



The impact of over-irrigation on the cycling and fate of persistent organic pollutants in the environment

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Abstract

Over-irrigation, driven by intensive agricultural demands and changing climatic patterns, significantly alters the hydrological cycle and terrestrial ecosystems. Persistent Organic Pollutants (POPs) remain a global environmental and public health concern due to their toxicity, long-range transport potential, and resistance to degradation. This review provides a comprehensive synthesis of how excessive water application influences the environmental fate, transport, and cycling of POPs. It examines the mobilization of POPs via surface runoff, soil erosion, and enhanced leaching into groundwater systems. Furthermore, this article evaluates the impacts of over-irrigation on soil physicochemical properties such as redox potential, dissolved organic matter (DOM) dynamics, and microbial community structures which directly control POP bioavailability, volatilization, and biodegradation pathways. By critically analyzing recent literature, we highlight how altered hydrological regimes accelerate the cross-media transfer of legacy and emerging organic contaminants. Finally, this review identifies critical knowledge gaps and proposes future research directions to improve agricultural water management and mitigate environmental contamination risks.

Keywords: Persistent organic pollutants (POPs), over-irrigation, contaminant transport, soil redox potential, dissolved organic matter (DOM), bioavailability

Introduction

Persistent Organic Pollutants (POPs), including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs), are highly toxic compounds characterized by environmental persistence, bioaccumulation, and long-range atmospheric transport. While global regulations like the Stockholm Convention have restricted legacy POPs, their residues endure in agricultural soils, accompanied by an increasing influx of emerging hydrophobic organic contaminants. Concurrently, modern agricultural intensification has led to widespread over-irrigation the application of water exceeding crop evapotranspiration requirements and soil water-holding capacities. This anthropogenic alteration of the hydrological cycle does not merely waste water; it fundamentally transforms the environmental matrices governing contaminant behavior.

Over-irrigation induces rapid shifts in soil moisture, hydraulic gradients, and redox conditions. These physical and chemical transitions alter the equilibrium partitioning of POPs between solid soil phases, aqueous pore water, and the atmosphere. Understanding these dynamics is critical, as agricultural soils act as both historical sinks and contemporary sources of toxic organic pollutants ^[1]. While standard hydrological models track water movement, they often oversimplify the chemical and biological feedback loops triggered by excessive watering ^[2]. Consequently, predicting the fate of toxic residues under modern farming practices remains a complex challenge ^[3].

This review systematically addresses the nexus between unsustainable irrigation practices and the environmental fate of POPs. We evaluate the mechanisms driving surface and subsurface contaminant transport, examine the shifts in soil biogeochemistry that dictate pollutant bioavailability, and discuss the subsequent risks of food chain transfer. By

synthesizing recent empirical findings, this paper delivers a cohesive framework to guide future ecotoxicological research and sustainable water management strategies.

Overview Of Persistent Organic Pollutants (Pops) And Over-Irrigation

Characteristics and Environmental Behavior of POPs

POPs are distinguished by high lipophilicity, low water solubility, and exceptional resistance to photolytic, chemical, and biological degradation ^[4]. Structurally, the presence of halogenated functional groups, particularly chlorine, shields these molecules from enzymatic attack and nucleophilic substitution. Because of their hydrophobic nature, quantified by high octanol-water partition coefficients ($\log K_{ow}$), POPs strongly adsorb to soil organic matter (SOM) ^[5].

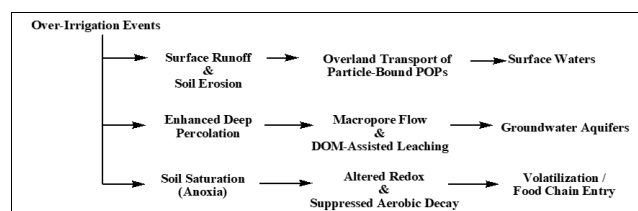
Once bound to the soil matrix, these compounds undergo slow aging processes, becoming increasingly entrapped within the micropores of organic fractions ^[6]. However, desorption remains a dynamic process. It is continuously influenced by ambient temperature, matrix moisture, and the presence of mobile carriers. The environmental behavior of POPs is therefore a balance between secure sequestration and episodic mobilization into adjacent environmental compartments.

Causes and Extent of Over-Irrigation

Over-irrigation stems from a combination of inefficient farming techniques, subsidized water utilities, and inaccurate climate-adaptive planning ^[7]. Flood irrigation and uncalibrated furrow systems routinely deliver water volumes far exceeding the field capacity of agricultural soils ^[8]. In arid and semi-arid regions, farmers frequently practice deliberate over-irrigation to leach accumulated salts out of

the root zone, inadvertently triggering secondary environmental issues [9].

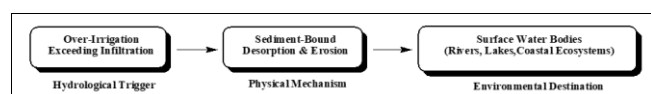
Globally, excessive water application alters local water tables and drives widespread secondary salinization [10]. It also modifies regional microclimates by increasing surface energy partitioning toward latent heat flux [11]. This chronic over-wetting creates unstable hydrological conditions across millions of hectares of arable land. As a result, it transforms stable terrestrial sinks into highly dynamic zones of chemical transport.



Mechanisms of Pop Transport Induced by Over-Irrigation

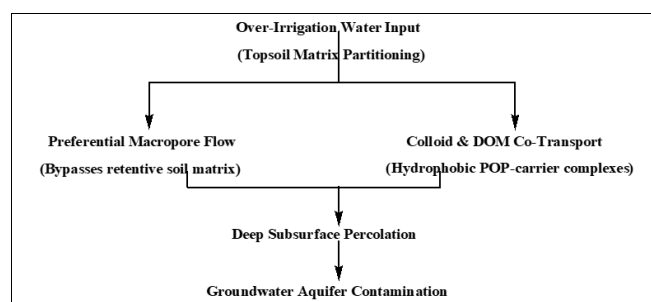
Runoff and Soil Erosion

When irrigation rates exceed the infiltration capacity of the soil, surface ponding occurs, generating overland runoff [12]. This moving water exerts shear stress on the soil surface, detaching fine particles, colloids, and associated organic matter [13]. Because POPs are highly hydrophobic, they attach preferentially to this fine, carbon-rich sediment fractions [14].



During heavy runoff events, sediment-bound POPs are carried away from agricultural fields and deposited directly into downstream aquatic ecosystems [15, 16]. Simultaneously, the sudden increase in the water-to-soil ratio shifts the chemical equilibrium [17]. This triggers the desorption of the less tightly bound fraction of POPs into the dissolved phase [18]. This dissolved fraction is highly bioavailable and poses an immediate toxicological threat to aquatic organisms. Consequently, over-irrigation serves as a primary driver for moving legacy terrestrial contaminants into vulnerable aquatic food webs.

Leaching and Groundwater Contamination



While POPs are traditionally viewed as immobile in subsoil profiles due to their low water solubility, over-irrigation accelerates their downward migration via preferential flow pathways. Chronic over-watering forces water rapidly through macro-pores, structural cracks, and earthworm burrows. This fast-moving water bypasses the chemically

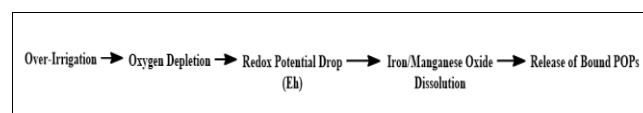
retentive soil matrix, allowing hydrophobic contaminants to travel deep into the subsurface.

This downward migration is further accelerated by colloid-mediated transport and dissolved organic matter (DOM) co-transport [8]. The abundant organic matter mobilized by excessive irrigation acts as a chemical carrier. Hydrophobic compounds associate with these mobile organic complexes, effectively masking their hydrophobicity and allowing them to move freely through the soil profile. This process facilitates the steady accumulation of persistent organic pollutants in underlying groundwater aquifers, threatening clean drinking water reserves.

Impact of Over-Irrigation on Soil Physicochemical Properties and POP Dynamics

Soil Moisture and Redox Potential

Persistent over-irrigation displaces soil air with water, cutting off the diffusion of atmospheric oxygen. As aerobic microorganisms consume the remaining dissolved oxygen, the soil matrix rapidly transitions from oxic to anoxic states, dropping the redox potential (Eh) [19]. This shift in redox status alters the stability of iron and manganese oxides, which serve as primary sorptive surfaces for organic pollutants.

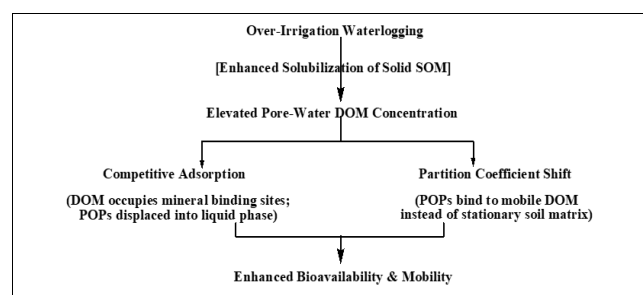


The reductive dissolution of these mineral oxides releases previously trapped POPs back into the soil solution [20]. Furthermore, changed redox conditions alter the chemical structure of the organic matter itself, changing its polarity and reducing its overall capacity to adsorb hydrophobic compounds. Therefore, the anaerobic cycles caused by over-irrigation directly unlock bound pollutants, increasing their mobility in the local environment.

Dissolved Organic Matter (DOM) Dynamics

Over-irrigation significantly increases the generation and flushing of DOM from surface soils. The extended waterlogging promotes the breakdown of solid organic matter, releasing soluble humic and fulvic acids. This spike in pore-water DOM concentrations drives competitive adsorption processes on soil particles.

Because DOM molecules occupy available binding sites on the soil minerals, POPs are displaced into the liquid phase. Additionally, the partition coefficient of POPs shifts in favor of the mobile DOM phase rather than the stationary solid matrix [18]. This chemical partitioning increases the apparent solubility of otherwise insoluble organic chemicals, boosting both their environmental mobility and their availability to living organisms.



Volatilization and Air-Soil Exchange

The wetting of dry soils during over-irrigation triggers a rapid displacement of gases from the pore space, accelerating the volatilization of semi-volatile POPs. Water molecules compete directly with organic chemicals for adsorption sites on soil mineral grains. As water fills these spaces, it displaces the adsorbed organic molecules, driving them into the soil vapor phase.

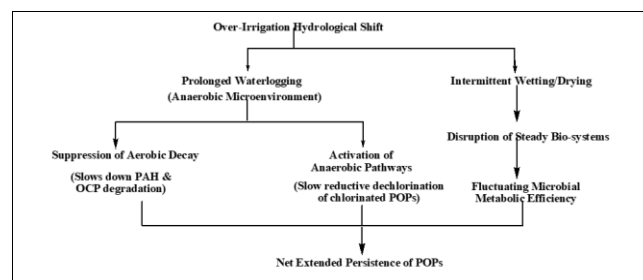
This moisture-induced desorption significantly increases the upward flux of volatile contaminants into the atmosphere. Once in the air, these gaseous compounds are subjected to wind currents, fueling long-range atmospheric transport and deposition in pristine ecosystems far from the agricultural source. Over-irrigation thus acts as a mechanical pump that drives legacy soil contaminants back into global atmospheric cycles.

Influence of Over-Irrigation on the Bioavailability and Degradation of Pops

Microbial Community and Biodegradation

The shift from aerobic to anaerobic conditions caused by over-irrigation fundamentally restructures the soil microbial community. Aerobic bacteria and fungi, which possess efficient oxygenase enzymes capable of breaking down complex aromatic structures,

are suppressed during prolonged water logging. Consequently, the oxidative degradation pathways of compounds like PAHs and certain OCPs slow down dramatically.



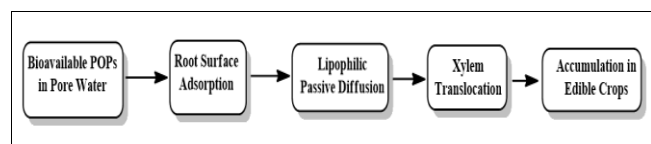
Conversely, anaerobic conditions favor facultative and obligate anaerobes, such as sulfate-reducing and methanogenic bacteria. These organisms utilize reductive dechlorination pathways, which can break down highly chlorinated POPs into less chlorinated sometimes more toxic intermediates [21]. However, these anaerobic pathways operate at much slower rates than aerobic metabolism. The overall result of over-irrigation is a net reduction in the self-cleaning capacity of the soil, leading to extended persistence of toxic organic residues.

Table 1. Comparative Analysis of POP Degradation Half-Lives under Soil Hydro-Regimes.

POP Class	Specific Compound	Aerobic Half-life	Aerobic Half-life	Dominant Anoxic mechanism	Primary Risk of Residues
OCPs	p,p'-DDT	2 to 15 years	16 to 100 days	Reductive dechlorination	Converts to highly toxic, persistent DDE and DDD.
OCPs	Hexachlorobenzene	3 to 6 years	10 to 20+ years	Suppressed oxidative decay	Severe matrix accumulation and groundwater leaching
PCBs	Highly Chlorinated	5 to 12+ years	1 to 3 years	Microbial dechlorination	Strips chlorine to yield more volatile/mobile congeners.
PAHs	Benzo[a]pyrene	200 to 500 days	3 to 8+ years	Halt of oxygenase pathways	Topsoil accumulation and physical splash risks.

Bioavailability and Plant Uptake

By increasing the concentrations of POPs in pore water through DOM complexation and mineral dissolution, over-irrigation enhances the bioavailability of these contaminants to crop root systems. Hydrophobic contaminants can enter plant roots via passive lipophilic diffusion, moving across cell membranes into the vascular system. Inside the plant, compounds with moderate lipophilicity are translocated through the xylem to harvestable tissues, such as leaves and grains.

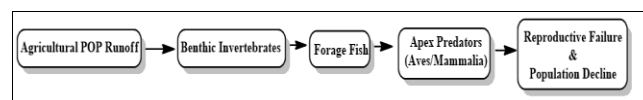


For highly hydrophobic compounds, accumulation is often concentrated in the lipid-rich root cortex. However, when these root crops or low-hanging leafy vegetables come into direct contact with splashed, contaminated soil particles during intense furrow irrigation, surface contamination rises. This dual pathway of systemic uptake and physical splash contamination increases the accumulation of toxic compounds in food crops, elevating food safety risks for consumers.

Environmental and Health Implications

Ecotoxicological Risks

The movement of POPs from over-irrigated fields into nearby streams and wetlands poses severe ecotoxicological risks [16]. Aquatic organisms, including macroinvertebrates, amphibians, and fish, experience continuous exposure to elevated levels of dissolved and sediment-bound organic contaminants. Because these compounds resist metabolic breakdown, they bioaccumulate within organism tissues and biomagnify across trophic levels.



Apex predators, such as piscivorous birds and mammals, suffer the highest body burdens of these contaminants. Chronic exposure leads to endocrine disruption, reproductive failure, and suppressed immune systems, destabilizing vulnerable aquatic and terrestrial populations. The environmental footprint of unsustainable irrigation practices thus extends far beyond farmland boundaries, damaging regional biodiversity.

Human Health Risks

Human exposure to POPs mobilized by over-irrigation

occurs primarily through the consumption of contaminated agricultural crops, groundwater, and animal products. When livestock graze on forage irrigated with contaminated water or contaminated by soil splash, these lipophilic pollutants accumulate in milk, fat, and meat tissues. This creates a direct pathway for highly toxic compounds to enter the human diet.

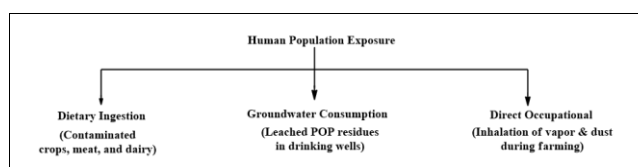


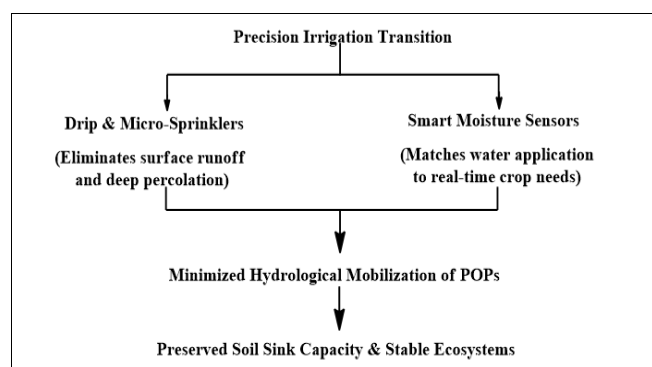
Table 2. Toxicological Hazard Index for Specific Dietary Exposure Pathways

POP Category	Representative Compounds	Primary Dietary Exposure Pathway	Molecular Mechanism	Target Organs & Chronic Pathologies	RfD Range (mg/kg/day)	BAF Class
OCPs	DDT, DDE, DDD, Lindane	Root vegetable ingestion, dairy fat, fish consumption.	Inhibits ATPase; disrupts sodium channels.	CNS; induces hepatic carcinomas, reproductive failure.	5.0e-4 to 5.0e-5	Extremely High (>5000)
PCBs	Aroclor 1254, PCB-138, PCB-153	Fat-rich beef, pork, dairy, bottom fish.	Binds to AhR; alters gene expression.	Thymic atrophy, chloracne, neuro-delays, liver cancer.	2.0e-5 to 7.0e-5	Very High (1000-5000)
PAHs	Benzo[a]pyrene, Chrysene	Leafy greens (soil splash), well water.	Metabolic activation into diol-epoxides.	Pulmonary & GI tracts; mutagenic DNA adducts.	BaP equivalence basis	Mod to High (100-1000)
PAHs	Benzo[a]pyrene, Chrysene	Leafy greens (soil splash), well water.	Metabolic activation into diol-epoxides.	Pulmonary & GI tracts; mutagenic DNA adducts.	BaP equivalence basis	Mod to High (100-1000)

Once inside the human body, POPs disrupt endocrine functions by mimicking or blocking natural hormones, which can lead to developmental abnormalities and reproductive disorders. Chronic exposure is also linked to increased risks of hepatic diseases, neurological impairment, and various forms of cancer. By accelerating the movement of these compounds into food and drinking water, over-irrigation amplifies the long-term public health risks of persistent chemical pollution.

Mitigation Strategies and Future Research Directions Sustainable Water Management Practices

Mitigating the environmental impacts of over-irrigation requires transitioning to precision water management technologies. Adopting drip and micro-sprinkler systems drastically reduces total water application volumes, preventing surface ponding, runoff, and deep percolation. These systems deliver water directly to the plant root zone, minimizing the hydrological forces that mobilize organic contaminants.



Implementing real-time soil moisture sensors and weather-based irrigation scheduling ensures water is applied only when needed. This approach prevents the prolonged soil saturation that triggers anaerobic conditions, iron oxide dissolution, and subsequent pollutant release. Maintaining stable, optimal soil moisture levels preserves the soil's capacity to securely bind persistent organic pollutants.

Farm-Level Implementation Protocols:

Precision System Conversion: Retrofit traditional flood configurations with sub-surface drip irrigation systems buried 15–30 cm deep. Maintain drip emitter flow rates between 1.0 to 2.4 L/h to match fine-textured soil capacities and eliminate ponding.

Real-Time Moisture Networks: Install tri-depth Frequency Domain Reflectometry (FDR) moisture probes at 15 cm, 30 cm, and 60 cm. Configure automated controllers to cut off water as soon as deep probes detect moisture reaching 85% of field capacity.

Tailwater and Sediment Control: Dig lined tailwater recovery ponds at field topographic lows. Establish permanent, 5-meter-wide vegetative filter strips of deep-rooted perennial grasses (e.g., *Vetiveria zizanioides*) to slow runoff velocity and trap sediment-bound POPs.

Future Research Needs

To develop better pollution control strategies, future research must focus on clarifying the exact mechanisms driving contaminant transport under shifting field conditions. Key critical targets include:

- Developing integrated models that couple multi-phase hydrodynamic transport with real-time chemical partitioning.
- Investigating how climate change-driven alterations in wetting and drying cycles affect long-term pollutant binding and aging.
- Exploring the role of nano-scale colloids and specific fractions of dissolved organic matter in accelerating subsurface contaminant transport ^[2].
- Assessing the long-term impacts of reclaimed wastewater irrigation on the accumulation and cycling of emerging polar organic pollutants ^[22].

Addressing these gaps will enable scientists and policymakers to design more effective agricultural management strategies. This research is vital for

safeguarding global food security, protecting vital water resources, and minimizing environmental contamination risks (8).

Conclusion

Over-irrigation acts as a major environmental catalyst, fundamentally altering how Persistent Organic Pollutants cycle through our ecosystems. By triggering excessive surface runoff, soil erosion, and deep subsoil leaching, irresponsible water application transforms agricultural soils from stable chemical sinks into active sources of pollution. The resulting shifts in soil properties including low oxygen levels, altered redox states, and increased dissolved organic matter directly increase the mobility, volatilization, and availability of toxic compounds to living organisms. These changes increase the risk of pollutant accumulation in food crops and vital drinking water sources, threatening both ecological balance and human health. To break this cycle of contamination, agricultural systems must adopt precision irrigation technologies, implement proactive water conservation practices, and advance research into soil-pollutant dynamics. Balancing water management with environmental chemistry is essential to ensuring sustainable food production while protecting global ecosystems from long-term chemical risks.

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