Chapter 16
Impacts of Agriculture-Based Contaminants on Groundwater Quality

Pooja Singh, Abhay Raj, and Basant Yadav

16.1 Introduction

All across the world, groundwater pollution due to agricultural activities is of significant concern. Agriculture has been identified as a significant source of water pollution in many countries and is considered a primary cause of nonpoint source pollution that releases agrochemicals, mainly Nitrogen and phosphorous (Xu et al. 2020), into the surrounding environment. The contaminants generated during crop production and post-processing may alter the quality and quantity and drastically affect environmental processes (Grimene et al. 2022). The goal to boost agricultural output by utilizing many agrochemicals is wreaking havoc on the natural ecosystem. Many developing nations cannot quantify agro-pollution, particularly in the case of chemical inputs like pesticides, hindering them from adopting action plans to minimize agrochemicals detrimental environmental effects (Jayasiri et al. 2022). Agriculture contaminants cause significant degradation of groundwater quality, and hence there is an urgent need to understand the sub-surface fate and transport of these contaminants. The growing population and resulting food demand have pressured the agriculture sector to increase crop productivity using pesticides and fertilizers (Wang 2022). The fertilizer and pesticides are two primary sources of agricultural contaminants, which leads to more percentage of the Nitrogen (N) -phosphorous(P)-potassium (K) in the sub-surface.

The fertilizer induces heavy metal, nitrogenous compounds, and greenhouse gas emissions, contaminate groundwater, and threaten the environment (Yuan et al. 2017). Figure 16.1 depicts the comparative availability of fertilizer minerals worldwide in 2022. China is now the world's most significant producer of nitrogen-based fertilizers, followed by India, the United States, and Russia, while Egypt is the world's

P. Singh · A. Raj · B. Yadav (✉)
Department of Water Resources Development and Management, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand 247667, India
e-mail: basant.yadav@wr.iitr.ac.in

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top consumer. In 2018 global consumption of pesticides was 5.89 million tons, a 34.7% increase compared to 2000 (FAO, 2020a). Fertilizer use has increased in the last two decades: Nitrogen, Potassium, and Phosphorous rose by 33.1%,97.9%, and 18.4%, respectively, from 2000 to 2018 (FAO 2020b). Globally the use of fertilizer in 2018 was 235 million tons, which consisted of 20.6% phosphorus, 58.2% nitrogen, and 21.1% potassium fertilizers. In 2019, Nigeria had the greatest average annual increase in nitrogen fertilizer production (51.9%). Guinea had the second-highest annual nitrogen fertilizer usage growth (+48.4%) (FAO 2020b). The high concentration of Nitrate in agricultural areas has also been linked to the over-usage of animal dung and garbage (Wang et al. 2019). Figure 16.2a and b show the global demand for ammonia, phosphoric acid, and potash from 2016 to 2020.

Pesticides have a crucial function in increasing agricultural productivity, but they come at a cost to the environment and human health in the long run. The plant only consumes 5% of the pesticide sprayed, and the rest harms the soil and groundwater (Sim et al. 2022). Similarly, fertilizers increase agricultural productivity, however, higher than recommended use of nitrogen and phosphorus results in transport of these contaminants through runoff into other ecosystems like wetlands, rivers, ponds, lakes, etc. One of the most significant environmental effects of such contaminated runoff is eutrophication, which causes changes in various physio-chemical processes, including the formation of low oxygen zones (Qian et al. 2018) and changes in water quality nutrient cycling (Dorgham 2014; Jayasiri et al. 2022). Eutrophication causes algal blooms to emit harmful chemicals, hindering photosynthesis and changing

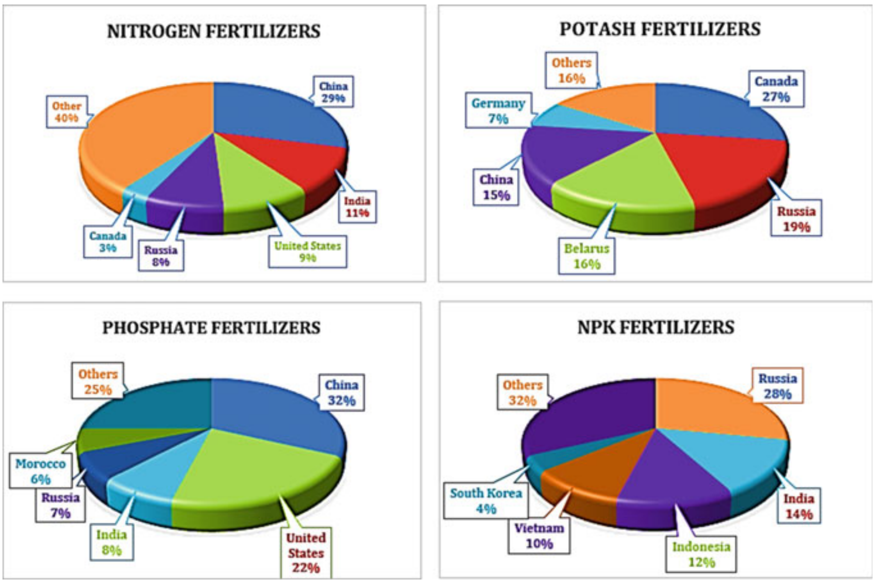

Fig. 16.1 Top five producers of fertilizer minerals account for more than half of global production. *Source* (FAO 2020b)

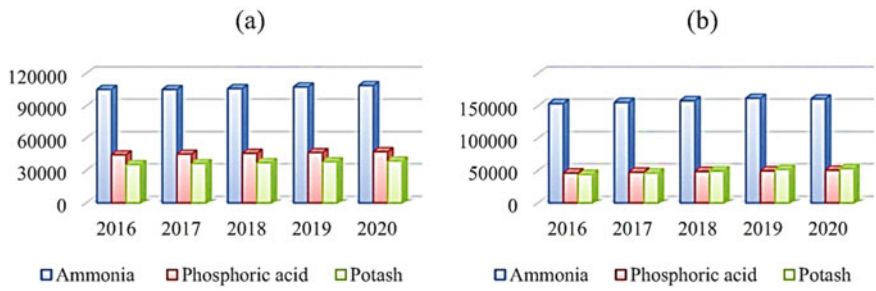

Fig. 16.2 **a** World demand for ammonia, phosphoric acid, and potash (thousand tonnes) from 2016 to 2020, **b** World supply of ammonia, phosphoric acid, and potash from 2016 to 2020. (thousand tonnes). *Source* (FAO 2020b)

aquatic life's behavior. It mainly influences the food web quality by altering the benthic diversity and habitat (Dorgham 2014).

Agricultural runoff contains a significant chemical ingredient that promotes groundwater pollution, mainly Nitrate from fertilizers (USEPA, 2014). The harmful substance contaminates groundwater via dispersed sources, such as the use of fertilizer and pesticides on farms. Irrigation methods are mostly used on permeable soils and has a substantial impact on groundwater quality. The dissolved salts in irrigated water enter the soil via infiltration into groundwater. Paddy is the most water-intensive crop since the fields must be flooded in its initial growth stage, and excessive fertilizers are used to increase yield (He et al. 2020). Pesticides and fertilizers containing hazardous elements such as Cd, Pb, Ni, Cr, Cu, As, and Zn are used for paddy production (Calvo et al. 2021). Hence, paddy fields are a significant source of toxic metals in drinking water. Groundwater is negatively impacted by the improper management of agrochemicals in rural and urban regions (Redwan et al. 2020). Due to the increasing use of fertilizers and pesticides in agriculture to increase profits, the soil's capacity to support agriculture is degrading, causing erosion and nitrate leakage into groundwater (Filintas 2005). Wastewater released from urban areas also contributes to the increase in Nitrate concentration in groundwater. Excessing groundwater extraction in urban areas also deteriorates the groundwater quality. Nitrate is a major pollutant in groundwater and if its concentration exceeds 10 mg/L, then it is toxic to infants and, over time, can cause stomach cancer (Wu and Sun 2016). According to the World Health Organization (WHO), a health hazard might emerge if an individual consumes water with a nitrate concentration of more than 50 mg/L. Moreover, excessive levels of nutrients in Groundwater can increase the risk of a variety of disorders, including (a) methemoglobinemia, (b) diabetes, (c) spontaneous abortions, (d) cancer, (e) thyroid, (f) mutagenesis, and (g) teratogenesis.

16.2 Agro-Chemicals Used in Crop Cultivation

Many natural substances like manure and synthetic materials like nitrogen, phosphorous, and potassium compounds are applied to soil to boost its ability to support plant growth. The USGS, 2014 often examined Agricultural contaminants as Nutrients to plants, including fertilizer components such as Nitrogen, Potassium, Phosphorus, pesticides, including herbicides, insecticides, and fungicides. Nutrients are mainly classified into the following four types: (a) Natural nutrients- carbon, hydrogen, oxygen; (b) Primary nutrients- nitrogen, phosphorous, and potassium; Urea (46%-0%-0%), monopotassium phosphate (0-54-34); (c) Secondary nutrients-calcium, sodium, sulfur, magnesium and; (d) Micronutrients- copper-molybdenum, manganese, cobalt, zinc, boron, Iron.

16.3 Fertilizers Used for Crop Cultivation

The commonly used fertilizer for agriculture can be divided into three types. They are: (a) Potassium fertilizer- KCl, K_2SO_4, KNO_3; (b) Nitrogen fertilizer- NH_4NO_3, NH_4CL; (c) Phosphorus fertilizer- $(NH_4)_2PO_4$, $(NH_4)_3PO_4$. For the previous five decades, nitrogen fertilizers used to increase agricultural yields include heavy metals (Tyagi et al. 2022). These kinds of agrochemicals employed as fertilizers negatively impact all the environment segments, including water, soil, air, etc. (Ahmed et al. 2017). Long-term usage of these chemical compounds affects livestock and eventually enters the food chain; long-term use will have a lasting impact on biodiversity. Slow utilization of fertilizer by plant is one main reason for contamination of Groundwater and surface water. The plants can absorb just a limited quantity of these nutrients. Excessive nutrients result in soil salinity and alkalinity rise, rendering the soil infertile (Folina et al., 2021). Plant uses only 61–65% of fertilizer and remaining 50% is absorbed by soil or microorganisms and leached to groundwater, contaminating the water table via percolation (Ahmed et al. 2017). When these contaminants reach the surface water bodies, they contribute to the formation of algal bloom, which releases harmful toxins rendering the water undrinkable. The algal bloom consumes all dissolved oxygen present in water and causes oxygen deficit in water bodies. Table 16.1 Shows Nitrogen-based fertilizers such as Nitrous Oxide (N_2O), Nitrogen dioxide (NO_2), Ammonia (NH_3), Nitrate (NO_3^-), Nitrite (NO_2^-), Nitric oxide (NO), Nitrogen (N_2), Urea, Organic Nitrogen, etc. The mean concentration of NO_3^--N was higher than NH_4^+-N and NO_2^--N in groundwater (Wang 2022), The hydrochemistry of groundwater in recharge zones was influenced by water–rock interactions. In the transition and discharge zones, there were high levels of NO_3 and NH_4^+ in groundwater (Mao et al. 2022).

Table 16.1 Shows the category of, pesticide, fertilizer with the type of agrochemical

Category	Parameter	Source
Pesticide		
Herbicide	Pretilachlor, MCPA, sodium, bispyribac propanil, oxyfluorfen, cyhalofop butyl, glyphosate, fenoxaprop-p-ethyl	(Rahman et al. 2012)
Insecticide	Etofenprox, chlorantraniliprole, carbosulfan, fipronil, Tau-Fluvalinate Pyrethroid, Flumethrin, thiamethoxam, fenobucarb, diazinon, carbofuran,	(Jayasiri et al. 2022)
Fungicide	Hexaconazole, captan carbendazim, tebuconazole	(Jayasiri et al. 2022)
Minerals	Phosphate, nitrogen (ammoniacal nitrogen, nitrite, nitrate), sulphate, magnesium, Iron, calcium, sodium	(Meng et al. 2020)
Fertilizer	Nitrogen dioxide (NO_2) Nitrate (NO_3^-) Nitrite (NO_2^-) Nitrous oxide (N_2O) Ammonia (NH_3) Nitric oxide (NO) Nitrogen (N_2) Urea Organic nitrogen	(Zhao et al. 2022)

16.4 Pesticide Used for Crop Cultivation

Chemical substances are used to eliminate fungus, insects, bacteria, weeds, etc., since these organisms damage crops. The persistent use of such chemicals has made theme emerging contaminants with the potential to damage human health (Kurakalva 2022). The two key features of a pesticide are that it should not be damaging to plants and it destroys itself in sunlight, e.g., hydrogen sulfate, lead arsenate, nicotine sulfate, parathione, and DDT. The widespread use of lead arsenate as a pesticide in fruit orchards numerous times each year to control gypsy and codling moth or caterpillar infestations which harms crops by eating their leaves and fruits. The degradation process and sorption may decrease pesticide migration through the soil matrix. Both biotic and abiotic variables govern the degradation, and the pace is based on the soil's chemical, physical, and biological properties and the pesticide's properties (Mascarelli 2013). Once inside the soil, the pesticide partitions between the liquid and solid phases. The sorption level depends on pesticide and organic matter concentrations. Due to its physical entrapment in the soil and covalent link to soil organic matter, the clay mineral portion of the soil may contain pesticide residues (Gevao et al. 2000). Several studies have described the transport of pesticides from the soil to depth within different groundwater systems (Panno and Kelly 2004). A major pathway for contaminant transport to groundwater is leaching from soils following pesticide application. The transport of these contaminants without natural attenuation in the shallow aquifers is quicker specially in area where it is supported by drains, soakpits, sumps and fractures (Lapworth et al. 2006). The Pesticide fate information helps public authorities, spatial planners, agricultural extension services, farmers, and scientists better relate agricultural activities to groundwater preservation by estimating, in time and space, specific groundwater vulnerability based on the natural filtering capacity of soils under different crop and pesticide use conditions (Bancheri et al. 2022).

16.5 Herbicide Used for Crop Cultivation

The most commonly used herbicides are pretilachlor, MCPA, bispyribac sodium, glyphosate, fenoxaprop-pethyl, propanil, oxyfluorfen and cyhalofop butyl. These chemicals are excessively used in agriculture for weed control and have the potential to leach their active ingredients and metabolites into the groundwater. After application, the portion of the dissolved chemical neither absorbed by the plant nor transported to surface water moves downward and percolates through the soil to reach groundwater. The size and connection of soil's water-filled pores significantly govern the movement of water and contaminants through the soil (Jarvis 2007). Soil, chemical, management, and climate conditions all influence herbicide loadings in groundwater. There are many easy evaluation processes for ranking pesticides based on their possible influence on groundwater. The majority of these techniques aren't unique to any particular climate, farming strategy, or soil (Leonard et al. 1988).

16.6 Insecticides Used for Crop Cultivation

The insecticides which are used frequently to support the higher yield of crops are chlorantraniliprole, carbosulfan, thiamethoxam, fenobucarb, fipronil, diazinon, carbofuran, etofenprox. According to recent research, insecticides account for 20% of all agrochemicals used in crop production (Tang et al. 2018). Pyrethroid insecticide was developed to enhance effectiveness and light stability compared to pyrethrin insecticide (Lopez-Lopez et al. 2001). In recent years, organophosphorus insecticides such as pyrethroid have been prohibited. Excessive use of pyrethroid in agriculture has the potential to pollute soil, taint surface and Groundwater, and disrupt aquatic life (Feo et al. 2010). Tau-fluvalinate (N-[2-chloro-4-(trifluoromethyl) phenyl]-D-valine (RS)-cyano (3phenoxyphenyl) methyl ester), Flumethrin (cyano(4-fluoro-3-phenoxyphenyl) methyl 3-[2-chloro-2-(4chlorophenyl) vinyl]-2,2-dimethylcyclopropanecarboxylate) are insecticides belonging to the type II pyrethroid family and used to treat cereal and oilseed crops for controlling a broad spectrum of ectoparasites and very harmful for Plant, animal, and beehives (Bodian et al. 2022). In the nineteenth and twentieth centuries, lead, mercury, and arsenic were used to a limited extent for the purpose. After the 2nd world war, these synthetic insecticide organochlorines and organophosphates were widely accepted. Groundwater pollution caused by pesticides is a worldwide problem. Groundwater includes at least 143 different pesticides and 21 transformation products, according to the USGS, including pesticides from every major chemical family. During one survey in India, 58% of drinking water samples collected from multiple hand pumps and wells in Bhopal were found to be contaminated with Organo Chlorine pesticides in excess of EPA standards (Kole and Bagchi 1995). When hazardous pollutants contaminate ground water, it might take years for the pollution to dissipate or be removed. Cleanup could be very expensive and complex if not impossible.

16.7 Fungicide Used for Crop Cultivation

Copper-based fungicide are mostly used in agriculture which has a lasting effect on soil biota. These fungicides alter soil qualities such as microbiological activity, bioturbation, and earthworm activity at very low copper concentrations (Van-Zwieten et al. 2004). Alternately, it contaminates groundwater and has an impact on human health. Regulators monitoring watersheds with crops requiring intensive fungicide application should consider including copper salt, copper oxide, copper hydroxide, copper chelate, and copper oxychloride, as well as copper complexes and combinations of components into their surveillance systems, otherwise, they would risk missing the detection of new pollutants in surface and groundwater systems (Reilly et al. 2012).

16.8 Agrochemicals and Their Impacts on Groundwater

Soil provides nutritional support for the agricultural land by regulating the biogeochemical cycle, waste degradation, nutrient cycle, etc. The biggest threat to soil health is the agrochemical. The behaviour of agrochemicals in the soil is governed by a number of complex physical, chemical, and biological phenomena, such as desorption-sorption, biological and chemical degradation, evaporation, runoff, and leaching through soil. The contamination in groundwater can be triggered by a variety of factors, such as excessive agrochemical application, rainfall pattern, soil texture, bacterial population, microbial degradation, leaching through the soil, surface runoff, and agrochemical percolation in the water table, among others.

Excessive use of nitrate fertilizer is a problem in many parts of India or the world. Leaching of nitrates from the soil to groundwater is a global phenomenon due to less retention by soil particles and high solubility in water. Nitrate concentrations in agriculture are often related to microbial and pesticide activity, and nitrogen fertilizers are the nonpoint source of groundwater pollution (Mahvi et al. 2005). The bacterial population oxidises the ammonium ions into nitrate ions, and nitrate ions

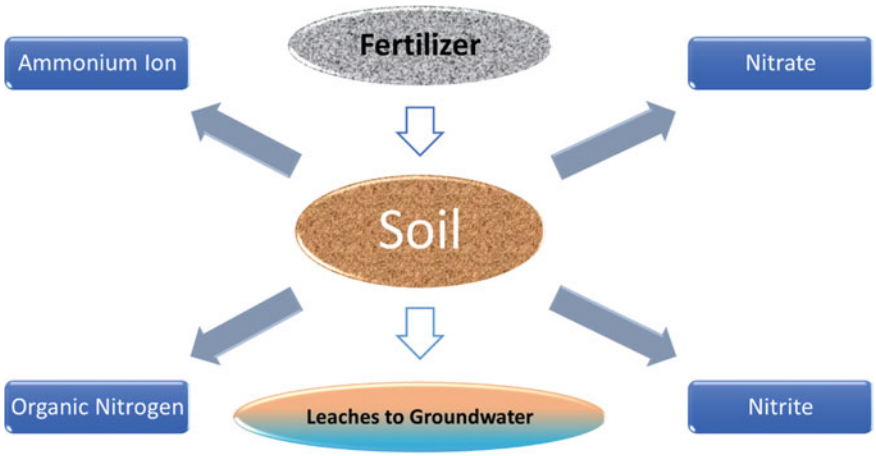

Fig. 16.3 Fertilizer process from nitrogen to other forms

are the predominant contaminant in the groundwater. Nitrate ions, which are negatively charged, pollute groundwater more than ammonium ions, which are positively charged. Soluble nitrates can reach up to root level or up to groundwater due to surface water infiltration. Unconfined strata having shallow water tables are particularly susceptible to agricultural contamination. As shown in Fig. 16.3, several studies have demonstrated the effect of irrigation on the accelerated leaching of nitrate in aquifers and the atmosphere. The most critical determinants of nutrient leaching to groundwater and surface water are hydrological conditions governing nutrient transport (Oenema et al. 2005).

According to the estimated Groundwater Ubiquity Score (GUS) index, the herbicide was found in 14.7% of groundwater in the study area of Pampean Plain of Cordoba, Argentina (0.14–1.26 g/L), making it a leachable herbicide with moderate potential for groundwater contamination (Lutri et al. 2022). Atrazine has high mobility in areas with a predominance of course-textured sediments (sands and gravels), low clay percentages, and lower K_{oc}, permitting it to reach the unconfined aquifer at sites with a deep water table (25 m below surface). Herbicide spraying is typically timed to coincide with wet seasons, resulting in high leaching rates (Lutri et al. 2022). Hydrogeological features impacted its spread in the unconfined aquifer. The highest atrazine levels were found in places with a thin unsaturated zone (UZ), and the lithology of the UZ was also significant. Several processes, along with microbial metabolism and chemical or photo-degradation, induce atrazine and other agrochemicals to degrade over time and are influenced by pH, climate, soil type, clay and organic matter content (OM), and geological characteristics of the site, such as lithology (Urseler et al. 2022). It is also vital to understand the pesticide features that govern their breakdown rates. The most essential variables are the sorption distribution coefficient (K_d) between the aqueous and soil phases and the chemical stability in the environment as shown by the compound's half-life ($t_{1/2}$).

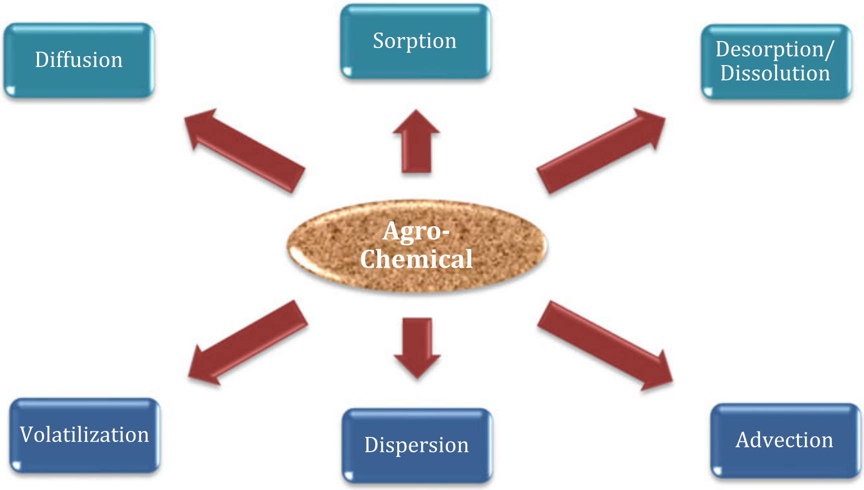

Fig. 16.4 Shows the process of agro-chemical from surface to sub-surface

Due to the fact that the sorption coefficient varies substantially with soil type and organic matter concentration, one of the most often used sorption constants is the sorption coefficient standardized to soil organic carbon content (K_{oc}).

Insecticides that are as water-accessible as ions are expected to have similar effects. There have been few efforts to pinpoint the source of chemical contamination in agriculture (Warner et al. 2021). Pesticides are carectorized into two groups: short-term and long-term usage. It was observed that the results of the first type were seasonal and geographically restricted, whereas for the second type their transformation products were more persistent (TP). Degradation is crucial for diminishing pesticide residue in soil. It is influenced by abiotic and biotic variables and follows a complicated journey through the subsurface structure, i.e., the saturated and unsaturated zone to reach groundwater (Tetteh 2015). Sorption is crucial to the dynamics of advective–dispersive transport, transformation, etc. Extensive research indicates that the sorption of the neutral chemical depends on the soil's organic matter concentration. It has been shown that the molecular weight is crucial in affecting the sorption of non-ionic insecticides (Ahmed et al. 2017). Figure 16.4 depicts the adsorption, chemical degradation, and volatilization processes that allow applied agro-chemicals to reach the groundwater table.

16.9 Remedial Measures

The presence of agricultural contaminants has a negative impact on groundwater and their contamination levels varies according to application of fertilizer and chemicals which are used in agriculture field. Remediation techniques are required to ensure adequate water supply from groundwater sources. Some of the following technique are there such as bio-char, bio-remediation, adsorption, nitrate remediation by nanoparticles and biological denitrification improves the quality and health of polluted water and soil (Karimi et al. 2022). Bioremediation uses microorganisms to clean up polluted soil and water (Singh and Strong 2016; Singh et al. 2016b; Vimal et al. 2017). In-situ bioremediation includes bioventing, biostimulation, air-sparging, natural atten-uation, landfarming, and phytoremediation (Juwarkar et al. 2010). Among them, biostimulation and phytoremediation are the most effective remediation for nitrate in groundwater. Biosorption is cheap, possibility of pollutant recovery and regeneration and environmentally friendly (Othmani et al. 2022). Nanotechnology is cheap, effective, and environmentally friendly in most cases (Jassby et al. 2018) In subsurface environments, lack of available organic carbon has often been reported as the most common hindrance to denitrification (Jahangir et al. 2012). However, phytoremediation is time-consuming compared with physical or chemical remediation. Phytoremediation is also limited by the depth of plant roots (Martino et al. 2019).

16.10 Conclusion

Agriculture based contamination has been a longstanding threat for both soil and groundwater. In this study, we attempted to investigated the impacts of various agro-chemicals such as fertilizers and pesticides on groundwater using the available literature. It it observed that the fertilizers based nutrient like Nitrate is the biggest threat for groundwater. Excessive application of nitrogen based fertilizers coupled with favourable conditions results into leaching of Nitrate into the shallow groundwaters. Similarly, pesticides including herbicides, fungicides and insecticides contaminante groundwater if used in excess quantity. Various remedial measures such as using organic faming in place of chemical fertilizer, application of Bio-Char (Absorbent) in agriculture field ion exchange, membrane separation, catalytic reduction and, nano-remediation, reverse osmosis, chemical denitrification, biological denitrification, ion exchange, electrodialysis, and adsorption process are available, catalytic reduction is effective in removing NO_3^-, nano-remediation is a potentially developing tool for dealing with contamination of the environment, particularly POPs (persistent organic pollutants). is suggested as the most effective strategy to control the agro-chemicals based contamination of groundwater. It is possible, although difficult, to trace the migratory route of contaminants in nonpoint source samples. In addition, investigating groundwater quality may enhance our understanding of the human health risk caused by indirect discharge of pollutants into aquifers. Conducting regular quality assessments with sufficient sample sites or in-situ measurements may provide a clear understanding of agro-chemical based pollution sources and the underlying patterns of water contamination at the landscape scale.

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