

Partitioning of Pesticide-Related Residues Between Dissolved and Particulate Phases in River Water

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Abstract

The environmental behaviour of pesticides in river systems is strongly influenced by their partitioning between dissolved water and suspended particulate matter (SPM). While regulatory monitoring programs primarily target dissolved-phase concentrations of pesticide active ingredients, increasing evidence indicates that a substantial fraction of pesticide-related residues—including parent compounds, transformation products, and formulation-derived additives—preferentially associate with particulate phases. This review synthesizes recent advances in understanding the mechanisms governing phase partitioning of pesticide-related residues in river water. Emphasis is placed on physicochemical drivers, hydrological controls, analytical strategies—particularly GC–MS-based non-target screening—and the role of SPM as both a transport vector and environmental reservoir. The implications of phase partitioning for monitoring design, exposure assessment, and ecological risk evaluation are critically discussed. The review highlights the need for integrated dissolved–particulate monitoring frameworks to accurately characterize pesticide contamination in riverine environments. The implications of phase partitioning for environmental monitoring, exposure assessment, and risk evaluation are discussed, highlighting the need for integrated water–SPM monitoring strategies.

Keywords : Pesticide residues, suspended particulate matter, partitioning, river water, environmental fate

1. Introduction

Pesticides remain indispensable tools in modern agriculture, yet their widespread use has led to persistent concerns regarding contamination of surface water systems. Rivers draining agricultural catchments frequently receive pesticide inputs through runoff, erosion, spray drift, and irrigation return flows. Traditionally, assessments of pesticide pollution in river water have relied almost exclusively on measurements of dissolved-phase concentrations of active ingredients. While this approach has provided valuable regulatory benchmarks, it fails to capture the full environmental complexity associated with pesticide use. Pesticides are applied as commercial formulations, which consist not only of active substances but also of solvents, surfactants, stabilizers, emulsifiers, and other auxiliary compounds. These formulation-derived components, together with transformation products formed during environmental degradation, are collectively referred to in this review as pesticide-related residues. Increasing evidence indicates that many of these residues exhibit environmental behaviours distinct from those of the parent active ingredients, particularly with respect to their interaction with suspended particulate matter (SPM) (Mesnage et al., 2021).

Suspended particulate matter is a dynamic and heterogeneous component of river systems, comprising mineral particles, organic matter, and biological debris. It plays a central role in controlling the transport, persistence, and bioavailability of hydrophobic organic contaminants. Numerous field studies have demonstrated that pesticide-related residues are often preferentially associated with particulate phases, leading to underestimation of total pesticide loads when monitoring is restricted to dissolved water samples (Zhang et al., 2023).

Advances in analytical techniques have further revealed the presence of complex mixtures of pesticide-related residues in riverine SPM. These findings challenge the long-standing assumption that non-detectable pesticide concentrations in water necessarily indicate low agrochemical pressure. Instead, they point to a more nuanced scenario in which residues persist and are transported primarily in particulate-bound forms (Ferrante et al., 2022).

This review discusses the partitioning of pesticide-related residues between dissolved and particulate phases in river water on the basis of recent literature. In this first part, emphasis is placed on the conceptual framework and physicochemical mechanisms governing phase distribution. Subsequent parts address hydrological drivers, ecological implications, and regulatory perspectives.

2. Dissolved–Particulate Partitioning

2.1 Environmental phases

In river systems, pesticide-related residues can be distributed among several operationally defined phases: (i) the truly dissolved phase, (ii) suspended particulate matter, (iii) colloidal material, and (iv) bed sediments. Environmental monitoring studies typically separate dissolved and particulate phases through filtration, often using pore sizes between 0.45 and 1.0 μm . While such separation is operational rather than absolute, it provides a practical framework for assessing phase-specific contaminant distributions (Li et al., 2023).

Partitioning between dissolved and particulate phases is governed by a combination of equilibrium sorption processes and kinetic factors. Unlike closed laboratory systems, river environments are highly dynamic, with continuous inputs, transport, deposition, and resuspension of particles. Consequently, partitioning may not reach equilibrium, particularly during high-flow events or episodic pesticide applications (Tang et al., 2021).

2.2 Suspended particulate matter as a transport vector

SPM acts not merely as a passive sink but as an active transport vector for pesticide-related residues. Particle-bound contaminants can be conveyed over long distances, enabling downstream propagation of agricultural signals far beyond the point of application. During periods of reduced flow, SPM may settle, transferring residues to sediments, which can later serve as secondary sources during resuspension events (Zhang et al., 2023). This dynamic behavior has important implications for exposure assessment. While dissolved-phase concentrations may fluctuate rapidly due to dilution and degradation, particulate-associated residues often exhibit greater temporal persistence, contributing to chronic exposure of benthic organisms and sediment-associated food webs (Brack et al., 2019).

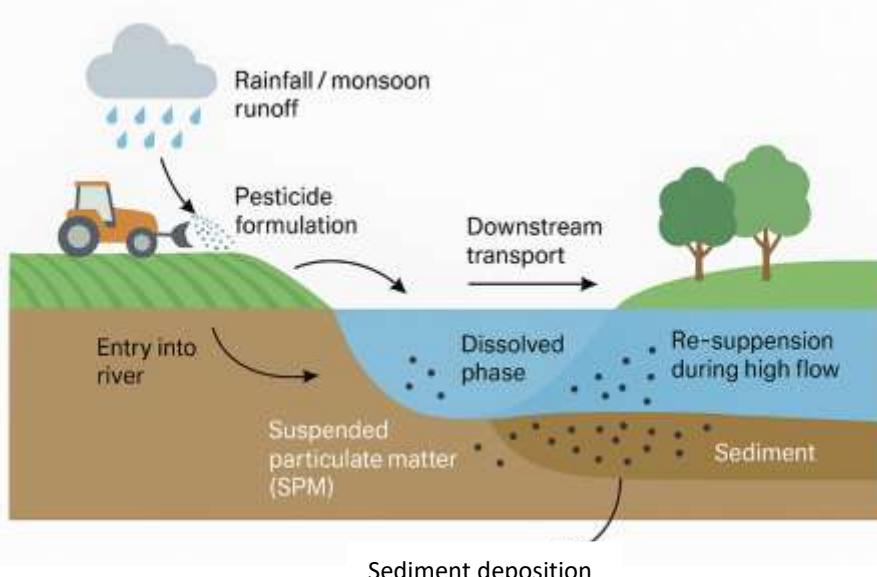


Fig 1. Fate of pesticides

3. Physicochemical Drivers of Partitioning

3.1 Hydrophobicity and octanol–water partitioning

Hydrophobicity, commonly expressed as the octanol–water partition coefficient ($\log K_{ow}$), is one of the most important determinants of sorption behavior. Compounds with higher $\log K_{ow}$ values tend to associate more strongly with organic matter and particulate phases. Many pesticide active ingredients fall within moderate to high $\log K_{ow}$ ranges, while formulation components such as aromatic solvents, long-chain aliphatics, and antioxidants often exhibit even higher hydrophobicity (Pérez et al., 2021). Sorption behavior in natural systems is influenced by molecular structure, aromaticity, and functional groups, as well as by interactions with heterogeneous particle surfaces. Consequently, compounds with similar $\log K_{ow}$ values may display markedly different partitioning behaviors in field conditions.

3.2 Role of molecular structure and functional groups

Molecular size and structure exert additional control over partitioning. Larger molecules with planar or aromatic structures generally exhibit stronger sorption to organic-rich particles due to π – π interactions and van der Waals forces. Functional groups such as hydroxyl, nitro, or amine moieties can either enhance or reduce sorption depending on their influence on polarity and hydrogen bonding (Maldonado-Reina et al., 2022). Heterocyclic compounds, which are increasingly reported in non-target GC–MS studies of surface waters, often exhibit intermediate behavior. These compounds may remain partially dissolved while still associating with finer particulate fractions, complicating simple dissolved–particulate classification.

3.3. Influence of Particle Characteristics

Organic carbon content

The organic carbon content of SPM is a critical determinant of sorptive capacity. Numerous studies have demonstrated strong correlations between particulate organic carbon and concentrations of hydrophobic organic contaminants. Organic-rich particles provide sorption sites that stabilize pesticide-related residues, reducing their susceptibility to rapid degradation or volatilization (Zhang et al., 2023).

Seasonal variations in organic carbon content—driven by primary productivity, leaf litter inputs, and agricultural runoff—can therefore alter partitioning patterns. This effect is particularly pronounced in monsoon-influenced river systems, where large pulses of organic-rich material are transported during high-flow events (Chakraborty et al., 2022).

Table 1 Octanol–water partition coefficient ($\log K_{ow}$) ranges of major pesticide classes and implications for environmental partitioning

Pesticide class	Typical $\log K_{ow}$ range	Dominant environmental phase	Partitioning implication
Organochlorine insecticides	3.5 – 6.5	Suspended particulate matter & sediments	Strong sorption to organic-rich particles; long-term persistence
Organophosphate insecticides	2.0 – 5.0	Dissolved + particulate (compound-dependent)	Moderate to strong particle association; event-driven transport
Carbamate insecticides	1.5 – 3.0	Predominantly dissolved	Higher mobility; short-term water exposure
Pyrethroid insecticides	4.0 – 7.0	Strongly particulate-bound	High affinity for SPM; low dissolved concentrations
Triazine herbicides	2.0 – 3.5	Mostly dissolved	Moderate mobility; detected mainly in water phase
Phenoxy acid herbicides	2.0 – 3.0	Dissolved	High water solubility; limited particle sorption
Chloroacetanilide herbicides	2.5 – 4.0	Dissolved + particulate	Transitional behavior; influenced by SPM organic carbon
Neonicotinoid insecticides	0.5 – 1.5	Dissolved	Low sorption; high leaching and runoff potential
Azole fungicides	3.0 – 4.5	Dissolved + particulate	Moderate hydrophobicity; sorption increases with organic matter
Strobilurin fungicides	2.5 – 4.0	Mixed	Partitioning sensitive to formulation and SPM
Urea herbicides	2.5 – 3.5	Mixed	Moderate particle association; sediment interaction possible
Sulfonylurea herbicides	0.0 – 2.0	Dissolved	Very high mobility; minimal sorption

3.4 Particle size and mineral composition

Particle size distribution also plays an important role. Fine-grained particles and colloids offer larger surface areas relative to mass, enhancing sorption efficiency. Clay minerals, iron oxides, and organic coatings further influence sorptive interactions. Fine particles tend to remain suspended longer, facilitating long-range transport of associated pesticide-related residues (Li et al., 2023).

3.5. Influence of Formulation Chemistry

Role of surfactants and solvents

Formulation-derived surfactants and solvents can significantly modify partitioning behaviour. Surfactants may increase the apparent solubility of hydrophobic pesticide actives, promoting their presence in the dissolved phase and facilitating transport. Conversely, hydrophobic solvents and carriers are often detected predominantly in particulate matter, reflecting their strong affinity for organic phases (Kalyabina et al., 2021).

These interactions help explain why formulation residues are frequently detected in SPM even when parent pesticide actives are not. GC–MS non-target screening studies increasingly reveal such compounds as dominant features in particulate extracts, underscoring their environmental relevance (Ferrante et al., 2022).

3.6 Implications for interpreting monitoring data

The presence of formulation residues complicates interpretation of pesticide monitoring results. Dissolved-phase non-detects of active ingredients may coexist with substantial particulate-bound contamination, leading to false assumptions of low environmental impact. Recognizing formulation chemistry as a driver of partitioning is therefore essential for accurate interpretation of field data.

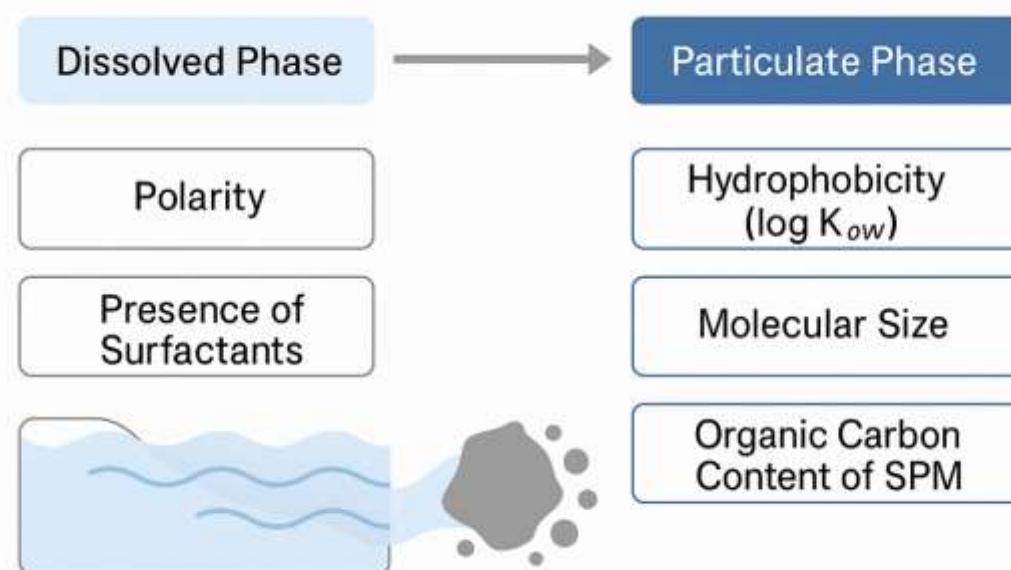
3.7 Hydrological Controls on Partitioning of Pesticide-Related Residues

Role of river hydrodynamics

Hydrological conditions exert a dominant influence on the partitioning of pesticide-related residues between dissolved and particulate phases in river systems. Flow velocity, discharge variability, and water residence time collectively control dilution, transport, and particle dynamics. During base-flow conditions, dissolved-phase concentrations of pesticide residues may reflect relatively steady-state inputs and degradation processes. In contrast, high-flow events introduce non-equilibrium conditions in which large quantities of particulate-bound residues are mobilized and transported downstream (Oldenkamp et al., 2020). Hydrodynamic forcing can therefore decouple dissolved and particulate concentrations. While dissolved-phase pesticide levels may decline rapidly during high discharge due to dilution, particulate-associated residues may increase substantially due to enhanced erosion and SPM mobilization.

3.8 Rainfall- and monsoon-driven systems

In monsoon-influenced regions, hydrological variability is particularly pronounced. Intense rainfall events generate rapid surface runoff, transporting both dissolved contaminants and soil-bound residues into river systems. Several studies have shown that post-monsoon river samples exhibit markedly higher suspended particulate loads and more complex chemical signatures compared to pre-monsoon conditions (Giri et al., 2021). Importantly, dilution during monsoon flows often leads to reduced concentrations of pesticide active ingredients in the dissolved phase. Observations suggest that monsoon hydrology preferentially enhances the transport of particulate-bound residues, reinforcing the importance of SPM-inclusive monitoring strategies (Kumar et al., 2022).



Composition and sources of SPM

Suspended particulate matter is a heterogeneous mixture derived from multiple sources, including soil erosion, bank collapse, resuspension of sediments, phytoplankton biomass, and organic detritus. The relative contribution of these sources varies spatially and temporally, influencing the chemical composition and sorptive properties of SPM (Rügner et al., 2020).

Agricultural catchments often generate SPM enriched in organic matter and fine mineral particles, providing favorable conditions for sorption of hydrophobic pesticide-related residues. In contrast, SPM dominated by coarse mineral particles may exhibit lower sorptive capacity but still function as a transport medium over long distances.

Seasonal variability in SPM characteristics

Seasonal changes in land use, vegetation cover, and hydrology lead to pronounced variability in SPM concentration and composition. During dry seasons, SPM loads are typically low, and particulate-bound residues may accumulate in sediments. During wet seasons, increased erosion and runoff result in elevated SPM concentrations and remobilization of previously deposited contaminants (Giri et al., 2021). This seasonal cycling has important implications for contaminant fate. Particulate-associated pesticide-related residues may undergo repeated cycles of deposition and resuspension, prolonging their environmental residence time and expanding their spatial footprint.

Interaction between SPM and dissolved organic matter

Dissolved organic matter (DOM) can act as a bridge between dissolved and particulate phases. Pesticide-related residues may associate with DOM, forming colloidal complexes that behave differently from truly dissolved or particulate-bound compounds. These interactions complicate operational definitions of phase partitioning and can influence apparent distribution coefficients (Oldenkamp et al., 2020).

4. Ecotoxicological Implications of Dissolved and Particulate-Bound Pesticide-Related Residues

The partitioning of pesticide-related residues between dissolved and particulate phases fundamentally alters exposure pathways for aquatic organisms. Dissolved residues primarily affect pelagic organisms such as phytoplankton, zooplankton, and fish through direct uptake across biological membranes. In contrast, particulate-bound residues disproportionately impact benthic organisms, including macroinvertebrates, sediment-dwelling larvae, and benthic-feeding fish species (Brack et al., 2022). Because suspended particulate matter (SPM) and sediments serve as long-term reservoirs for hydrophobic contaminants, benthic organisms may experience chronic exposure, even when dissolved-phase concentrations fluctuate or fall below detection limits. This decoupling between dissolved concentrations and biological exposure represents a critical limitation of water-only monitoring approaches.

Particle association does not necessarily imply reduced ecological risk. While sorption to SPM may temporarily reduce immediate bioavailability, several studies have demonstrated that particulate-bound contaminants remain biologically accessible through ingestion, desorption in gut conditions, or sediment–water exchange processes (van der Oost et al., 2020). Changes in pH, redox conditions, and microbial activity within sediments can further influence desorption and transformation, leading to delayed or secondary exposure. Consequently, particulate-bound pesticide-related residues may exert long-term ecological effects that are not captured by short-term dissolved-phase measurements.

5. Regulatory and Policy Challenges

Most regulatory frameworks for pesticide risk assessment are based on dissolved-phase concentrations of active ingredients, with limited consideration of particulate-bound residues or formulation components. Environmental quality standards (EQS) are rarely available for formulation residues, and sediment guidelines for pesticides remain sparse or absent in many jurisdictions (Brack et al., 2022).

Additionally, formulation composition is often protected as confidential business information, limiting transparency and hindering independent environmental assessment. This lack of disclosure poses significant challenges for both monitoring and risk evaluation. The exclusion of SPM and sediments from routine monitoring programs creates a disconnect between measured concentrations and actual ecological exposure. As demonstrated throughout this review, particulate-bound residues may dominate total pesticide loads, particularly in rivers influenced by intensive agriculture and seasonal hydrology. Bridging this gap requires regulatory recognition of particulate-associated contamination and the development of guidance frameworks that integrate dissolved, particulate, and sediment phases.

6. Conclusion

This review demonstrates that partitioning between dissolved and particulate phases is a defining feature of pesticide-related residue behaviour in river systems. Suspended particulate matter plays a central role in controlling transport, persistence, and ecological exposure, particularly for hydrophobic and formulation-derived compounds. Reliance on dissolved-phase monitoring alone can substantially underestimate total pesticide loads and associated ecological risks. Integrating SPM analysis, non-target GC-MS screening, and mixture-aware assessment frameworks represents a critical step toward more realistic and protective monitoring strategies.

By adopting an integrated dissolved–particulate perspective, future research and regulatory programs can move beyond simplistic interpretations of pesticide contamination and better reflect the complexity of real-world exposure scenarios in riverine environments.

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