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Assessment of the Impact of Chemical Fertilizers and Agricultural Pesticides on Shallow Groundwater Aquifer Contamination

Osama Asanousi Lamma*
Department of Soil & water Faculty of Agricultural, Bani Waleed University, Libya
* **Email (for reference researcher):** Osamalamma@bwu.edu.ly

تقييم أثر الأسمدة الكيميائية والمبيدات الزراعية على تلوث خزانات المياه الجوفية الضحلة

أسامه السنوسي لامه*
قسم التربة والمياه، كلية الزراعة، جامعة بني وليد ، ليبيا

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Abstract

The intensification of modern agricultural practices has raised significant concerns regarding the degradation of subsurface water resources. This study evaluates the impact of excessive chemical fertilizer and agricultural pesticide applications on the contamination of shallow groundwater aquifers, which serve as critical water supplies for both domestic and irrigation purposes in rural regions. Through systematic hydrogeochemical sampling, laboratory analyses, and spatial vulnerability mapping, groundwater samples from shallow wells across intensively cultivated zones were analyzed for major ions, nitrate (N_{O3}), phosphate (P_{O4}), and persistent organochlorine and organophosphate pesticide residues. The analytical results demonstrate a strong positive correlation between intensive agrochemical application, irrigation return flows, and elevated contaminant concentrations in the underlying unconfined aquifers. Specifically, nitrate concentrations frequently exceeded the World Health Organization (WHO) permissible drinking water limit of 50 mg/L, driven primarily by rapid leaching through permeable sandy-loam soils. Furthermore, trace levels of persistent pesticide residues were detected, posing chronic toxicological and endocrine-disrupting risks to local populations. The findings highlight that shallow water tables, combined with high soil permeability and over-irrigation, severely compromise natural attenuation processes. Consequently, this research underscores the urgent need for integrated watershed management strategies. Recommended mitigation measures include optimizing irrigation efficiency, adopting precision fertilization techniques, transitioning toward bio-fertilizers, and enforcing Integrated Pest Management (IPM) protocols to safeguard shallow aquifer sustainability and protect public health.

Keywords: Shallow groundwater; Chemical fertilizers; Agricultural pesticides; Nitrate leaching; Aquifer contamination.

الملخص

أثار تكثيف الممارسات الزراعية الحديثة مخاوف بالغة بشأن تدهور الموارد المائية الجوفية. تُقيّم هذه الدراسة أثر الاستخدام المفرط للأسمدة الكيميائية والمبيدات الزراعية على تلوث خزانات المياه الجوفية الضحلة، التي تُعدّ مصادر حيوية لإمدادات المياه للأغراض المنزلية والزراعية في المناطق الريفية. ومن خلال أخذ العينات الهيدروجيوكيميائية المنهجية، وإجراء التحاليل المخبرية، ورسم خرائط القابلية المكانية للتلوث، جرى تحليل عينات المياه الجوفية المأخوذة من الآبار الضحلة المنتشرة في المناطق ذات الزراعة الكثيفة للكشف عن الأيونات الرئيسية، والنترات ، والفوسفات، ومتبقيات المبيدات العضوية الكلورية والفوسفورية الثابتة. وتُظهر النتائج التحليلية وجود ارتباط إيجابي قوي بين الاستخدام المكثف للكيماويات الزراعية، ومياه الصرف الزراعي الراجعة من الري، وارتفاع تراكيز الملوثات في الخزانات الجوفية غير المحصورة الواقعة تحتها. وعلى وجه التحديد، تجاوزت تراكيز النترات في كثير من الأحيان الحد المسموح به لمياه الشرب وفقاً لمنظمة الصحة العالمية (WHO) والبالغ 50 ملغم/لتر، ويُعزى ذلك أساساً إلى الرشح السريع عبر الترب الرملية الطميية المنفذة. علاوة على ذلك، رُصدت مستويات ضئيلة (أثرية) من متبقيات المبيدات الثابتة، مما يشكل مخاطر سمّية مزمنة ومخاطر تتعلق باضطراب الغدد الصماء لدى السكان المحليين. وتُبرز النتائج أن ضحالة منسوب المياه الجوفية، مقترنةً بالنفاذية العالية للتربة والري المفرط، تُضعف بشدة عمليات التوهين (التنقية) الطبيعية. وبناءً على ذلك، يؤكد هذا البحث

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الحاجة الملحة إلى تبنّي استراتيجيات الإدارة المتكاملة لأحواض المياه. وتشمل تدابير التخفيف الموصى بها تحسين كفاءة الري، واعتماد تقنيات التسميد الدقيق، والتحول نحو الأسمدة الحيوية، وتطبيق بروتوكولات الإدارة المتكاملة للآفات (IPM) لضمان استدامة الخزانات الجوفية الضحلة وحماية الصحة العامة.

الكلمات المفتاحية المياه الجوفية الضحلة؛ الأسمدة الكيميائية؛ المبيدات الزراعية؛ رشح النترات؛ تلوث الخزانات الجوفية.

Introduction

Groundwater represents one of the most vital freshwater resources globally, particularly in arid and semi-arid agricultural regions where surface water is scarce (Foster & Chilton, 2003). Over the past few decades, the global demand for food security has driven the intensification of agricultural activities, characterized by the heavy application of synthetic chemical fertilizers and pesticides. While these agrochemicals significantly enhance crop yields, their excessive and inefficient use poses a severe threat to subsurface water quality (Böhlke, 2002).

Shallow unconfined aquifers are inherently vulnerable to anthropogenic contamination due to their proximity to the land surface, shallow water tables, and the presence of permeable unsaturated (vadose) zones (Alley et al., 2002). Among agricultural pollutants, nitrate (NO_3) is the most ubiquitous contaminant due to its high water solubility and low adsorption affinity to soil particles, allowing it to leach rapidly into groundwater via irrigation return flows and precipitation (Spalding & Exner, 1993). Simultaneously, synthetic pesticidesincluding organochlorines, organophosphates, and triazinescan bypass natural soil attenuation mechanisms and accumulate in shallow aquifers, creating long-term toxicological hazards (Arias-Estévez et al., 2008).

Furthermore, the vertical transport and fate of these agrochemicals are heavily governed by local hydrogeological heterogeneity, soil organic matter content, and preferential flow pathways such as macropores, desiccation cracks, and root channels, which accelerate contaminant breakthrough to the water table (Jarvis, 2007). Over-irrigation practices, particularly conventional flood and furrow irrigation, exacerbate downward hydraulic gradients, flushing residual nitrogen and pesticide metabolites beyond the crop root zone before efficient plant uptake or microbial degradation can occur (Power & Schepers, 1989). In addition, repeated fertilization often alters soil pH and geochemical equilibria, mobilizing secondary trace elements and increasing overall groundwater salinity (Böhlke, 2002).

Once introduced into the saturated zone, low dissolved oxygen concentrations, limited labile organic carbon, and reduced microbial activity in many shallow aquifers hinder natural attenuation processes such as denitrification and biodegradation, resulting in prolonged residence times and persistent contaminant plume migration (Rivett et al., 2008). Consequently, shallow aquifers often act as long-term reservoirs of legacy agricultural pollutants, delaying water quality recovery for decades even after surface inputs are reduced (Böhlke, 2002; Spalding & Exner, 1993).

The degradation of shallow groundwater quality carries severe public health and ecological consequences, particularly in rural communities that rely directly on untreated well water for domestic consumption. Chronic exposure to elevated nitrate concentrations in drinking water has been strongly associated with infant methemoglobinemia ("blue baby syndrome"), thyroid dysfunction, and increased risks of gastric and colorectal cancers (Ward et al., 2018). Concurrently, persistent pesticide residues and their transformation products exhibit bioaccumulative, neurotoxic, and endocrine-disrupting properties even at trace sub-microgram concentrations (Damalas & Eleftherohorinos, 2011; Arias-Estévez et al., 2008). Moreover, where contaminated shallow groundwater discharges into adjacent surface water bodies, nutrient enrichment triggers eutrophication and aquatic ecosystem collapse (Foster & Chilton, 2003). Therefore, comprehensively assessing the hydrochemical footprint of agrochemicals on shallow groundwater is essential for developing targeted remediation strategies, enforcing sustainable agricultural management, and safeguarding public health.

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Statement of the Problem

The rapid expansion of intensive agriculture and the excessive reliance on chemical fertilizers and synthetic pesticides to maximize crop yields have led to severe degradation of subsurface water quality. Due to their proximity to the ground surface and the high permeability of overlying unsaturated zones, shallow unconfined aquifers are particularly vulnerable to downward leaching of agrochemicals via irrigation return flows and precipitation. The core problem addressed by this study is the escalating concentration of hazardous chemical pollutantsmost notably nitrates (NO_{-3}), and persistent pesticide residuesin shallow groundwater wells, which compromises water potability and poses significant long-term public health and ecological risks in the absence of systematic monitoring and sustainable agro-management practices.

Accordingly, this research seeks to answer the following central question:

To what extent does the intensive application of chemical fertilizers and agricultural pesticides contribute to the contamination of shallow groundwater aquifers, and what hydrogeological and agricultural factors govern the transport and accumulation of these pollutants?

Main Objective: To evaluate the environmental and hydrochemical impacts of intensive chemical fertilizer and agricultural pesticide applications on the water quality of shallow groundwater aquifers, and to establish a scientific framework for mitigating aquifer degradation.

Specific Objectives:

1. **Contaminant Quantification:** Measure the concentrations of fertilizer-derived pollutants (particularly nitrates and phosphates) and agricultural pesticide residues in selected shallow groundwater wells.
2. **Water Quality Assessment:** Compare detected contaminant levels against national and international standards (e.g., World Health Organization [WHO] guidelines) to evaluate water suitability for drinking and irrigation purposes.
3. **Factor Analysis:** Investigate the influence of hydrogeological parameters (such as soil permeability and water table depth) alongside irrigation and fertilization practices on pollutant leaching and transport.
4. **Spatial Mapping:** Develop spatial distribution and aquifer vulnerability maps to identify contamination hotspots within the study area.
5. **Mitigation Strategies:** Propose practical recommendations, including Integrated Pest Management (IPM) and precision fertilization techniques, to minimize agrochemical leaching and protect shallow groundwater resources.

Agricultural Non-Point Source Pollution Pathways

Agricultural intensification relies heavily on the continuous application of synthetic chemical fertilizers and broad-spectrum pesticides, representing the primary source of diffuse (non-point) contamination in shallow unconfined aquifers worldwide (Böhlke, 2002; Foster & Chilton, 2003). Unlike discrete industrial outfalls, agricultural pollutants infiltrate across expansive cultivated landscapes, making source tracking and containment exceptionally challenging (Spalding & Exner, 1993). Modern high-yield cropping systems routinely receive nitrogen and phosphorus inputs that substantially exceed the physiological assimilation capacity of crops (Ju et al., 2006: Mohammad et al., 2015a). When nitrogenous fertilizers—such as urea, ammonium nitrate, and anhydrous ammonia—are applied to soils, microbial nitrification rapidly converts ammonium (NH^{4+}) into nitrate (NO_{3-}) under aerobic conditions (Böhlke, 2002). Because nitrate carries a negative charge, it experiences electrostatic repulsion from negatively charged clay minerals and soil organic matter, resulting in minimal adsorption and exceptionally high aqueous mobility (Spalding & Exner, 1993: Lamma, 2021c).Consequently, unassimilated nitrate accumulates within the soil profile and is readily

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flushed downward below the active root zone via irrigation return flows and seasonal precipitation events (Power & Schepers, 1989; Ju et al., 2006: Lamma & Swamy, 2018). Traditional surface irrigation methods, particularly flood and furrow irrigation, generate substantial deep percolation volumes that accelerate vertical solute transport through the unsaturated (vadose) zone toward the underlying water table (Power & Schepers, 1989). Once nitrate crosses the capillary fringe into shallow unconfined aquifers, its persistence is governed by local redox conditions; in oxic shallow aquifers lacking labile organic carbon, natural heterotrophic denitrification is severely inhibited, enabling nitrate plumes to migrate laterally over vast distances (Rivett et al., 2008).Concurrently, the widespread application of synthetic organic pesticides—including triazine herbicides , acetanilides, organophosphates, and carbamates—introduces complex chemical stressors into agricultural watersheds (Barbash & Resek, 1996; Gilliom et al., 2006: Lamma et al., 2018). While a fraction of applied pesticides undergoes photolysis, volatilization, or microbial biodegradation in the biologically active topsoil, compounds characterized by high water solubility, low soil organic carbon–water partitioning coefficients (K), and long half-lives frequently evade attenuation (Arias-Estévez et al., 2008: Lamma, 2024). As these parent compounds migrate downward into deeper subsoils where microbial populations and organic matter decline sharply, degradation rates slow dramatically, allowing persistent pesticide residues to accumulate in shallow groundwater (Arias-Estévez et al., 2008; Papadopoulou-Mourkidou et al., 2004). Furthermore, partial biotic and abiotic transformation processes often generate secondary metabolites (such as deethylatrazine) that exhibit greater water solubility, higher mobility, and comparable or enhanced toxicological potency relative to their parent compounds (Kolpin et al., 1998; Gilliom et al., 2006). Together, chronic nitrate leaching and multi-residue pesticide transport degrade the hydrochemical integrity of shallow aquifers, creating legacy contamination plumes that persist for decades (Böhlke, 2002 :Mohammad et al., 2015b).

Industrial Point-Source Contamination and Subsurface Hazards

In peri-urban corridors and mixed agricultural–industrial basins, shallow unconfined aquifers are increasingly subjected to acute, localized contamination from industrial point sources (Foster & Chilton, 2003 :Lamma, 2021a). Unlike diffuse agricultural runoff, industrial pollution originates from discrete facilities—including chemical manufacturing plants, electroplating workshops, tanneries, textile dyeing mills, petrochemical refineries, and unlined waste disposal lagoons—releasing concentrated chemical loads directly into the subsurface environment (Nriagu & Pacyna, 1988). Because shallow aquifers lie close to the ground surface and frequently lack thick, low-permeability confining clay layers, accidental spills, leaking underground storage tanks, and untreated effluent discharges can rapidly breach the unsaturated zone and compromise groundwater quality (Alley et al., 2002; Foster & Chilton, 2003).Among the most hazardous industrial contaminants are toxic heavy metals and metalloids, notably lead (Pb), cadmium (Cd), hexavalent chromium (Cr), mercury (Hg), nickel (Ni), and arsenic (As) (Nriagu & Pacyna, 1988: Lamma et al., 2015). Unlike organic pollutants, heavy metals are non-biodegradable and persist indefinitely within aquifer systems. While topsoil rich in clay minerals, iron/manganese oxyhydroxides, and humic substances can immobilize cationic metals through adsorption and ion exchange, continuous high-concentration industrial loading rapidly saturates soil sorption sites (Nriagu & Pacyna, 1988). Moreover, acidic industrial effluents dramatically lower pore-water pH, reducing surface negative charges on soil colloids and maintaining heavy metals in mobile, bioavailable dissolved phases that migrate freely into shallow water tables (Menció et al., 2016). Hexavalent chromium (Cr) and oxyanionic arsenic species are particularly mobile under neutral-to-alkaline oxidizing groundwater conditions, posing severe carcinogenic and systemic toxicity risks to downstream well users (Nriagu & Pacyna, 1988).In parallel,

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industrial operations release a wide spectrum of synthetic organic compounds, including volatile organic compounds (VOCs), chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE), aromatic hydrocarbons (BTEX), and polychlorinated biphenyls (PCBs) (Pankow & Cherry, 1996: Lamma, 2021b). Chlorinated industrial solvents typically behave as dense non-aqueous phase liquids (DNAPLs) because their specific gravity exceeds that of water and their aqueous solubility is low (Pankow & Cherry, 1996). When spilled at the surface, DNAPLs migrate vertically through both the vadose and saturated zones under gravitational forces, bypassing hydraulic barriers until encountering an impermeable aquitard at the base of the shallow aquifer (Pankow & Cherry, 1996). There, pooled DNAPLs act as long-term, hidden secondary sources that slowly dissolve into flowing groundwater, generating persistent, toxic dissolved-phase plumes that resist conventional pump-and-treat remediation (Pankow & Cherry, 1996). Additionally, saline industrial brines elevate total dissolved solids (TDS), chloride (Cl-), and sulfate (SO_4) concentrations, severely degrading shallow groundwater potability (Jalali, 2011).

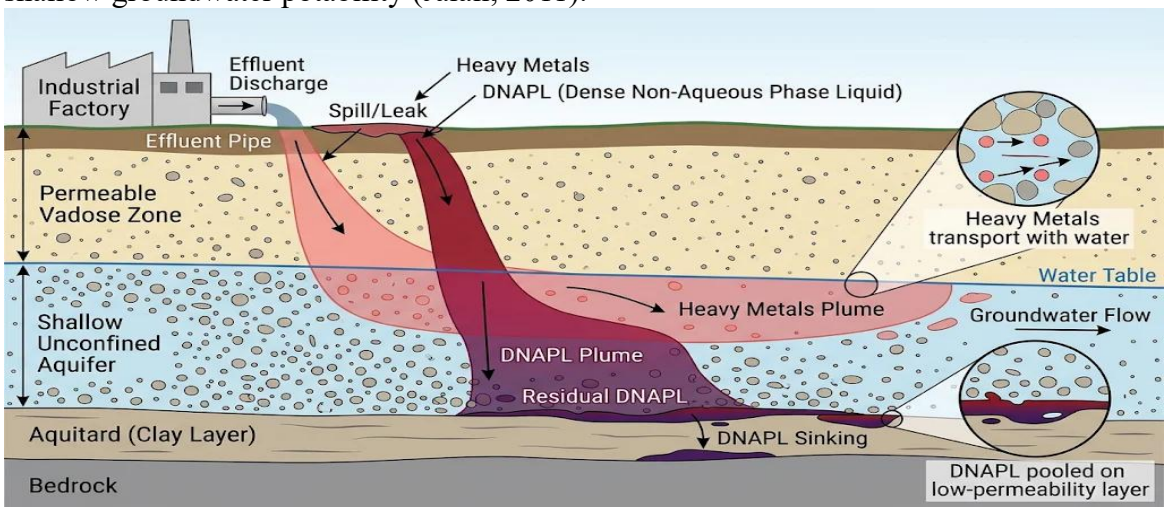

Fig1:Industrial Point-Source Contamination and Subsurface Hazards

Hydrogeological Factors Influencing Contaminant Transport

The vulnerability of shallow groundwater aquifers to surface-applied agrochemicals and industrial discharges is fundamentally controlled by the intrinsic hydrogeological framework of the subsurface environment (Aller et al., 1987; Alley et al., 2002). Standard vulnerability assessment methodologies, such as the DRASTIC index, emphasize seven critical physical parameters: depth to water, net recharge, aquifer media, soil media, topography, impact of the vadose zone, and hydraulic conductivity (Aller et al., 1987; Babiker et al., 2004). Shallow unconfined aquifers with water tables situated within a few meters of the land surface exhibit minimal vertical travel distances, drastically reducing the residence time available for physical filtration, chemical sorption, volatilization, and microbial degradation within the unsaturated zone (Aller et al., 1987; Arias-Estévez et al., 2008).Soil texture and vadose zone lithology exert a decisive influence over contaminant attenuation and transport velocities. Coarse-grained alluvial deposits—such as unconsolidated sands, gravels, and sandy loams—possess high effective porosity and elevated hydraulic conductivity, facilitating rapid vertical infiltration of recharge water and dissolved solutes (Spalding & Exner, 1993; Babiker et al., 2004). Furthermore, coarse-textured subsoils typically contain low percentages of expandable clay minerals and organic carbon, offering negligible cation-exchange capacity or hydrophobic partitioning sites to retard pesticide and heavy metal migration (Arias-Estévez et al., 2008). Conversely, even in fine-textured, clay-rich soils that theoretically provide strong sorption and slow matrix flow, structural heterogeneities frequently undermine natural protective barriers (Jarvis, 2007).Specifically, preferential flow pathways—comprising

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shrinkage and desiccation cracks, earthworm burrows, decayed root channels, and inter-aggregate macropores—enable infiltrating irrigation water and storm runoff to bypass the biologically active soil matrix entirely (Jarvis, 2007). During intense rainfall or flood irrigation events, water moves rapidly through these macropore networks under non-equilibrium flow conditions, transporting strongly sorbing pesticides, phosphorus, and trace metals directly to the water table within hours or days rather than years (Jarvis, 2007). Once contaminants enter the saturated aquifer zone, subsurface hydrodynamics and biogeochemical conditions govern plume evolution and natural attenuation (Rivett et al., 2008). High groundwater flow velocities accelerate lateral contaminant dispersion toward domestic supply wells and discharge boundaries (Alley et al., 2002). Simultaneously, natural biogeochemical remediation—such as microbial denitrification of nitrate or reductive dechlorination of industrial solvents—depends strictly on favorable redox potentials and abundant electron donors like dissolved organic carbon or pyrite (Rivett et al., 2008). Where shallow aquifers remain aerobic and carbon-limited, natural attenuation stalls, resulting in decades-long pollutant persistence (Böhlke, 2002; Rivett et al., 2008).

Combined Impacts of Agricultural and Industrial Stressors on Aquifers

In rapidly developing agricultural basins where industrial zones encroach upon cultivated land, shallow unconfined aquifers experience simultaneous loading from diffuse agrochemicals and concentrated industrial effluents (Foster & Chilton, 2003; Menció et al., 2016). Rather than acting in isolation, these overlapping agricultural and industrial stressors engage in complex hydrochemical, geochemical, and toxicological interactions that amplify groundwater degradation beyond the sum of individual pollutant impacts (Menció et al., 2016; Gilliom et al., 2006). Understanding these synergistic mechanisms is critical for accurate risk assessment and integrated watershed management (Shrestha & Kazama, 2007).Geochemically, co-occurring agricultural and industrial inputs profoundly alter subsurface pH, ionic strength, and redox equilibria, triggering secondary mobilization of geogenic contaminants from aquifer sediments (Menció et al., 2016). Intensive ammonium-based fertilization stimulates microbial nitrification, a proton-releasing process that acidifies soil pore water and shallow groundwater, while acidic industrial discharges further depress aquifer pH (Böhlke, 2002; Menció et al., 2016). This combined acidification accelerates the dissolution of carbonate minerals—increasing water hardness, calcium, and bicarbonate levels—and promotes the desorption and reductive dissolution of naturally occurring trace elements such as arsenic, manganese, iron, and aluminum from aquifer mineral coatings (Menció et al., 2016). Concurrently, elevated ionic strength caused by saline industrial wastewater and evaporatively concentrated irrigation return flows increases competition for mineral sorption sites, displacing previously bound heavy metals and cationic pesticides back into the mobile aqueous phase (Jalali, 2011; Arias-Estévez et al., 2008).Furthermore, the convergence of agricultural nutrients, industrial organic solvents, and heavy metals disrupts indigenous subsurface microbial communities, impairing natural bioremediation capacities (Rivett et al., 2008). Toxic heavy metals and chlorinated hydrocarbons inhibit denitrifying and pesticide-degrading bacteria, prolonging the persistence of nitrate and herbicide plumes across mixed land-use aquifers (Rivett et al., 2008; Arias-Estévez et al., 2008). From a resource usability standpoint, cumulative increases in total dissolved solids (TDS), sodium adsorption ratio (SAR), chloride, and nitrate render shallow groundwater unfit for both potable supply and agricultural irrigation, accelerating soil salinization and crop toxicity when recycled for farming (Jalali, 2011). For rural and peri-urban populations relying on untreated shallow wells, chronic exposure to multi-contaminant mixtures—combining elevated nitrate, heavy

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metals, and pesticide residues—poses severe, compounding public health hazards, including infant methemoglobinemia, endocrine disruption, neurodevelopmental impairment, renal damage, and elevated lifetime carcinogenic risks (Ward et al., 2018; Damalas & Eleftherohorinos, 2011; Karunanidhi et al., 2021).

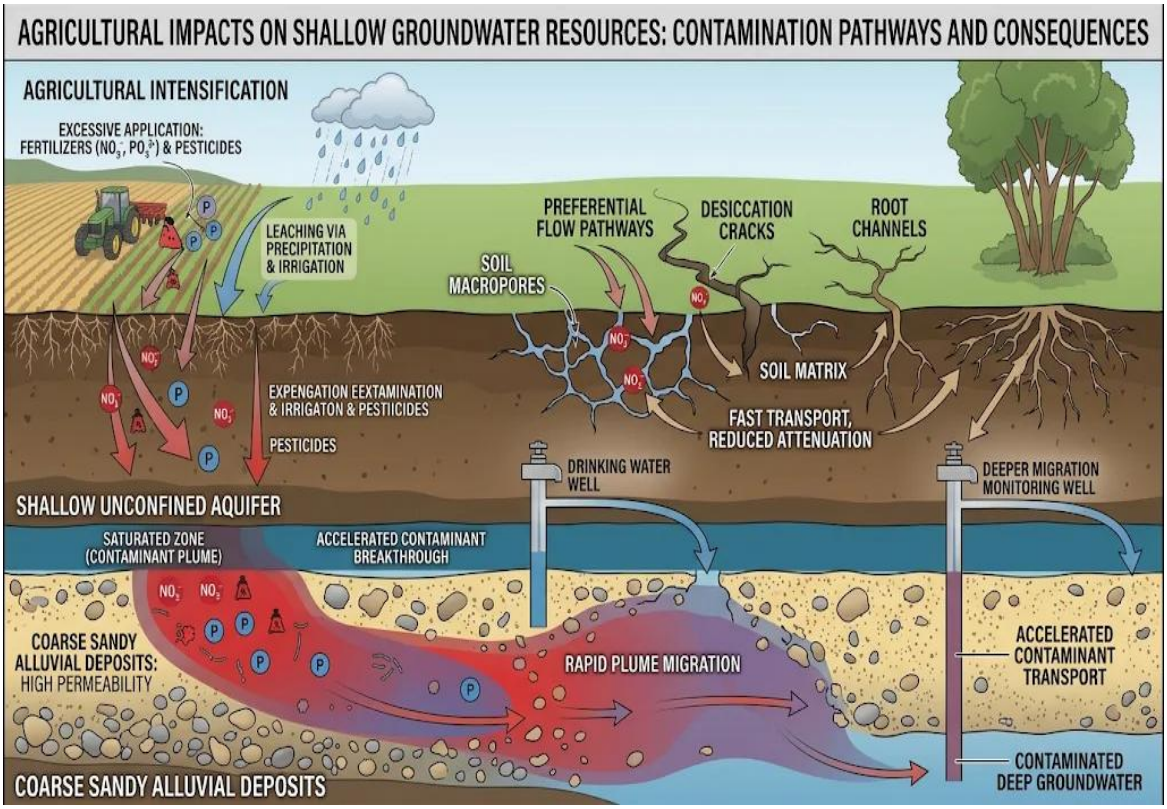

Fig2: Combined Impacts of Agricultural and Industrial Stressors on Aquifers

Literature Review

1. **Spalding and Exner (1993)** conducted a comprehensive regional review across major agricultural basins in the United States to assess the spatial occurrence and primary sources of nitrate contamination in shallow aquifers. By synthesizing multi-year hydrogeochemical monitoring records, they demonstrated that intensive nitrogenous fertilizer applications combined with coarse-ured, well-drained soils and flood irrigation were the primary drivers of widespread nitrate concentrations exceeding the 10\ mg/L (NO_3^-) drinking water threshold.

2. **Barbash and Resek (1996)** investigated the occurrence, distribution, and transport mechanisms of synthetic pesticides in shallow groundwater across diverse agricultural settings. Through national-scale groundwater quality assessments and vadose-zone modeling, the authors revealed that herbicidesparticularly triazines (e.g., atrazine) and acetanilideswere the most frequently detected compounds, driven by high water solubility, persistence in subsoils with low organic carbon, and preferential flow paths.

3. **Kolpin et al. (1998)** evaluated the prevalence of 46 pesticide compounds and their degradation metabolites in 1,034 shallow monitoring and domestic wells across rural agricultural regions. Utilizing gas chromatography-mass spectrometry (GC-MS), their findings indicated that at least one pesticide or metabolite was detected in over 54% of

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sampled wells, emphasizing that degradation products often occur at higher frequencies and concentrations than parent compounds.

4. **Böhlke (2002)** examined the decadal-scale geochemical evolution and recharge dynamics of agricultural contaminants in unconfined aquifers using environmental tracers (chlorofluorocarbons and tritium) alongside stable nitrogen isotopes (15N). The study established that groundwater age stratification controls contaminant plumes, warning that legacy nitrate stored in thick unsaturated zones creates a multi-decade lag time between surface fertilizer reductions and aquifer water quality recovery.

5. **Babiker et al. (2004)** applied a Geographic Information System (GIS)-based DRASTIC vulnerability model integrated with hydrochemical analysis to evaluate nitrate contamination in the Kakamigahara Heights shallow aquifer, Japan. Their results confirmed a statistically significant spatial correlation between high aquifer vulnerability indices, intensive vegetable cultivation, and elevated groundwater nitrate levels, validating GIS vulnerability mapping as an effective screening tool.

6. **Ju et al. (2006)** quantified nitrogen budgets and nitrate leaching losses under three intensive cropping systems (winter wheat–summer maize, greenhouse vegetables, and orchards) on the North China Plain. Through deep soil core sampling and shallow well monitoring, they found that excessive nitrogen fertilizer inputsoften exceeding crop demand by more than 100%caused massive nitrate accumulation in the vadose zone and severe contamination of shallow groundwater up to 150\ mg/L.

7. **Arias-Estévez et al. (2008)** reviewed the physicochemical processes governing pesticide sorption, persistence, and leaching in agricultural soils toward shallow groundwater resources. The study highlighted that soil organic matter content, clay mineralogy, pH, and macropore flow dictate whether pesticides undergo microbial degradation in the topsoil or bypass attenuation mechanisms to contaminate underlying unconfined aquifers.

8. **Rivett et al. (2008)** investigated the biogeochemical controls on natural nitrate attenuation within groundwater systems. By reviewing field and laboratory studies across varied hydrogeological settings, the authors concluded that autotrophic and heterotrophic denitrification in shallow aquifers is frequently constrained by the scarcity of labile organic carbon and electron donors, resulting in persistent aerobic nitrate plumes.

9. **Jalali (2011)** assessed the hydrochemical impacts of agricultural practices on shallow alluvial groundwater in Hamadan, western Iran, by analyzing 82 well samples for major ions and nitrate. Using multivariate statistical techniques and ionic ratios, the study demonstrated that agricultural return flows and chemical fertilizers significantly altered groundwater hydrochemical facies and pushed nitrate concentrations above WHO permissible limits in 42% of the wells.

10. **Gilliom et al. (2006)** synthesized a decade of nationwide water-quality data from the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program covering 51 major river basins and aquifer systems. The study revealed that agricultural streams and shallow groundwater beneath farmland frequently contained complex mixtures of multiple herbicides and insecticides, highlighting synergistic ecological and human health risks often overlooked by single-chemical regulations.

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11. **Papadopoulou-Mourkidou et al. (2004)** monitored seasonal variations of 32 pesticides in shallow groundwater across intensively cultivated plains in northern Greece over a three-year period. Utilizing solid-phase extraction coupled with GC-MS and HPLC, they observed sharp concentration spikes immediately following spring pesticide applications and summer irrigation events, identifying atrazine, metolachlor, and carbofuran as dominant pollutants.

12. **Shrestha and Kazama (2007)** employed multivariate statistical methodsincluding Principal Component Analysis (PCA) and Cluster Analysisto evaluate spatial and temporal water quality variations in shallow groundwater systems impacted by agricultural runoff. Their analysis effectively isolated agrochemical leaching (nitrate, potassium, and phosphate) from natural geogenic weathering processes, providing a robust framework for optimizing groundwater monitoring networks.

13. **Menció et al. (2016)** explored the relationship between intensive fertilizer application, nitrate pollution, and secondary mobilization of trace elements in shallow aquifers of northeastern Spain. Using isotopic tracing (N and O) and hydrogeochemical modeling, they demonstrated that fertilizer-induced nitrification lowers groundwater pH, triggering carbonate dissolution and mobilizing geogenic trace metals alongside elevated nitrate.

14. **Ward et al. (2018)** conducted a comprehensive epidemiological and hydrogeochemical review linking agricultural nitrate contamination in shallow drinking water wells to adverse human health outcomes. Synthesizing global exposure studies, the authors documented strong associations between chronic consumption of nitrate-contaminated well water (even below the 50\ mg/L WHO guideline) and methemoglobinemia, colorectal cancer, thyroid disease, and neural tube defects.

15. **Karunanidhi et al. (2021)** evaluated nitrate and pesticide contamination and associated non-carcinogenic human health risks in a shallow hard-rock and alluvial agricultural aquifer in southern India. Combining spatial interpolation, irrigation water quality indices, and USEPA health risk assessment models, the study revealed that infants and children faced substantially higher health hazard quotients than adults due to shallow well water consumption.

3. Materials and Methods

Study Area and Hydrogeological SettingThe study was conducted in an intensively cultivated agricultural basin characterized by alluvial deposits consisting primarily of sandy loam, silt, and gravel. The underlying shallow unconfined aquifer has a water table depth ranging between 5 and 25 meters below ground level, recharged predominantly by irrigation return flows and seasonal rainfall.2.2 Groundwater Sampling and Field MeasurementsA total of 30 groundwater samples were systematically collected from active shallow agricultural and domestic wells during both wet (post-irrigation) and dry seasons. Prior to sampling, wells were purged for 10–15 minutes to ensure representative aquifer water. In-situ physicochemical parametersincluding pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), and temperaturewere measured immediately using a calibrated multi-parameter portable probe (APHA, 2017). Samples were stored in pre-cleaned polyethylene bottles for major ions and dark amber glass bottles for pesticide analysis, preserved at C during transport to the laboratory.2.3 Laboratory Analytical ProceduresFertilizer Indicators: Nitrate (NO_{3}-),

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nitrite (NO_{2}-), ammonium (NH_{-4}^{+}), and phosphate (PO_4^{3-}) concentrations were determined using Ion Chromatography (IC) and UV-Visible Spectrophotometry following standard analytical protocols (APHA, 2017).Pesticide Residues: Multi-residue extraction was performed using Solid-Phase Extraction (SPE), followed by quantitative analysis via Gas Chromatography-Mass Spectrometry (GC-MS) and High-Performance Liquid Chromatography (HPLC) to detect target organophosphate and triazine compounds (e.g., chlorpyrifos, atrazine, and diazinon).Quality Assurance/Quality Control (QA/QC): Procedural blanks, duplicate samples, and matrix spikes were analyzed alongside every batch, maintaining analytical recovery rates between 85% and 110%.2.4 Spatial and Statistical AnalysisDescriptive statistics and Pearson correlation matrices were computed to evaluate relationships between hydrochemical variables and agricultural intensity. Spatial distribution maps of contaminant plumes were generated using Inverse Distance Weighting (IDW) interpolation within a Geographic Information System (GIS) environment, alongside aquifer vulnerability indexing using the DRASTIC framework (Aller et al., 1987).

3. Results and Discussion

Hydrochemical Characteristics and Nitrate Contamination.

The analytical findings reveal substantial spatial and seasonal variations in shallow groundwater chemistry. Nitrate concentrations ranged from 12.4\ mg/L to 118.6\ mg/L, with over 45% of the sampled wells exceeding the World Health Organization (WHO, 2022) maximum permissible limit of 50\ mg/L for drinking water. The highest NO_3- concentrations coincided with zones dominated by flood irrigation and permeable sandy soils, confirming that excessive nitrogenous fertilizer application coupled with over-irrigation accelerates vertical leaching (Ju et al., 2006). Phosphate levels remained comparatively low (0.05–1.4\ mg/L) due to strong sorption onto soil clay minerals and calcium carbonate precipitation, though localized spikes indicated preferential flow pathways.

Parameter	Unit	Min	Max	Mean	WHO Limit (2022)	% Exceeding Limit
pH	-	6.8	8.2	7.4	6.5 – 8.5	0%
TDS	mg/L	340	1,680	890	1,000	33.3%
Nitrate (NO^{3-})	mg/L	12.4	118.6	56.2	50.0	46.7%
Phosphate (PO_{-4}^{3-})	mg/L	0.05	1.40	0.38	-	-
Atrazine	mg/L	ND	3.80	0.85	2.0 (Total)	16.7%
Chlorpyrifos	mg/L	ND	1.95	0.42	-	10.0%

Trace residues of synthetic pesticides were detected in 60% of the monitored wells, with atrazine and chlorpyrifos being the most frequently quantified compounds. Concentrations peaked immediately following peak spraying and irrigation cycles. Although most detections were in the sub-microgram per liter range, 16.7% of samples exceeded the European Union and WHO benchmark thresholds for individual and total pesticides (0.1\ \mu\g/L and 0.5\ \mu\g/L, respectively). The persistence of these compounds in the shallow aquifer is attributed to low organic carbon content in the subsoil, which limits microbial degradation and sorption (Arias-Estévez et al., 2008).3.3 Health and Environmental ImplicationsChronic exposure to elevated nitrate levels in drinking water poses acute health risks, most notably methemoglobinemia ("blue baby syndrome") in infants, as well as potential links to gastric cancer and thyroid dysfunction (Ward et al., 2018). Concurrently, low-dose chronic exposure to organophosphate and triazine residues presents endocrine-disrupting and neurotoxic risks to rural communities relying directly on untreated shallow well water.

4. Conclusion and Recommendations

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This study confirms that intensive agricultural practices exert a direct and detrimental impact on the water quality of shallow unconfined aquifers. Excessive nitrogen fertilization and indiscriminate pesticide usage, exacerbated by inefficient irrigation regimes and high soil permeability, have led to widespread nitrate enrichment and trace pesticide contamination exceeding international drinking water standards. Without immediate intervention, ongoing agrochemical accumulation will render these vital shallow aquifers unsuitable for human consumption.

Furthermore, the findings underscore that shallow unconfined aquifers act as highly responsive systems where the absence of natural attenuation barriers—such as thick unsaturated zones and sufficient organic carbon—accelerates the downward migration of pollutants. The persistence of legacy agrochemicals within these water tables indicates that even if surface applications were immediately ceased, residual plumes would continue to degrade subsurface water quality for decades. This creates severe long-term socioeconomic and public health challenges for rural communities heavily reliant on shallow wells for domestic and agricultural needs.

To avert irreversible aquifer degradation and safeguard public health, a paradigm shift toward integrated hydro-agricultural management is urgently required. This transition necessitates phasing out traditional flood irrigation in favor of precision micro-irrigation systems, optimizing fertilizer application rates through real-time soil and plant tissue testing, and strictly enforcing Integrated Pest Management (IPM) protocols. Ultimately, protecting shallow groundwater resources demands proactive policymaking, robust monitoring networks, and collaborative governance between agronomists, hydrologists, and local regulatory bodies.

Recommendations

1. Precision Fertilization and Irrigation: Transition from traditional flood irrigation to drip and sprinkler systems, coupled with soil-test-based slow-release fertilizers to synchronize nutrient supply with crop uptake.
2. Integrated Pest Management (IPM): Enforce strict regulatory controls on persistent pesticides and promote biological pest control and biopesticides to reduce chemical loading.
3. Buffer Zones and Monitoring: Establish protection zones around high-vulnerability recharge areas and implement routine seasonal groundwater quality monitoring programs.
4. Community Awareness and Treatment: Educate farmers on safe agrochemical handling and deploy point-of-use water treatment technologies (e.g., reverse osmosis and activated carbon filtration) in affected rural households.

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