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From Abiotic Filters to Dynamic Biofilm Reactors for the Treatment of Diffuse Agricultural Pollution: A Comprehensive Review

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Abstract

Diffuse pollution from agricultural runoff, characterized by intermittent discharges of complex contaminant mixtures—including nutrients, pesticides, and heavy metals (HMs)—poses a persistent threat to global water quality. Conventional "end-of-pipe" strategies often fail to address these decentralized, nonpoint sources. This review examines the evolution of Permeable Reactive Barriers (PRBs) from static, abiotic filters into modern Permeable Reactive Bio-Barriers (PRBBs), engineered as dynamic, fixed-bed biofilm reactors. A key advancement in PRBB efficacy is the exploitation of biofilm plasticity, particularly in response to coexistence with organic and inorganic pollutants. While heavy metals are traditionally viewed as inhibitors, this review synthesizes evidence showing that sub-inhibitory HM levels can act as structural and functional drivers. These metals induce the upregulation of Extracellular Polymeric Substances (EPS), creating a "protective shield" that sequesters metals and confers functional resilience on the microbial consortia responsible for nutrient removal and pesticide biodegradation. The review analyzes contaminant removal mechanisms, highlighting the bio-chemo synergy between reactive media and biofilms, and proposes a classification framework based on target contaminants, media, and technological integration. Significant focus is placed on emerging hybrid multi-media systems designed to protect the "biological engine" from toxic metal shocks, alongside the integration of artificial intelligence for predictive control. While challenges in hydraulic sustainability and field validation remain, PRBBs represent a compact, low-energy, and scalable eco-technology. They offer a strategically targeted solution within the Nature-Based Solutions toolkit for building resilient protection of aquatic ecosystems at the critical land-water interface.

Keywords: permeable reactive bio-barrier; biofilm reactor; diffuse agricultural pollution; pesticide biodegradation; heavy metals; biofilm plasticity; functional resilience; hybrid systems; smart eco-technology

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1. Introduction: The Imperative for In-Situ Solutions to Diffuse Agricultural Pollution

1.1. The Scale and Nature of the Problem

The protection of freshwater resources is a defining challenge of the 21st century, with agricultural activities among the most prevalent and complex pressures. Pollution from agricultural landscapes is predominantly "diffuse" or "non-point" in nature, originating from spatially distributed activities across vast areas and mobilized by rainfall and irrigation events [1]. This contrasts sharply with treatable point-source discharges from industrial or municipal outfalls. Agricultural runoff and subsurface drainage transport a complex and variable cocktail of contaminants, including soluble nutrients (nitrate, phosphate) from fertilizers and manure, a diverse

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array of pesticides and fungicides, and emerging contaminants such as veterinary pharmaceuticals and hormones [2].

The environmental consequences are profound and well-documented. Nutrient enrichment drives eutrophication, leading to toxic algal blooms, hypoxia, and the degradation of aquatic habitats. Pesticides and fungicides can exert direct toxicity on non-target aquatic organisms, disrupting food webs and biodiversity [3]. The intermittent, weather-dependent nature of this pollution makes it exceptionally difficult to manage with conventional centralized treatment infrastructure, which is designed for continuous, predictable flows.

1.2. Limitations of Conventional and Nature-Based Management Strategies

Traditional management has often focused on "end-of-pipe" treatment or broad landscape measures. However, treating large volumes of dilute, intermittent runoff in centralized plants is economically and energetically prohibitive. Consequently, the most effective strategy is preventive in situ remediation, which intercepts pollutants within hydrologic pathways before they enter sensitive water bodies [4].

Nature-Based Solutions (NBS) such as constructed wetlands, riparian buffers, and vegetated drainage ditches have been widely adopted for this purpose. These systems provide valuable ecosystem services, including sediment trapping, nutrient assimilation, and habitat creation [5]**.** However, their effectiveness can be constrained by several factors: (1) substantial land requirements that conflict with agricultural production, (2) limited ability to intercept and treat subsurface tile drainage; a major pathway for nitrate and soluble pesticides, and (3) variable performance under high hydraulic or contaminant loading, where short residence times and toxic pulses can overwhelm natural attenuation processes [6].

1.3. The Emergence of Engineered Permeable Reactive Bio-Barriers (PRBBs)

This context has driven innovation toward more compact, targeted, and resilient eco-technologies. The Permeable Reactive Barrier (PRB), a well-established technology for in situ groundwater remediation, has been adapted to this new challenge [7]. Originally designed as subsurface "walls" containing reactive media like zero-valent iron (ZVI) to treat chlorinated solvent plumes, the PRB concept has been reimagined for near-surface applications in agricultural settings [8].

The critical evolution is the shift from an abiotic, consumable filter to a biologically active, self-regenerating system: the Permeable Reactive Bio-Barrier (PRBB)**.** In this model, the reactive media—which can range from organic carbon sources (e.g., wood chips) to mineral-based materials (e.g., slag, biochar) serve a dual purpose. It provides initial sites for physicochemical reactions (e.g., sorption, precipitation) and, more importantly, serves as a high-surface-area substrate for the intentional cultivation of complex microbial communities in the form of biofilms [9,10].

This intentional engineering transforms the barrier into a fixed-bed biofilm reactor. The biofilm is not a passive coating but a dynamic, resilient ecosystem. Microbial consortia within biofilms exhibit significant structural and functional plasticity, allowing them to adapt to fluctuating environmental conditions, degrade a wide range of organic pollutants, and withstand transient toxic shocks [11,12]. This biological resilience is the cornerstone of the PRBB's ability to handle the variable and complex nature of agricultural pollution.

1.4. Scope and Objectives of This Review

This review aims to provide a comprehensive synthesis of the current state of knowledge regarding PRBBs as biofilm reactors for mitigating diffuse agricultural pollution, and expects:

(1) Trace the conceptual and technological evolution of PRBs into dynamic PRBBs.

(2) Expose the fundamental mechanisms of contaminant removal, emphasizing the synergy between abiotic and biofilm-mediated processes.

(3) Examine the evidence for biofilm plasticity and functional resilience as key performance attributes.

(4) Analyze advanced designs, including hybrid multi-media systems and the emerging frontier of AI-enabled “smart” PRBBs.

(5) Propose a classification framework to organize a diverse range of PRBB technologies.

(6) Critically assess advantages, limitations, and future research directions.

By positioning PRBBs within the broader landscape of sustainable water management, this review highlights their role as a targeted, efficient, and resilient complement to traditional NBS for safeguarding water quality in agricultural watersheds.

2. The Conceptual and Technological Evolution of Permeable Reactive Barriers

The development of Permeable Reactive (Bio-)Barriers represents a journey from simple geochemical constructs to sophisticated bio-engineered ecosystems. This evolution can be categorized into distinct, overlapping stages that reflect advancements in scientific understanding and engineering practice.

2.1. Stage 1: Abiotic and Static Permeable Reactive Barriers

The original PRB concept emerged in the 1990s as an innovative in-situ strategy for groundwater remediation. These early systems were designed to intercept contaminant plumes (e.g., chlorinated solvents, hexavalent chromium, acid mine drainage) using a trench or wall filled with reactive media [13,14].

Mechanism and Media: Removal relied almost exclusively on abiotic mechanisms. Zero-valent iron (ZVI) was the predominant medium, facilitating reductive dechlorination of solvents such as trichloroethylene (TCE) and reduction-precipitation of metals like Cr(VI) [15]. Other media, such as steel slag **or** alum residuals, were used for phosphorus removal via sorption and precipitation of phosphate minerals [16,17]

System Characteristics: These were essentially static, flow-through chemical reactors. Performance was governed by the intrinsic reactivity and finite capacity of the media. They demonstrated the core PRB advantages: passive operation, in-situ treatment, and containment without extraction. However, significant limitations included media passivation (e.g., iron oxide coating on ZVI), pore clogging from precipitation reactions, and a narrow focus on specific inorganic or chlorinated organic contaminants [7,18,19].

2.2. Stage 2: Natural Carbon-Based Biofilm PRBs

A pivotal shift occurred with the recognition that organic carbon substrates could support microbial processes. This led to the development of denitrification walls and woodchip bioreactors, primarily targeting nitrate in agricultural tile drainage [20–23]**.**

Mechanism and Media: The primary removal mechanism shifted to microbial denitrification. Heterotrophic bacteria used organic carbon from media such as woodchips, sawdust, or compost as an electron donor, reducing dissolved nitrate (NO_3^-) to nitrogen gas (N_2) under anoxic conditions [24,25].

System Characteristics: These systems introduced biology as a central treatment driver. Microbial biofilms naturally develop on carbon media, driven by environmental conditions. They proved highly effective for nitrate removal, were passive and low-cost, and became widely implemented in temperate agricultural regions [26,27]. However, their functionality was largely restricted to nitrate removal, with incidental removal of other contaminants. The microbial communities were not engineered; they assembled spontaneously, limiting predictable performance against pesticides or emerging contaminants [28,29]. This stage marked the transition from “PRB” to “PRBB,” acknowledging the essential role of biological activity.

2.3. Stage 3: Engineered, Dynamic Biofilm PRBBs

This stage represents a paradigm shift, moving from utilizing natural biofilm assembly to actively engineering and leveraging biofilm communities for targeted treatment and resilience.

Core Concept: The PRBB is explicitly designed as a biofilm reactor. The focus is on cultivating specific, acclimated microbial consortia immobilized on tailored support media. The key operational principle is the harnessing **of** biofilm plasticity; the inherent ability of microbial communities to alter their structure, composition, and function in response to environmental perturbations [11].

Mechanism and Media: Treatment expands beyond denitrification to include the biodegradation of recalcitrant organic pollutants. Research has demonstrated that immobilized consortia can degrade hydrophobic pesticides such as chlorpyrifos and bifenthrin [49] and adapt structurally to increasing loads of fungicides such as carbendazim [12]. Media selection becomes strategic, including biochar (for sorption and biofilm support), porous ceramics**,** or polymeric carriers that favor biofilm formation and stability.

Evidence of Dynamic Response: Studies show that under toxic stress, biofilms increase production of Extracellular Polymeric Substances (EPS) for protection, reorganize their spatial architecture, and shift community composition to favor tolerant or degrading species [30]. This dynamic response allows the PRBB to maintain functional performance (e.g., pesticide removal rate) even as biomass viability fluctuates, a phenomenon not captured by static models [12].

2.4. Stage 4: Hybrid Multi-Functional PRBBs

Recognizing that agricultural runoff includes a complex mix of organic and inorganic contaminants, the logical next step was to develop systems capable of treating multiple contaminants.

Core Concept: Hybrid PRBBs integrate two or more reactive media types within a single structure to create sequential or synergistic treatment zones. They combine abiotic and biotic mechanisms to address a broader spectrum of pollutants [31].

Designs and Examples:

Woodchips + Steel Slag: A classic design for simultaneous nitrate (via denitrification on woodchips) and dissolved phosphorus (via sorption/precipitation on slag) removal [32].

Biochar + Carbon Substrate: Biochar provides superior sorption capacity for hydrophobic pesticides and pharmaceuticals, while also serving as a stable habitat for degrading biofilms. The adjacent carbon substrate (e.g., woodchips) supports denitrification [33,34].

Layered Media Configurations: Systems with sequential layers of different media (e.g., limestone for pH adjustment, organic carbon for denitrification, iron oxide for metal removal, biochar for organics) can treat complex leachates or runoff [35,36]**.**

Advantages: Hybrid systems move closer to a “treatment train” in a compact footprint, addressing the reality of co-contamination. They can also extend the system’s lifespan by distributing the treatment load across multiple mechanisms [37].

2.5. Stage 5: Toward AI-Enabled “Smart” PRBBs

The latest frontier involves integrating digital intelligence with biological systems to create adaptive, predictive, and optimized treatment units.

Core Concept: “Smart” PRBBs incorporate sensors, data transmission, and computational analytics (AI/ML) to monitor real-time performance, predict system stress, and enable autonomous or guided adaptive control [31,38].

Components:

Sensor Networks: Monitor parameters like nitrate, dissolved oxygen, redox potential, pH, flow rate, and surrogate markers for pesticides (e.g., specific fluorescence) [31,39]**.**

Data Analytics & Machine Learning: Algorithms analyze sensor data and external inputs (e.g., weather forecasts) to predict contaminant pulses, diagnose clogging, or forecast media exhaustion [40].

Digital Twins: Virtual replicas of the physical PRBB that simulate hydraulic and biochemical processes under various scenarios, used for design optimization and operational decision support [41].

Adaptive Control: Based on analytics, systems could automatically adjust flow distribution, activate bypasses during extreme toxic loads, or modulate aeration (in hybrid aerobic/anaerobic designs) [42].

This integration aims to transition PRBBs from resilience (reactive recovery) to robustness (proactive adaptation), thereby maximizing treatment efficiency and lifespan while minimizing maintenance interventions.

Table 1. The Evolutionary Stages of Permeable Reactive (Bio-)Barriers.

Stage	Technology Descriptor	Primary Mechanism	Media Examples	Key Advantage	Major Limitation
1	**Abiotic / Static PRBs**	Physicochemical (Sorption, Precipitation, Redox)	Zero-Valent Iron (ZVI), Steel Slag, Alum	Robust for specific metals/solvents	Media passivation and finite capacity
2	**Natural Carbon-Based PRBBs**	Microbial Denitrification (Incidental Biofilm)	Woodchips, Sawdust, Compost	Low-cost; excellent nitrate removal	Narrow focus; limited to nitrate
3	**Engineered Dynamic PRBBs**	**Biofilm Plasticity** & Biodegradation	Biochar, Porous Ceramics, Porous stones, Polymeric Carriers	Resilient to toxic pulses and load shifts	Requires acclimated inocula
4	**Hybrid Multi-Media Systems**	Synergistic (Sequential Biotic/Abiotic)	Layered Woodchips + Slag + Biochar	Treats complex “contaminant cocktails.”	Increased design complexity
5	**AI-Enabled “Smart” PRBBs**	Predictive & Adaptive Control	Sensors + Digital Twins + Reactive Media	Proactive optimization maximizes lifespan	High upfront cost and tech expertise

3. Fundamental Mechanisms of Contaminant Removal in PRBBs

The treatment efficacy of a PRBB arises from a combination of interconnected physical, chemical, and biological processes. The dominant mechanisms depend on the reactive media, the developed microbial community, and the prevailing hydrologic and geochemical conditions.

3.1. Biological Mechanisms: The Biofilm Engine

Biofilms are the catalytic heart of dynamic PRBBs, facilitating a suite of contaminant biotransformations.

Microbial Denitrification: Is the most well-established process in agricultural PRBBs. Heterotrophic denitrifying bacteria use organic carbon from the media (e.g., woodchips) as an electron donor, sequentially reducing nitrate (NO_3^-) to nitrite (NO_2^-), nitric oxide (NO), nitrous oxide

(N_2O), and finally nitrogen gas (N_2) under anoxic conditions [43]. Performance is sensitive to temperature, carbon availability, and hydraulic residence time (HRT) [44].

Biodegradation of Organic Micropollutants: This includes pesticides, fungicides, and pharmaceuticals.

Direct Metabolism: Specialized microorganisms use the pollutant as a carbon and energy source. Genes for degrading compounds like atrazine (*atz*, *trzN* genes) [45] or organophosphates (*opd* gene) are well-documented [46,47].

Co-metabolism: Contaminants are fortuitously transformed by enzymes produced for other substrates. This is crucial for many recalcitrant compounds that do not support microbial growth [48]. The presence of labile organic carbon in PRBB media (e.g., from woodchip decay) can stimulate co-metabolic degradation of pesticides.

Biofilm Adaptation: As shown in PRBB studies, biofilms adapt to pesticide stress through genetic up-regulation, community shifts, and EPS production, allowing sustained degradation activity across a range of concentrations [12,49].

Redox-Mediated Transformations: Biofilms naturally create gradients of oxygen, nitrate, iron, and sulfate. This allows for sequential anaerobic/aerobic processes. For example, reductive dechlorination of pesticides may occur in anoxic zones, while oxidation of resulting metabolites happens in aerobic microsites [50,51].

EPS-Mediated Sorption and Buffering: The biofilm matrix, composed of EPS, acts as a sorptive sponge for hydrophobic organic compounds and metal cations. This not only facilitates removal but also buffers the microbial cells within from sudden toxic pulses, thereby enhancing community resilience [52].

3.2. Abiotic Mechanisms: The Media's Inherent Reactivity

The selected media provide essential removal pathways, particularly during initial system operation or in hybrid designs.

Sorption: Physical and chemical adsorption to media surfaces is a primary mechanism for many contaminants.

Biochar/Activated Carbon: Exceptional for hydrophobic pesticides, pharmaceuticals, and some metals due to high surface area and porous structure [53].

Steel Slag/Iron Oxides: Effective for phosphate sorption and subsequent precipitation as iron or calcium phosphate minerals [54,55].

Zeolites/Clay Minerals: Used for cation exchange of ammonium (NH_4^+) and some metals [56].

(Co-)Precipitation: The formation of insoluble solids removes contaminants from solution. This is dominant for phosphorus removal with media rich in calcium, iron, or aluminum (e.g., slag, alum residuals) [57].

Reductive Reactions: Media like ZVI provide a strong reducing potential, directly reducing contaminants like chlorinated solvents, nitroaromatic pesticides, and oxyanions like Cr(VI) [18].

3.3. Coupled and Synergistic Mechanisms

The true power of advanced PRBBs lies in the interaction between biotic and abiotic processes.

Biochar-Biofilm Synergy: This is a paradigm for hybrid performance. Biochar rapidly sorbs hydrophobic pesticides, effectively concentrating them at the solid-liquid interface. This increases their local bioavailability to biofilm-associated degraders, potentially enhancing biodegradation rates. Simultaneously, microbial activity can help regenerate sorption sites on the biochar [58]. Biochar can also act as an electron shuttle, facilitating redox reactions mediated by the biofilm [59].

ZVI-Biofilm Synergy: ZVI creates a locally reducing environment and corrodes to produce H_2 gas, which can serve as an electron donor, including dechlorinating bacteria [60]. Thus, ZVI can stimulate and sustain microbial processes that complete the degradation of products from abiotic reduction [61].

Sequential Treatment in Layered Systems: In hybrid PRBBs, water passes through distinct zones. For example, a first layer of woodchips removes nitrate via denitrification, creating anoxic conditions; a second layer of slag removes phosphate; and a final layer of biochar/biofilm removes residual pesticides. This prevents competition between processes and optimizes conditions for each [62].

3.4. Hydrologic and Physical Controlling Factors

All biochemical and geochemical processes are governed by hydraulics.

Hydraulic Residence Time (HRT): The contact time between contaminated water and reactive media/biofilm is the master variable controlling removal efficiency. Design must ensure sufficient HRT for slow processes like denitrification or biodegradation to occur [63].

Flow Distribution and Clogging: Uniform flow through the barrier is essential to utilize the full reactive volume. Clogging—from biomass accumulation, EPS, mineral precipitation, or sediment ingress—is a major failure mode, causing flow channeling (short-circuiting) and reduced performance [64].

Temperature: Microbial activity and reaction kinetics are temperature-dependent. Performance, particularly for biological processes, typically declines in cold weather, a key consideration for design in temperate climates.

4. Biofilm Plasticity and Functional Resilience: The Core of Dynamic PRBB Performance

The ability of PRBBs to function under the highly variable conditions of agricultural systems is predicated on the dynamic nature of the biofilms they harbor. This section delves into the concept of biofilm plasticity and its direct link to system resilience.

4.1. Defining Biofilm Plasticity and Functional Resilience

Biofilm Plasticity refers to the capacity of a microbial community to alter its phenotypic traits—including structure, composition, metabolism, and gene expression—in response to environmental cues and stresses [65].

Functional Resilience in the context of a PRBB is the system's ability to maintain its core treatment function (e.g., nitrate or pesticide removal) despite experiencing disturbances such as toxic pulses, hydraulic shocks, or temperature shifts. Plasticity is the microbial-scale mechanism that enables this ecosystem-scale resilience [11,66].

4.2. Manifestations of Biofilm Plasticity in PRBBs

Research, particularly on pesticide-degrading systems, has illuminated specific adaptive responses:

(1) Structural and EPS Plasticity:

EPS Modulation: Under chemical stress (e.g., benzimidazole fungicide), biofilms often increase EPS production [52]. EPS acts as a diffusion barrier, slowing the penetration of the toxicant, and as an adsorptive matrix, binding contaminants and reducing their bioavailable concentration within cells [67,68].

Architectural Changes: Biofilms may alter their thickness, density, and porosity. A thicker, denser biofilm can protect inner cells, while a more porous structure may maintain mass transfer under high organic loading [69].

(2) Community Composition Plasticity:

Population Shifts: Exposure to selective pressure (like a specific pesticide) drives changes in the microbial community. Tolerant or degrading taxa increase in relative abundance, while sensitive taxa decline. This is not a failure but an adaptive restructuring [70]. Studies on PRBBs show that community shifts are correlated with sustained degradation rates of chlorpyrifos and bifenthrin [49].

(3) Functional and Metabolic Plasticity:

Metabolic Switching: Biofilms can utilize different metabolic pathways depending on available electron acceptors and donors. [69].

Stress Response Activation: Up-regulation of genes for efflux pumps, detoxification enzymes, and oxidative stress defenses is a common plasticity response to toxicants [70,71].

Spatial Stratification: Functional plasticity can be spatial. Aerobic degraders may dominate the biofilm surface, whereas anaerobic processes such as reductive dechlorination occur in deeper, anoxic layers, thereby allowing parallel treatment pathways [72,73].

4.3. Evidence from PRBB-Specific Research

Laboratory and pilot-scale studies provide compelling evidence for this plasticity-resilience link:

Pesticide Degradation under Increasing Loads: Arias-Ruiz et al. [49] demonstrated that immobilized consortia maintained chlorpyrifos and bifenthrin removal rates across a wide range of increasing loading rates, indicating functional stability despite changing conditions.

Response to Fungicide Stress: Alvarado-Gutiérrez et al. [12] meticulously documented the "dynamic and structural response" of a multispecies PRBB biofilm to increasing benzimidazole fungicide loads. The biofilm underwent significant changes in EPS and community composition, enabling it to maintain partial removal efficiency even at high, stressful concentrations, demonstrating adaptive plasticity.

Recovery from Perturbation: The inherent stability of biofilm communities allows for functional recovery after a temporary change in toxic exposure, a feature absent in suspended culture systems.[74]

4.4. Implications for PRBB Design and Management

Understanding plasticity leads to a better design and operation of a biofilm reactor; for example:

Inoculation and Acclimation: PRBBs can be inoculated with diverse, pre-acclimated consortia possessing known catabolic abilities, rather than relying on stochastic natural colonization.

Media Selection for Biofilm Support: Choosing porous, high-surface-area, and chemically compatible media (such as certain biochars) that promote robust, diverse biofilm formation is crucial.

Operational Buffering: Designs should include mechanisms to buffer extreme pulses (e.g., flow equalization basins, bypass options) to keep stresses within the biofilm's adaptive range, preventing collapse.

Monitoring for Plasticity Indicators: Tracking parameters like EPS content, community structure (via molecular tools), and specific degradation genes can provide early warnings of stress and insights into adaptation, moving beyond simple effluent concentration monitoring.

5. Classification of Permeable Reactive Bio-Barriers

To facilitate effective communication and selection across diverse designs, Permeable Reactive Bio-Barriers (PRBBs) can be organized into a multi-dimensional classification framework based on four primary attributes. When classified by target contaminants, systems range from nitrogen-focused designs, such as denitrifying woodchip bioreactors and walls, to phosphorus-focused units that use slag or alum residuals. Specialized barriers also target pesticides and fungicides with biochar-supported acclimated biofilms, and metals with zero-valent iron (ZVI) and limestone drains. Increasingly, hybrid multi-contaminant PRBBs integrate multiple media, such as woodchips combined with slag and biochar, to address complex chemical mixtures simultaneously.

The reactive media employed further define the system, ranging from purely abiotic media to carbon-based biofilm supports such as woodchips, compost, or mulch. Advanced engineered biofilm support systems employ specialized materials, such as porous ceramics, specific biochars, or plastic carriers, to optimize microbial attachment. These are often integrated into hybrid multi-media systems that combine two or more material types within a single unit to enhance performance. From a hydrologic and placement perspective, PRBBs are strategically positioned to intercept pollution pathways. Interception PRBBs are placed perpendicular to shallow groundwater, while in-line systems are integrated directly into tile drainage networks. Surface-flow or filtration variants treat runoff within ditches or channels; bank filtration systems are embedded in riparian zones; and infiltration galleries provide treatment prior to aquifer recharge.

Finally, the level of technological integration distinguishes between passive systems, which rely solely on natural gradients and assembly, and managed PRBBs, which require minimal human intervention for flow regulation or media maintenance. The modern frontier includes smart or active PRBBs that incorporate sensor networks, data telemetry, and AI-informed automated control systems to enable proactive and adaptive management.

Table 2. Multi-Dimensional Classification Framework for Permeable Reactive Bio-Barriers (PRBBs).

Classification Attribute	Category	Key Examples and Characteristics
Primary Target Contaminant(s)	**Nitrogen-Focused**	Denitrifying woodchip bioreactors; denitrification walls.
	Phosphorus-Focused	Steel slag filters; alum residual beds; iron-based barriers.
	Pesticide/Fungicide	Biochar-based barriers; systems with specialized acclimated biofilms.
	Metal-Removal	Zero-Valent Iron (ZVI) barriers; organic/limestone drains for AMD.
	Multi-Contaminant	Hybrid systems combining media for N, P, and pesticides (e.g., woodchip + slag + biochar).
Reactive Media Type	**Abiotic Media**	Mineral or chemical-based reactive filters without intentional biological engineering.
	Carbon-Based	Woodchips, compost, or mulch serve as both a carbon source and a biofilm support.
	Engineered Support	Porous ceramics, specific biochars, or plastic carriers optimized for biofilm attachment.
	Hybrid Multi-Media	Integration of two or more of the above media types within a single unit.
Hydrologic Configuration	**Interception**	Placed perpendicular to shallow groundwater flow to intercept subsurface plumes.
	In-Line	Installed within tile drainage networks or at their specific outlets.
	Surface/Filtration	Positioned in ditches or channels as check dams to treat surface runoff.
	Bank/Riparian	Integrated into streambanks or riparian zones for lateral filtration.
	Infiltration	Designed as galleries for water treatment prior to aquifer recharge.
Technological Integration	**Passive**	Relying entirely on natural hydraulic gradients and spontaneous processes.
	Managed	Involving human intervention for flow control, media replacement, or vegetation.
	Smart / Active	Incorporating **AI-informed control**, sensors, and telemetry for adaptive management.

6. Advantages, Limitations, and Implementation Challenges

A balanced assessment of Permeable Reactive Bio-Barriers (PRBBs) reveals a sophisticated eco-technology characterized by distinct operational advantages and persistent engineering challenges.

Among the key advantages, PRBBs offer a passive, low-energy treatment solution that operates under natural hydraulic gradients, thereby significantly reducing long-term operational costs and complexity. Their small footprint and subsurface compatibility enable installation within existing drainage infrastructure or underground, thereby avoiding land-take conflicts with agricultural production. This flexibility enables targeted intervention at hydrologic “choke points,” such as drain outlets or ditch confluences, ensuring maximum impact where contaminant loads are most concentrated. Furthermore, the inherent biofilm plasticity within these systems provides functional resilience, serving as a buffer against variable and intermittent loading, whereas hybrid designs offer broad multi-contaminant capacity to address the “cocktail effect” of agricultural runoff. The technology is also highly scalable and modular, enabling transitions from edge-of-field units to larger catchment-scale installations, potentially using modular cartridges to simplify maintenance protocols.

However, these benefits are countered by several persistent limitations and challenges that define the current research agenda. All reactive media possess a finite capacity and longevity; carbon sources eventually deplete, sorption sites reach saturation, and reactive metals undergo passivation, making the prediction and management of media exhaustion a central hurdle. Clogging remains perhaps the most common cause of system failure, as biomass overgrowth, mineral precipitation, and sediment accumulation can drastically reduce permeability, leading to surface ponding or flow bypass. Performance variability is also a significant concern, as efficiency can fluctuate with temperature—often resulting in lower winter performance—and with shifting hydraulic loading rates and influent compositions.

Designers must also account for the potential production of harmful by-products, such as the greenhouse gas N_2O from incomplete denitrification or toxic intermediates generated during abiotic reduction processes. These technical risks are compounded by a lack of extensive real-world data on complex contaminants, as robust long-term field studies on the removal of pesticides, fungicides, and pharmaceuticals under actual agricultural conditions remain scarce. Finally, the move toward hybrid and “smart” PRBBs increases design complexity, necessitating sophisticated media selection and potentially higher upfront costs and technical expertise for effective management.

7. Future Directions and Emerging Frontiers

The field of PRBBs is a dynamic landscape defined by several promising research and development trajectories aimed at transforming these systems into more efficient, sustainable, and intelligent filters. A primary focus is the development of next-generation media and materials, in which “designer”- engineered composites—such as biochar impregnated with iron nanoparticles—combine sorption, redox activity, and biofilm support into a single substrate. Research is also moving toward slow-release and self-regenerating media to extend system longevity, alongside the exploration of waste-derived materials that align with circular economy principles. Complementing these material advances is **advanced biological engineering**, which utilizes microbial ecology and synthetic biology to design synergistic consortia and bioaugmentation strategies that introduce specialized degraders to target persistent contaminant mixtures.

The deep **integration of digital technologies** represents another transformative trend, moving toward “Smart Remediation.” This includes developing robust, cost-effective sensor suites and advanced AI/ML models that transition from simple descriptive analytics to predictive and prescriptive control. By creating watershed-scale **digital twins**, researchers can integrate PRBB models into larger digital replicas of agricultural catchments to optimize the placement and operation of distributed networks. Furthermore, there is a growing emphasis on **system sustainability and lifecycle management**, encompassing standardized performance monitoring, sustainable end-of-life media management, and holistic environmental and economic assessments to guide future policy.

8. Effect of Heavy Metals on PRBBs

The coexistence of pesticides and heavy metals in agricultural runoff affects biological treatment systems, as metal toxicity can disrupt microbial activity, thereby compromising treatment performance. To understand the full scope of how Permeable Reactive Bio-Barriers (PRBBs) function in agricultural settings, the complex role of heavy metals (HMs) must be highlighted because heavy metals are not merely contaminants to be removed; they also act as drivers of biofilm plasticity and functional resilience.

8.1. Heavy Metals as Drivers of Biofilm Structure

Heavy metals have a double role within the PRBB system. While extreme concentrations cause metabolic perturbations, including cell death, sub-inhibitory or chronic levels trigger significant structural adaptations [76,77].

Induction of Biofilm Formation: Low levels of some metals (e.g., Pb, Cd, Ni) are recognized by microbial consortia as environmental stressors. This triggers a survival strategy in which microbes shift from a planktonic (free-floating) state to an immobilized biofilm state to seek safety in numbers [78,79].

EPS as a protective Barrier: The most profound structural change is the up-regulation of Extracellular Polymeric Substances (EPS). The EPS matrix acts as a physical and chemical shield. It contains functional groups (carboxyl, hydroxyl, and phosphate) that bind and sequester heavy metals, preventing them from penetrating the cell cytoplasm [80,81].

Architectural Changes: Metals can cause the biofilm to become thicker and denser. This increased density creates steeper redox gradients, which allows for sequential anaerobic and aerobic processes within the same barrier [78,82].

8.2. Impact on Biofilm Function and Metabolism

The functional resilience of a PRBB—its ability to continue treating nitrate or pesticides under stress is directly modulated by the presence of heavy metals.

Positive Functional Impacts (Resilience)

Metallotolerant Selection: Heavy metals exert selective pressure, favoring taxa that possess resistance genes (e.g., efflux pumps or detoxifying enzymes). This leads to an “adaptive restructuring” of the community that is more robust against the variable “contaminant cocktails” found in agricultural runoff [83,84].

Sorption Synergy: As metals are trapped in the EPS or adsorbed onto media like biochar (Stage 3 & 4 PRBBs), they can alter the surface charge of the media, potentially enhancing the secondary sorption of other organic micropollutants [85,86]

Negative Functional Impacts (Inhibition)

Enzymatic Interference: HMs can bind to the active sites of essential enzymes. This may lead to a decrease in oxygen uptake or the inhibition of specific pathways, such as denitrification (the reduction of $NO3^-$ to N_2) [87]

Metabolic Shifting: Under high metal stress, the community may redirect energy from growth and pollutant degradation toward maintenance and defense (e.g., pumping metals out of the cell), leading to a temporary decline in treatment efficiency [88]

8.3. Integration Into the PRBB Evolutionary Framework

The impact of heavy metals reinforces the need for the advanced stages of PRBB development.

Table 3. Effects of heavy metals on PRBBs.

Evolutionary Stage	Role of Heavy Metals (HM)
Stage 1: Abiotic PRBs	HMs are removed strictly via chemical precipitation or ZVI reduction; no biological feedback.
Stage 3: Engineered PRBBs	Focuses on Biofilm Plasticity. The system leverages EPS production and community shifts to maintain function despite HM toxicity.
Stage 4: Hybrid Systems	Uses media such as biochar or Steel Slag to abiotically capture the bulk of HMs, thereby protecting the sensitive "Biofilm Engine" from toxic shock.
Stage 5: Smart PRBBs	Uses sensors to detect metal pulses in real-time, allowing AI to predict when the biofilm might reach its "tipping point" of metabolic inhibition.

8.4. The Bio-Chemo Synergy

PRBB is not just a filter, but a living, adaptive shield. Heavy metals are key participants in this "biological engine." By inducing EPS production and selecting for hardier microbial species, moderate levels of heavy metals "train" the biofilm to become more resilient.

Future PRBB designs must therefore account for the HM-Biofilm feedback loop: ensuring that the reactive media (abiotic) and the microbial consortia (biotic) work together to sequester metals while maintaining the plasticity needed to degrade pesticides and nutrients.

Table 4. Comparative Removal Mechanisms: Heavy Metals vs. Organic Micropollutants in PRBBs.

Feature	**Heavy Metals (HMs)** (e.g., , ,)	**Organic Micropollutants** (e.g., Pesticides, PPCPs)
Primary Mechanism	**Immobilization & Transformation:** Metals are physically/chemically trapped or altered in valence.	**Biodegradation & Mineralization:** Complex molecules are broken down into simpler products.
Biotic Pathway	**Biosorption:** Binding to EPS functional groups; **Biomineralization** (e.g., forming or sulfides).	**Metabolic/Cometabolic degradation:** Enzymatic cleavage of aromatic rings or functional groups.
Abiotic Pathway	**Ion Exchange & Precipitation:** Adsorption onto reactive media (e.g., ZVI, Zeolites, Biochar).	**Adsorption & Photolysis:** Hydrophobic partitioning into media pores; surface-mediated reactions.
Role of Biofilm	**Protective Barrier:** EPS sequesters HMs to protect the inner microbial community from toxicity.	**Bioreactor:** Biofilm acts as a concentrated enzymatic zone for active catabolism.
Response to Stress	**Upregulation of EPS:** High metal stress increases matrix density, enhancing the "sponge effect."	**Metabolic Adaptation:** Horizontal gene transfer and shifts in consortia toward resistant degraders.
Final Fate	**Retention:** Accumulated within the barrier (requires eventual media replacement or recovery).	**Elimination:** Ideally converted to , , and biomass (mineralization).
AI/Modeling Target	**Saturation/Breakthrough:** Predicting the "sorption capacity" and exhaustion of the media.	**Degradation Kinetics:** Modeling half-lives () and predicting transformation products ().

9. Conclusions

The reviewed research reflects a definitive shift from purely chemical, static treatments—such as traditional Zero-Valent Iron (ZVI) barriers—to integrated Permeable Reactive Bio-Barriers (PRBBs) that leverage complex microbial activity. PRBBs have undergone a remarkable transformation from their origins as passive geochemical filters to their current status as dynamic, adaptive bioreactors uniquely suited to the challenges of diffuse agricultural pollution.

The fundamental strength of the PRBB lies in its microbial plasticity. This inherent ability of biofilm communities to alter their structure and metabolism enables the system to achieve functional resilience to the variable hydraulic and chemical loads characteristic of agricultural landscapes. A critical dimension of this resilience is the impact of heavy metals (HMs), which often coexist with nutrients and pesticides in runoff. Far from being simple inhibitors, HMs act as structural and functional modulators:

Structural Shielding of biofilms is affected by HMs: Sub-inhibitory concentrations of some metals (Pb, Ni, Cd) trigger the up-regulation of Extracellular Polymeric Substances (EPS). This matrix acts as a protective barrier, sequestering metals and creating dense architectural zones that protect sensitive pesticide-degrading microbes.

The microbial community forming the biofilm undergoes transient functional changes: while high metal pulses can temporarily inhibit enzymatic pathways (e.g., denitrification), the selective pressure of HMs often promotes the growth of “hardened” microbial consortia. These metallotolerant communities frequently exhibit enhanced capacity to degrade complex organic micropollutants.

While originally established for nitrate removal, PRBB research is rapidly advancing to treat complex contaminant mixtures—including pesticides, fungicides, and pharmaceuticals—through hybrid designs. These systems utilize a “treatment train” approach, where abiotic media (like biochar or slag) buffer extreme metal toxicity to protect the biological engine.

The nascent integration of artificial intelligence and smart sensing promises a future in which these systems are not only resilient but also predictive. By monitoring real-time shifts in biofilm health and metal loading, “smart” PRBBs can autonomously adapt to maximize lifespan and efficiency.

Finally, challenges in longevity, clogging, and large-scale field validation remain, defining a clear agenda for future research in materials science, microbial ecology, and hydraulic engineering. As part of a diversified portfolio of management strategies that complements improved upstream practices and other Nature-Based Solutions (NBS), PRBBs offer a targeted, compact, and sustainable engineering solution. By strategically deploying these living filters at critical nodes in the agricultural watershed, the gap between productive agriculture and the preservation of healthy aquatic environments can be bridged.

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