolysis

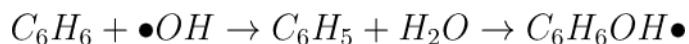
Many organic compounds undergo hydrolysis, where water molecules cleave chemical bonds. For example, organophosphate pesticides such as parathion hydrolyze into less toxic products:



The rate depends on pH, temperature, and substituents (Liu et al., 2015; Zhang et al., 2025).

### 4.2.2 Oxidation and Photolysis

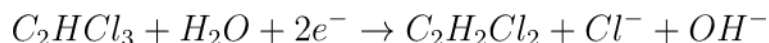
Hydrocarbons and chlorinated solvents undergo oxidation through natural oxidants or photolysis under UV light. For example:



This radical chain mechanism eventually mineralizes benzene to CO<sub>2</sub> and H<sub>2</sub>O, though intermediates like phenol and catechol can persist (Jaber et al., 2020; Xu & Wang, 2013; Yin et al., 2025).

#### 4.2.3 Microbial Degradation

Microorganisms play a central role in organic pollutant transformation. Aerobic microbes use oxygenases to hydroxylate hydrocarbons, while anaerobic microbes reduce chlorinated solvents. For example, trichloroethene (TCE) can be reductively dechlorinated:



Further stepwise dechlorination yields ethene, a non-toxic end product (Bolesch et al., 1997; Chung et al., 2008; Hnatko et al., 2023; Wang et al., 2024).

#### 4.2.4 Transformation Products

A key concern is that degradation often yields metabolites that are more mobile or toxic than the parent compound. For instance, atrazine degradation produces deethylatrazine, which is persistent in groundwater (Chen et al., 2019; Xie et al., 2021).

Thus, the mechanistic pathways of organic pollutant degradation illustrate the balance between detoxification and the generation of hazardous intermediates.

#### 4.3 Emerging Contaminants (PFAS, Pharmaceuticals, Microplastics)

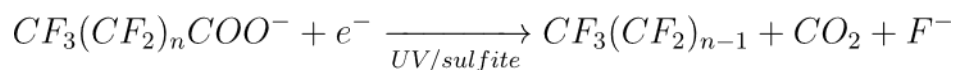
Emerging contaminants (pharmaceuticals, personal care products, endocrine disruptors, PFAS/PFAS-like substances, novel industrial chemicals) are chemically diverse but share features: continuous release at low concentrations, varying degradability, and potential for subtle chronic effects. PFAS are highly persistent and mobile due to C–F bonds; many pharmaceuticals undergo partial biodegradation to active metabolites and can persist

in effluents and receiving waters. Fate is governed by compound-specific processes — biodegradation, hydrolysis, photolysis, sorption and volatility — and by treatment efficacy. Environmental detection frequently relies on high-resolution mass spectrometry; One-Health syntheses emphasize sources (wastewater, runoff, biosolids), monitoring gaps, and the need for coordinated control and safer-by-design chemistry (Wang et al., 2024). Emerging contaminants present unique challenges due to their persistence, complex chemistry, and poorly understood toxicology.

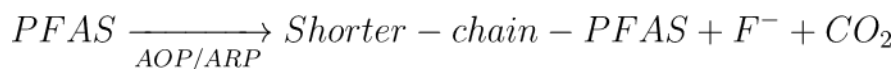
#### 4.3.1 Per- and Polyfluoroalkyl Substances (PFAS)

PFAS are characterized by strong C–F bonds (bond energy ~485 kJ/mol), making them resistant to hydrolysis, oxidation, and biodegradation. They are amphiphilic, with hydrophobic fluorocarbon tails and hydrophilic heads, enabling mobility in both surface and groundwater.

Their degradation requires advanced oxidation or reduction:



With a generalized degradation pathway as shown below

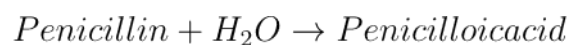


Yet these processes are energy-intensive, and incomplete defluorination produces shorter-chain PFAS, which remain mobile and toxic (Itumoh et al., 2024; Lin et al., 2024; Wackett, 2024)

#### 4.3.2 Pharmaceuticals and Personal Care Products (PPCPs)

Pharmaceuticals enter water systems through wastewater effluents. They exhibit diverse mechanisms:

- Hydrolysis of beta-lactam antibiotics:

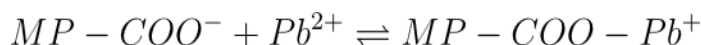


- Photodegradation of fluoroquinolones under sunlight.
- Sorption onto sediments, which may later desorb under changing pH or ionic strength.

Transformation products of pharmaceuticals often retain biological activity, such as antibiotic resistance selection in microbes (Goodarzi et al., 2024; Klein et al., 2021; Klementová et al., 2022; Löffler et al., 2023; Zhao et al., 2022).

### 4.3.3 Microplastics

Microplastics (<5 mm) act as contaminants and vectors. Their hydrophobic surfaces adsorb organic pollutants (hydrocarbons, PCBs) and heavy metals. Sorption occurs via hydrophobic interactions, van der Waals forces, and electrostatic attraction (Frost et al., 2022; Fu et al., 2021; Liang et al., 2023; Lu et al., 2022; Menéndez-Pedriza & Jaumot, 2020):



(where MP = microplastic surface)



They facilitate contaminant transport across ecosystems and into organisms. In addition, plasticizers such as bisphenol A leach out, exerting endocrine-disrupting effects.

These emerging pollutants exemplify how molecular stability and sorption mechanisms underpin persistence, mobility, and toxicity in aquatic systems.

**Table 1** Chemistry of Various Pollutants in Aquatic Systems

Pollutant (class & typical compounds)	Main chemical forms/speciation in water	Key chemical properties/behaviour in aquatic systems (brief)	Ref.
Mercury (methylmercury; inorganic Hg(II), Hg <sup>0</sup> )	Inorganic Hg(II) (dissolved complexes), elemental Hg <sup>0</sup> (gaseous), methylmercury	Hg(II) forms strong complexes with sulfides and natural organic matter (NOM); under anoxic/microbial conditions, Hg(II) → MeHg methylates microbes. MeHg is lipophilic, bioaccumulates, and biomagnifies; redox (photochemical and microbial) and	(Hong et al., 2012)

	(MeHg <sup>+</sup> , organometallic cation)	complexation control partitioning between water, sediment and biota.	
PFAS (per- and polyfluoroalkyl substances — e.g., PFOA, PFOS)	Dominant dissolved anionic forms at environmental pH (carboxylates/sulfonates); some neutral precursors occur	Very low biodegradability, high persistence; strong surfactant behaviour (high surface activity), low sorption of short chains but stronger partitioning to organic matter for long chains; mobile in water, resist hydrolysis/oxidation — termed “forever chemicals.”	(Fenton et al., 2020)
PCBs (polychlorinated biphenyl congeners / Aroclors)	Neutral(uncharged) chlorinated biphenyl congeners; degree of chlorination (mono → deca) determines properties	Hydrophobic (high log K <sub>ow</sub> for higher-chlorinated congeners), strongly sorb to sediments and particulate organic carbon; resist biodegradation (especially highly chlorinated congeners); undergo slow dechlorination (anaerobic reductive) and limited oxidation (aerobic) producing lower-chlorinated congeners/metabolites.	(Montano et al., 2022)
Microplastics & associated additives (polystyrene, polyethylene, PVC, plasticizers)	Solid particles (nano → micro → macro); additives (phthalates, stabilizers) may leach as dissolved organics.	Polymer density, crystallinity and surface chemistry control transport (float/sink/near-bed). Weathering (UV, mechanical) produces smaller particles and increases surface area; particles sorb hydrophobic organic contaminants (HOCs) and metals; additives can leach into water depending on partition coefficients and polymer-matrix diffusion.	(Ivleva, 2021)
Nutrients — Nitrogen (NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> ) & Phosphorus (PO <sub>4</sub> <sup>3-</sup> )	Dissolved inorganic: nitrate (NO <sub>3</sub> <sup>-</sup> ), ammonium (NH <sub>4</sub> <sup>+</sup> ); dissolved organic N/P; particulate organic forms	Nitrate: conservative, highly mobile; ammonium: sorbs/adsorbs and is transformed (nitrification → NO <sub>2</sub> <sup>-</sup> /NO <sub>3</sub> <sup>-</sup> ; denitrification → N <sub>2</sub> under anoxia). Phosphate strongly complexes with Fe/Al oxides and sorbs to sediments (low solubility at circumneutral pH when bound to Fe(III) oxides); redox and pH control release from sediments and bioavailability.	(Howarth & Paerl, 2008)
PAHs (polycyclic aromatic hydrocarbons; e.g., naphthalene, benzo[a]pyrene)	Neutral hydrophobic organic molecules (multiple fused aromatic rings)	Low water solubility (decreases with ring number), high log K <sub>ow</sub> → strong sorption to particles and sediments; subject to photochemical oxidation, aerobic/anaerobic biodegradation (rates vary widely by compound), and formation of more polar oxygenated/nitrated PAH derivatives. Many PAHs are bioaccumulative and genotoxic/carcinogenic.	(Patel et al., 2020)
Antibiotics & pharmaceuticals (e.g.,	Mostly neutral or ionizable organic molecules (pKa-dependent	Ionization state (pKa) controls sorption and aqueous mobility; many are polar and moderately persistent in wastewater treatment effluents; undergo photolysis,	(Kümmerer, 2009)



sulfonamide s, fluoroquinol ones, macrolides)	speciation), present as parent compound + metabolites	hydrolysis and microbial transformation to metabolites (some retain biological activity). Environmental concentrations can select for antibiotic-resistance genes.	
Lead (Pb) — inorganic Pb(II) and particulate Pb species	Dissolved Pb <sup>2+</sup> , Pb- organic complexes, adsorbed to particles/sediment, particulate oxide/hydroxide forms	Pb solubility and speciation are strongly controlled by pH, redox, hardness (Ca/Mg), and dissolved organic matter (complexation). Lower pH and low DOC usually increase free Pb <sup>2+</sup> (more bioavailable/toxic); Pb strongly partitions to particles and sediments and can be remobilized under changing geochemistry.	(Cullen & McAlister, 2017)

## 5.0 POLLUTION MECHANISMS

### 5.1 Geochemical mechanisms

#### 5.1.1 Adsorption

Adsorption involves the attachment of contaminants onto mineral surfaces such as clays, iron and manganese oxides, and organic matter present in sediments and aquifers (Mary Ugwu & Anthony Igbokwe, 2019; Molina-Fernández et al., 2025; Wang et al., 2023; Y. Wang et al., 2020). Factors such as pH, redox potential, ionic strength, and competing ions influence adsorption capacity. For example, heavy metals (Pb<sup>2+</sup>, Cd<sup>2+</sup>, As<sup>3+</sup>) adsorb strongly to ferric hydroxides under oxidizing conditions, reducing their mobility. Conversely, changes such as acidification or reducing environments can cause desorption and remobilization of contaminants (Fernandes et al., 2025; Yang et al., 2025).

#### 5.1.2 Precipitation and Co-precipitation

Contaminants may precipitate as insoluble mineral phases (e.g., PbCO<sub>3</sub>, FePO<sub>4</sub>) or co-precipitate within mineral lattices. Uranium can precipitate as uranyl phosphate under phosphate-rich conditions, while arsenic co-precipitates with iron hydroxides, immobilizing these contaminants. However, these precipitates may dissolve under shifting environmental parameters (Almeida et al., 2020; Foster et al., 2020; Jain & Maiti, 2021).

### **5.1.3 Redox Reactions**

Redox conditions are a primary control on contaminant speciation and mobility. For instance, arsenic is more mobile under reducing conditions as arsenite ( $\text{As}^{3+}$ ), which is released from iron oxides, while chromium exists as mobile Cr(VI) under oxidizing conditions but reduces to less toxic Cr(III) in the presence of organic matter or Fe(II) (Brookshaw et al., 2014; Kim et al., 2019; Sun et al., 2022). These redox-driven transformations are critical at redox interfaces in aquatic systems.

### **5.1.4 Complexation**

The formation of complexes with natural organic matter, ligands, or inorganic ions influences contaminant behavior. Metal-organic complexes (e.g., Cu-humate) increase solubility and mobility, affecting bioavailability and toxicity (Cai et al., 2024; Qin et al., 2024).

## **5.2 Biochemical mechanisms**

### **5.2.1 Microbial Degradation**

Microorganisms drive the biodegradation of organic contaminants through aerobic and anaerobic pathways. Aerobic degradation uses oxygen as the terminal electron acceptor to oxidize compounds such as petroleum hydrocarbons, while anaerobic degradation employs nitrate, sulfate, Fe(III), or  $\text{CO}_2$  for respiration, transforming contaminants like chlorinated solvents via reductive dichlorination (Li, Chen, et al., 2022; Li et al., 2024; Miles et al., 2024).

### **5.2.2 Biotransformation and Biosorption**

Microbial metabolism can convert contaminants into less toxic or more mobile forms. For example, mercury methylation by anaerobic bacteria produces methylmercury, a more bioaccumulative species (Pu et al., 2025). Biosorption involves binding contaminants to microbial biomass, temporarily immobilizing metals.

### **5.2.3 Biomineralization**

Microbes can induce mineral precipitation that sequesters contaminants. Sulfate-reducing bacteria produce sulfide ions, precipitating metals as insoluble metal sulfides (e.g., PbS, ZnS), a key attenuation process in acid mine drainage and metal-contaminated aquifers (Dong et al., 2024; Marques & Rodrigues, 2025).

### **5.3 Coupled geochemical-biochemical interactions**

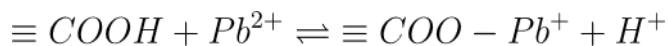
Geochemical and biochemical processes often occur simultaneously and interact synergistically or antagonistically. For example, microbial iron reduction dissolves Fe(III) oxides, releasing sorbed arsenic into groundwater, while microbial sulfate reduction immobilizes metals as sulfides (Nghiem et al., 2023; Wu et al., 2024). This interplay results in spatial and temporal heterogeneity of contaminant fate in aquatic environments.

Contaminant behavior in aquatic systems is governed by integrated geochemical and biochemical processes influenced by environmental conditions such as pH, redox potential, and microbial communities. Understanding these processes is critical for accurate prediction of contaminant fate and the design of remediation strategies. Future research should emphasize mechanistic models and in situ monitoring to capture these complex dynamics.

## **6.0 CASE STUDIES OF DIFFERENT POLLUTANTS IN AQUATIC SYSTEMS**

Kabwe is one of the world's most-cited modern case studies of mining-derived lead contamination. Historical lead–zinc mining and ore processing released large quantities of Pb-rich dust and tailings across the town and into nearby drainages, producing pervasive soil and surface-water contamination and chronic childhood lead exposure. Community surveys and environmental monitoring document extremely high blood lead concentrations in children, contamination of river sediments and floodplain soils, and ongoing exposure pathways via dust resuspension and locally grown foodstuffs. Recent analyses quantify the social and public-health costs and discuss remediation options (soil stabilization, targeted cleanups, and community interventions) as essential but resource-intensive measures to reduce long-term exposure (Yamada et al., 2023).

$Pb^{2+}$  sorbs onto clay and organic matter at neutral pH can be mobilized under acidic mine drainage conditions:



When pH drops, protonation weakens sorption, enhancing  $Pb^{2+}$  leaching.

Cadmium pollution in Japan's Jinzu River basin historically produced the classic itai-itai disease epidemic (mid-20th century), caused by Cd discharged from upstream mining into irrigation waters and rice paddies. Contemporary case reports show that cadmium hotspots persist in parts of Japan (and are detected elsewhere where former mining or industrial discharge occurred), producing renal tubular dysfunction, bone demineralization, anemia and fractures in long-exposed residents. Modern clinical follow-up, biomonitoring and a recent suspected itai-itai case from an Akita prefecture Cd-polluted area underscore that legacy cadmium in soils and sediments continues to produce human disease decades after emissions decline, and that sustained health surveillance plus remediation of agricultural soils remain priorities (Sasaki et al., 2024).

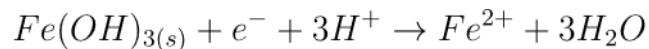
Artisanal and small-scale gold mining (ASGM) in Amazonian Andean foothills and lowlands releases elemental mercury that biomagnifies as methylmercury in river food webs. Recent regional studies report elevated Hg in stream waters, sediments, fish and human biomarkers (hair/blood) from mining-impacted provinces in Ecuador and from indigenous communities in the Brazilian Amazon; health risk assessments detect elevated exposure, particularly in children and frequent fish consumers. Field monitoring and probabilistic risk estimates identify hotspots tied to illegal mining activity, with recommendations for combined strategies: source-control (anti-mining enforcement, mercury-free techniques), fish-consumption advisories, ecosystem monitoring and targeted public-health screening to address neurodevelopmental risks (Mestanza-Ramón et al., 2023; Passarelli et al., 2024).

The Bengal Basin groundwater arsenic crisis remains a paradigmatic geogenic contamination case. Elevated inorganic arsenic (often as arsenite, As(III)) occurs in shallow Holocene alluvial aquifers across Bangladesh and parts of West Bengal; reductive

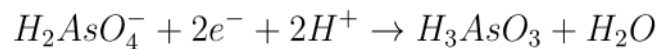
dissolution of As-bearing iron oxyhydroxides coupled with organic matter and microbial processes mobilizes arsenic into potable wells and irrigation water. Recent reviews and hydrogeochemical studies map persistent high-As zones, describe depth-dependent patterns and food-chain transfer (e.g., rice irrigated with As-rich groundwater), and evaluate mitigation options such as alternative safe wells, in-situ treatment, and irrigation management. Policy and remediation remain challenging because contamination is widespread, spatially heterogeneous, and driven by natural geochemistry as well as anthropogenic water-use patterns (Kanel et al., 2023; Sarkar et al., 2022).

Groundwater arsenic contamination in Bangladesh and India illustrates the interplay of redox and microbial processes. Arsenate (As(V)) is reduced to arsenite (As(III)) by iron-reducing bacteria in anoxic aquifers, releasing arsenic from Fe-oxyhydroxides:

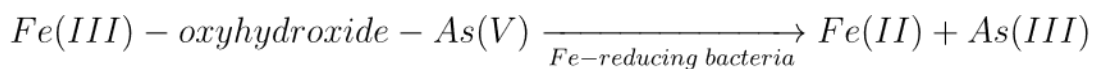
Reductive dissolution of Fe(III) oxyhydroxides (primary release mechanism)



Reduction of arsenate to arsenite



Coupled conceptual pathway



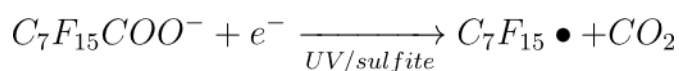
This mechanism explains why tube wells show high As(III) concentrations despite remediation efforts (Diba et al., 2023; Sathe et al., 2021).

Long-lived organic contaminants illustrate two global archetypes. In the Hudson River (USA), decades of PCB discharge produced extensive PCB-contaminated sediments, persistent bioaccumulation in fish, food-web transfer and ecological impacts; post-dredging monitoring and fish-advisories remain central components of remediation and risk management. Separately, the 2020 MV Wakashio grounding and fuel-oil release off Mauritius released complex low-sulfur fuel oil with hydrocarbon fractions (including PAHs) that contaminated mangroves, sediments and coastal biota; subsequent studies document

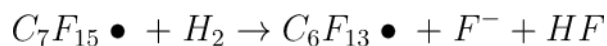
residual hydrocarbons, ecosystem damage, and the importance of rapid response, long-term monitoring, and habitat restoration after oil incidents. Both cases show that organic pollutants demand sediment-and-biota-focused assessment plus long timelines for recovery (Sathe et al., 2021; Wirgin et al., 2023).

Per- and polyfluoroalkyl substances (PFAS) are exemplary “emerging” persistent contaminants. The Cape Fear watershed (North Carolina) documented GenX and complex PFAS mixtures from fluorochemical production: downstream river and drinking-water intakes contained numerous PFAS congeners, prompting exposure studies, regulatory action and engineered source controls. Broader groundwater and national surveys show widespread PFAS detections (many sites and private wells), with predictive models highlighting likely occurrence at drinking-water depths. Case studies emphasize source attribution (manufacturing, firefighting foams, wastewater), challenges in detecting novel PFAS, the need for advanced treatment (e.g., granular activated carbon, ion exchange, advanced oxidation) and the policy/monitoring frameworks required to manage large numbers of related compounds (Pétre et al., 2022; Scarlett et al., 2021).

PFAS contamination from firefighting foams illustrates persistence due to strong C–F bonds. Mechanistic studies show partial degradation via reductive defluorination under UV/sulfite treatment:



Followed by subsequent defluorination



However, the process is incomplete, generating shorter-chain PFAS with similar mobility (Abusallout et al., 2021; Ren et al., 2021)

Microplastics in European rivers adsorb hydrophobic organics (PAHs, PCBs) and metals, transporting them downstream. Mechanistic models attribute sorption to hydrophobic partitioning and  $\pi$ – $\pi$  interactions between plastic polymers and aromatic

pollutants (Agboola & Benson, 2021; Prajapati et al., 2022; Tumwesigye et al., 2023; Wang et al., 2024).

These case studies reveal how mechanistic understanding supports prediction and remediation strategies in real-world polluted sites.

**Table 2** Case studies of different pollutants in aquatic systems

Pollutant (type)	Location / Case Study	Matrix Studied	Key Findings / Summary	Year	Ref
Mercury (methylmercury)	<i>Minamata Bay, Japan</i>	Fish, sediments, and human tissues	Industrial discharge of methylmercury from acetaldehyde production caused widespread neurotoxicity ("Minamata disease"). Methylmercury bioaccumulates in fish and is biomagnified through the food web.	1950s–present	(Semionov, 2018)
Crude oil (petroleum hydrocarbons)	<i>Deepwater Horizon Oil Spill, Gulf of Mexico</i>	Water column, deep-sea corals, coastal sediments, biota	Approximately 4.9 million barrels of oil were released; polycyclic aromatic hydrocarbons (PAHs) caused chronic toxicity and long-term ecological disruption.	2010	(Barron, 2012)
Polychlorinated Biphenyls (PCBs)	<i>Hudson River, USA</i>	Sediments, fish, floodplain soils	Discharge from GE capacitor plants led to one of the world's largest PCB-contaminated river systems. Strong sediment sorption and slow dechlorination led to decades-long contamination and remediation efforts.	1940s–present	(Carpenter & Welfinger-Smith, 2011)
Perfluorooctanoic Acid (PFOA)	<i>Mid-Ohio Valley, USA</i>	Drinking water, serum, groundwater	Chronic exposure from industrial discharges; strong persistence and mobility in water. Epidemiological evidence links exposure to kidney/testicular cancers and thyroid disorders.	2000s–2013	(Vieira et al., 2013)
Nutrients (N and P)	<i>Chesapeake Bay, USA</i>	Surface and bottom waters	Agricultural and wastewater nutrient inputs cause eutrophication, algal blooms, and seasonal hypoxia. Modelling studies link nutrient load reductions to improved dissolved oxygen levels.	2001–2014	(Testa et al., 2014)
Microplastics	<i>Yangtze River Basin, China</i>	Surface water and sediments	High abundance of polyethylene and polypropylene microplastics; major sources include wastewater and urban runoff. Microplastics act as vectors for	2023–2024	(S. Wang et al., 2024)

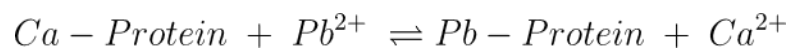
			heavy metals and hydrophobic organic contaminants.		
Antibiotics and Pharmaceuticals	<i>Ganges River, India / Global Rivers</i>	Water, sediment, microbial communities	High concentrations of antibiotics (ciprofloxacin, sulfamethoxazole, etc.) and antibiotic resistance genes from wastewater inputs. Rivers serve as hotspots for AMR dissemination.	2013–2023	(S. Li et al., 2022)
Mercury from Artisanal Gold Mining (ASGM)	<i>Madre de Dios, Peruvian Amazon</i>	Soil, water, and biota	Atmospheric and waterborne mercury emissions from ASGM lead to accumulation in forest canopies and aquatic food webs, causing widespread MeHg bioaccumulation.	2018–2023	(Gerson et al., 2022)

## 7.0 HUMAN HEALTH AND ECOLOGICAL IMPACTS

Contaminants in surface and groundwater exert both direct toxicological effects and indirect ecological disruptions.

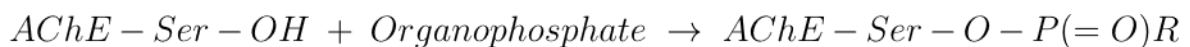
### 7.1 Health impacts

Lead interferes with calcium metabolism, impairing neurological function through substitution at calcium-binding sites:



This substitution mechanism underlies neurotoxicity, impaired synaptic transmission, and bone accumulation (Tobalu & Enogieru, 2025). Cadmium complexes with thiol groups in proteins, impairing kidney function, promoting oxidative stress, and disrupting calcium signaling, which contributes to bone demineralization (Yan & Allen, 2021). Mercury methylation produces methylmercury, a neurotoxin that bioaccumulates in fish and biomagnifies in food webs, posing dietary risks (Jeong et al., 2024).

Pesticides inhibit enzymes—most notably, organophosphates block acetylcholinesterase (AChE):





AChE = Acetylcholinesterase, Ser = Serine residue, AChE-Ser-OH = Active (native) acetylcholinesterase, AChE-Ser-O-P(=O)R = Phosphorylated (inhibited) acetylcholinesterase

Organophosphates form stable covalent bonds with AChE, preventing neurotransmitter breakdown and causing neurotoxicity (Toropova et al., 2023). PFAS bind strongly to serum albumin, altering lipid transport, endocrine regulation, and liver function (Zhao et al., 2023). Pharmaceuticals discharged into aquatic ecosystems disrupt microbial communities, facilitating the spread of antibiotic resistance genes (Świacka et al., 2023). Microplastics not only cause physical blockage in aquatic species but also act as vectors for hydrophobic pollutants and metals, enhancing their bioavailability and toxicological impact in higher trophic levels (Parashar et al., 2023; Wu et al., 2024).

## 7.2 Ecological Disruptions

Aquatic ecosystems face multiple stressors:

- Altered redox balance from organic pollutant degradation → hypoxia.
- Bioaccumulation of metals in fish and benthic organisms → trophic transfer.
- Endocrine disruption by pharmaceuticals and microplastics → reproductive impairments in fish and amphibians.

Mechanistically, these effects derive from the molecular-level interactions between pollutants and biological systems, linking environmental chemistry with toxicology.

## 7.3 Risk Assessment and Predictive Models

Risk assessment integrates chemical data, exposure pathways, and toxicological thresholds to evaluate threats posed by contaminants in surface and groundwater. The mechanistic understanding of contaminant chemistry is essential for accurate modeling.

## 7.4 Human Health Risk Assessment (HHRA)

Risk is quantified through hazard quotient (HQ) and carcinogenic risk (CR) values, based on contaminant concentration, exposure, and toxicity reference values.

$$HQ = \frac{C \times IR \times EF \times ED}{RfD \times BW \times AT}$$

Where:

C = contaminant concentration; IR = ingestion rate; EF = exposure frequency; ED = exposure duration

RfD = reference dose; BW = body weight; AT = averaging time

Mechanistically, the toxicity values (RfD, slope factor) derive from dose–response relationships demonstrated such risk calculations for Pb and Cd in polluted soils and their leachates.

## 7.5 Ecological Risk Assessment (ERA)

ERA incorporates species sensitivity distributions (SSDs), modeling contaminant effects across multiple taxa. For instance, LC<sub>50</sub> values for fish exposed to methylmercury inform protective threshold concentrations.

## 7.6 Predictive Geochemical Models

Models such as PHREEQC simulate aqueous speciation, adsorption, and precipitation:

- Pb<sup>2+</sup> partitioning between aqueous and solid phases is predicted by equilibrium constants.
- Arsenic mobility modeled through surface complexation reactions.

Reactive transport models couple hydrodynamics with geochemical kinetics, predicting contaminant plumes. Mechanistic redox pathways (e.g., Fe reduction releasing As) are embedded in such models to improve predictions (Tufenkji et al., 2022).

Risk assessment frameworks, therefore, rely on the integration of contaminant chemistry and transport mechanisms to identify high-risk scenarios and guide remediation priorities.

## **8.0 CONCLUSION**

The chemistry and mechanisms of contaminants in surface and groundwater define their environmental persistence, ecological risks, and health impacts. This review has highlighted the complex interplay of geochemical and biochemical processes — adsorption, redox transformations, hydrolysis, microbial degradation, and complexation — that govern contaminant fate at polluted sites. Heavy metals such as Pb, Cd, Hg, and As exhibit speciation-dependent toxicity, with redox and sorption dynamics controlling their mobility. Organic pollutants, including pesticides, hydrocarbons, and solvents, undergo hydrolysis, photolysis, and microbial degradation, often yielding toxic intermediates. Emerging contaminants such as PFAS, pharmaceuticals, and microplastics challenge existing remediation strategies due to their structural stability, amphiphilicity, and vector roles.

Mechanistic insights demonstrate that environmental chemistry provides predictive capacity: speciation models anticipate contaminant behavior under varying geochemical conditions, while toxicological mechanisms explain health impacts ranging from neurotoxicity to endocrine disruption. Risk assessment frameworks integrate these mechanistic details, supporting site-specific evaluations. Case studies across Asia, Africa, Europe, and North America illustrate how mechanistic understanding explains observed contamination patterns, from arsenic mobilization in South Asia to PFAS persistence in military sites.

Ultimately, the chemistry and mechanisms of contaminant behavior must remain central in monitoring, modeling, and remediation strategies. Bridging environmental chemistry with toxicology, risk science, and engineering is essential for sustainable management of polluted sites and protection of water resources. Future research should emphasize integrated mechanistic models and emerging contaminants, ensuring proactive rather than reactive responses to contamination challenges.

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