

Chapter 2

Groundwater Pollution by Geogenic and Industrial Pollutants



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Abstract The groundwater accounts for around 98% of the total freshwater available on the earth. Groundwater pollution is an emerging threat to our beloved planet. The chapter explains the two major sources of pollution, each from natural (geogenic) and anthropogenic (industrial) activities, which are responsible for degrading the quality of groundwater. It includes the physio-chemical characteristics of pollutants, governing factors to their fate and transport, their adverse effects on human health and earth as a whole, and possible strategies for their remediation. The latest studies conducted to understand the nature and treatment techniques of these pollutants are also discussed in the chapter. The chapter concludes with the countermeasures required to tackle the problem of groundwater pollution.

Keywords Groundwater pollution · Fluoride · Arsenic · Uranium · Geogenic · Industrial contamination · Nitrate

2.1 Introduction

The water found beneath the earth surface saturating the pores and fractures of subsurface materials is termed as groundwater. The upper layer of the saturated geological material is termed as water table (Fig. 2.1). Depth to the water table may vary from zero feet to a thousand feet below the ground level (bgl), depending on the prevailing geologic, meteorological, and topographical factors.

The groundwater stores in the cracks and voids of soil, sand, and rock in the same way water fills the sponge. It moves through the aquifer material typically at a rate of 7–60 cm per day. Groundwater moves through the vadose zone (containing numerous geological filters) to reach the water table and is generally free from any

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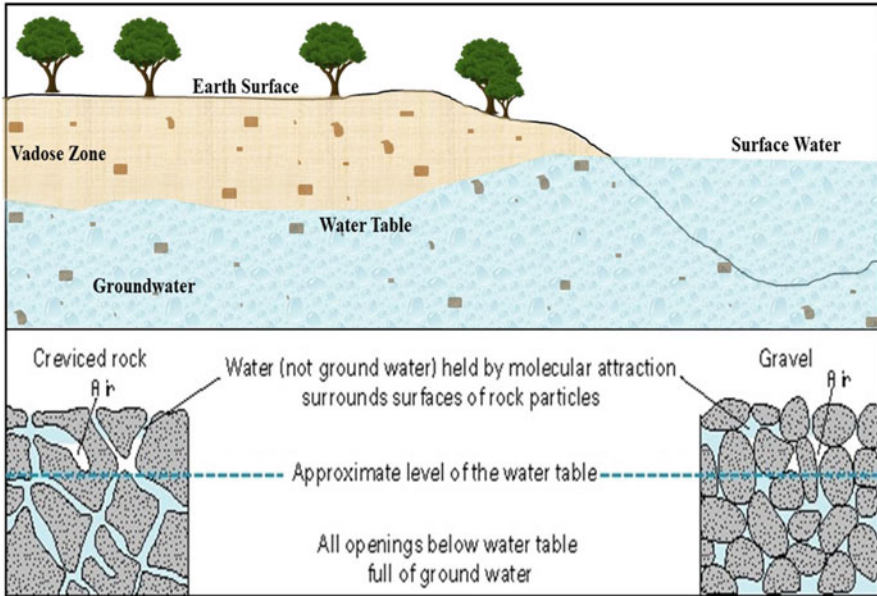


Fig. 2.1 The vadose zone (unsaturated zone), groundwater level, and pores in the subsurface

contaminant or impurity. It can be found all over the earth and hence is a very reliable source of fresh water for multiple uses as domestic, agricultural, and industrial water demand. It is the world's most extracted resource with withdrawal rates in the range of about $982 \text{ km}^3/\text{year}$ (Margat and Van-der 2013).

Groundwater fulfilled about 60% of the agriculture and half of the world domestic water requirement (Smith and Cross 2016). Although groundwater is less vulnerable to the pollution compared with the surface water resources but if contaminated, treatment of the same would be much challenging and costlier. There are numerous groundwater pollutants, but can be broadly categorized in two types:

1. Anthropogenic: caused by human activities like sewage, industries, mining, among others.
2. Geogenic: caused primarily by geological activities.

The scope of this chapter is limited to introduction, cause, effects, and possible remedial measures for geogenic and industrial pollution in groundwater.

2.2 Geogenic Pollution

Geogenic pollution denotes the state when certain naturally occurring elements in the groundwater rise to an objectionable level that can cause potential harm to mankind. It can emanate due to the geochemical decomposition of underlying aquifer material—contaminant the subsurface matrix as a result of dissolution during

geological interaction or may be due to other environmental factors like successive climatic changes, redox condition in an aquifer, change in groundwater flow regime. Anthropogenic activities like mining can also trigger the subsurface changes causing the geogenic pollution in groundwater. Table 2.1 lists some of the prime studies showing the status of geogenic pollutants in groundwater throughout the world. Major geogenic pollutants in groundwater that had proven to be a potential threat are listed below.

2.2.1 Fluoride (F^-)

It is the lightest member of halogens family and is found in varying concentration in rocks: granites (810 $\mu\text{g/g}$); basalt (360 $\mu\text{g/g}$); limestone (220 $\mu\text{g/g}$); shale (800 $\mu\text{g/g}$); sandstone (180 $\mu\text{g/g}$); oceanic sediments (730 $\mu\text{g/g}$), and soils (285 $\mu\text{g/g}$). Besides rocks, it is commonly found in plant, soil, and rock minerals like biotite, muscovite, mica, etc. Its existence in groundwater is predominantly geogenic due to weathering and dissolution of fluoride bearing minerals, hauled by calcite precipitation. Factors like pH, temperature, residence time, porosity, soil structure, depth, groundwater age, and ion exchange capacity of aquifer materials govern the extent of fluoride contamination in groundwater.

Human body needs small concentration of fluoride for prevention of dental caries. But intake of water with concentration more than a specific limit (1.5 mg/l) causes fluorosis, may be dental, skeletal, or non-skeletal fluorosis. Persistent intake of such fluoride contaminated water ultimately leads to severe joints related pain including knee-, pelvic-, and shoulder-joints, and may also restrict movements of cervical and lumbar spine, fluorosis is irreversible and the person once affected cannot be cured.

Treatment methods adopted for the treatment of groundwater contaminated with fluoride are broadly ex-situ techniques. These methods are based on adsorption and ion exchange (by active alumina, red mud, bone char, etc.), coagulation–precipitation (like Nalgonda technique), and membrane techniques (reverse osmosis, nano-filtration, etc.). Sustainable future solutions involve arranging alternate source of potable water, finding fluoride free aquifers by sampling at vulnerable sites, installation of de-fluoridation plants, and supply from appropriate surface water source, wherever available.

2.2.2 Arsenic (As)

Arsenic can be found abundantly in earth's crust and in small amount in soil, rock, air, and water. The typical concentration of arsenic in the interior crust is 1–2 mg/kg, 1.5–3.0 mg/kg in igneous rocks, and 1.7–400 mg/kg in sedimentary rocks. Various forms of arsenic, both organic and inorganic (more toxic), can be introduced to groundwater by geogenic, anthropogenic, or biogenic activities. It keeps circulating

Table 2.1 Some latest studies conducted to understanding the effect of geogenic pollutants in groundwater

S. no.	Reference	Study area	Target geogenic contaminants	Key findings	Possible remediation measures
1	Lapworth et al. (2017)	Bist-Doab region, India	Selenium and uranium	The contamination is due to dissolved minerals and iron oxide present on aquifer grains, the existing toxic and alkaline conditions, and carbonate complexation. The study concluded that the deeper aquifers are vulnerable to vertical breakthrough of mobile contaminants from shallow ones	Controlled groundwater extraction, adsorption-ion exchange process, and adopting redox technologies
2	Egbinola and Amanambu (2014)	Ibadan, South-West Nigeria	Arsenic and fluoride	The As concentration is above the WHO guidelines for drinking water in 98% and 100% of the dry and wet season samples, while 13% and 100% of the dry and wet season samples are having more fluoride. Questionnaire analyses concluded that 85% of respondents have never checked their wells, 55% have no knowledge of geogenic contamination	Dilution of affected areas, detailed geophysical investigation, isotopic and hydrochemical modeling studies
3	Harkness et al. (2017)	Southeast Wisconsin, United States	Molybdenum	The isotope signatures studies in correlation with mean groundwater residence times support a geogenic source of Mo to the groundwater, rather than CCR-induced contamination. The	Use of permeable reactive barriers (PRBs) and nanomaterials can be effective for the treatment

(continued)

Table 2.1 (continued)

S. no.	Reference	Study area	Target geogenic contaminants	Key findings	Possible remediation measures
				study exhibits the effectiveness of a multi-isotope approach to distinguish between anthropogenic and geogenic source of contaminant	
4	Selck et al. (2018)	Goshen Valley, UT, USA	Arsenic	The study finds out two distinct triggers that can lead to the release of As in groundwater: (1) development of high pH (>8.5) environment in semi-arid environments and (2) introduction of reducing situations at a neutral pH, which causes the reductive dissolution of As that is co-precipitated with Mn and Fe oxides. It may be from Paleozoic carbonate rocks or quaternary fill deposits found in the area	An integrated approach must be implemented for efficient, equitable, and sustainable groundwater management
5	Naeem et al. (2019)	Gaza coastal aquifer, Palestine	Salinity	Factor analysis (FA) comprised of three factors, viz. F1 as salinization, F2 as mixing of sewage invasion and water hardness, and F3 as carbonate dissolution, proved that high salinization in groundwater was the result of three main factors loadings accounts for 83.86% of the total variance. Areas dominantly	Techniques like micro-filtration and solar humidification can be implemented along with reactive barriers to control sea water intrusion

(continued)

Table 2.1 (continued)

S. no.	Reference	Study area	Target geogenic contaminants	Key findings	Possible remediation measures
				affected by the different hydro-geochemical processes are clarified by factors' scores. Ionic deltas and ionic ratios reveal the dominance of reverse ion exchange process	

all over the environmental compartments in a complex cycle. Due to alteration in gastrointestinal absorption, humans are more sensitive to arsenic contamination than animals and plants.

Arsenic contaminated groundwater has serious health impacts on human's in the form of respiratory distress (bronchitis or rhinitis, laryngitis, myocardial depolarization, etc.) and gastrointestinal effects (thirst, nausea, burning lips, painful swallowing, and abdominal colic). Overdue interaction with arsenic causes arsenic poisoning that leads to anemia and leucopenia. Ingestion of inorganic arsenic can cause neural failure, hallucinating, hypopigmentation spots generation, lungs or even skin cancer. Arsenic contamination in the unconsolidated aquifers of the world especially along alluvial and deltaic plains in southern and eastern parts of Asia is a chief concern for groundwater hydrologists.

The arsenic concentration in groundwater is intricately linked to the subsurface geometry, soil matrix, and groundwater flow regime. Planning of sustainable arsenic remediation techniques involves understanding of various physicochemical processes in subsurface, aquifer framework geometry, lithological information and flow regime of the study area. Treatment methods include options ranging from ex-situ treatment, searching alternative aquifers, dilution by artificial recharge. The arsenic free deep aquifers can be located beneath the affected shallow aquifers identified through detailed geophysical investigation, isotopic and hydro-chemical modeling studies.

2.2.3 *Salinity*

Salinity level is a suitable macro parameter defining the groundwater quality. It refers to the amount of salt (particles or ions) dissolved in water. The salinity is highly variable both in terms of quality (anhydrite, carbonates, halides, fluoride-salts, gypsum, and sulfate salts) and concentration levels throughout the world. It is generally expressed as either total dissolved solid (TDS) in milligram per liter of water or electrical conductivity (EC) in micro Siemen per centimeter. Geogenic phenomenon responsible for the salinity of groundwater includes deposition under

marine environment, sea water fluctuations (often accelerated by climate change), sea water intrusion, and various meteorological (like evaporation) and hydrological cycle (like carbon cycle).

High salinity levels in groundwater damage the plant growth, lower the crop yield, degrade aesthetic importance of groundwater, destroy aquatic life, and damage industrial equipment. These dissolved salts generally do not attenuate naturally and remain in groundwater for long time period of decadal scale. Intake of groundwater having higher concentration of salts like sodium can cause heart disease and high blood pressure.

Salinity reduction techniques in groundwater require a huge amount of financial as well as technical resources. The method of salinity reduction includes distillation methods (like vapor compression, solar humidification, multi-stage flash), membrane technologies (like reverse osmosis, micro-filtration, electro dialysis reversal), and providing freezing or hybrid facilities.

2.2.4 Uranium (Ur)

Uranium has an average concentration of only 0.0003% in the Earth's crust with three primary ore minerals, namely uraninite, pitchblende, and davidite. Naturally occurring igneous and sedimentary rocks contain uranium from 0.5 to 4.7 µg/g. It is gaining fast notoriety in the field of groundwater geogenic contaminants. Along with the radiotoxicity of uranium, its aqueous form has chemical toxicity also due to formation of complex compounds, hydrolytic processes, and redox properties. Uranium in groundwater is predominately geogenic but anthropogenic activities like groundwater table decline and nitrate pollution may further enhance uranium mobilization.

Uranium contamination in groundwater may lead to chronic kidney disease and cancer in humans. Its concentration in groundwater cannot exceed much due to inclination towards complex formations. Uranium generally found to accumulate in the soil and plant fruits irrigated by the uranium contaminated water. It may generate mutagenicity and reproductive toxicity on long exposure. World Health Organization (WHO) set up a provisional, owing to outstanding uncertainties regarding the toxicology and epidemiology of uranium, threshold limit of 30 µg/l for drinking water.

Treatment of uranium contaminated groundwater can be done in broadly two ways: (1) Ex-situ techniques (adsorption and ion exchange, reverse osmosis, reactive sorption, and precipitation) and (2) In-situ methods (phosphate precipitation, flushing, and redox technologies).

2.2.5 Radon (Rn)

It is a gas generally produced during decaying of uranium ore radium-226. It can be found in phosphate rock, uranium ores, black shales, metamorphic and igneous

rocks such as schist and granite. It may accumulate in small caves and fractures, but concentration of radon varies significantly with different seasons and environmental conditions. Radon has a solubility co-efficient of 0.254 at 20 °C in groundwater. Radon concentration in groundwater depends upon mineralogy of rocks, grain size, uranium content, permeability, fracture geometry in the host rock, and its tectonic history. The concentration of radon found to be inversely varying with the pH value of groundwater.

Consumption of radon contaminated groundwater can cause lung cancer, emphysema, respiratory lesions, and pulmonary fibrosis, chronic interstitial pneumonia, and silicosis. It can also generate genotoxic effects—higher incidence of chromosomal aberrations in humans.

The principal methods to remediate radon contaminated groundwater is stripping, aeration, and adsorption. Aeration technique of radon remediation from groundwater can ultimately proves to be a large source of air-borne radon.

2.2.6 Chromium (Cr)

It is the transition element found in groundwater either due to weathering and erosion of chromium-containing rocks or volcanic eruptions. Oxidation state of chromium varies from -2 to $+6$ and the distribution oxidation ratio governs by complex biochemical factors like pH, redox and nutrient levels that govern bacterial activity in the subsurface.

Chromium (III) compounds and metal are not included in potential geogenic contaminants, while chromium (VI) can be a serious threat to humans due to its toxicity and carcinogenic properties. Because of the selective transport mechanism of Cr, quantity of Cr (III) entering the cell is limited. Chromium (III) in the cell can lead to DNA damage as verified by several vitro studies. Acute oral toxicity for chromium ranges between 1.5 and 3.3 mg/kg. Once in contact with the blood stream, it can damage the kidneys, liver, and blood cells through oxidation reactions.

Remedial measures for chromium contamination include methods to reduce either its toxicity or concentration in groundwater. Chemical, microbial, and phyto-remediation techniques are used to reduce the toxicity of Cr by altering the oxidation state. Ex-situ measures for reducing the chromium concentration incorporates ion exchange methods, granular activated carbon, adsorbents, and membrane filtration techniques. In-situ methods involve soil flushing and electro kinetics.

2.2.7 Selenium (Se)

It is a non-toxic metalloid discovered by Swedish chemist Jons Jacob Berzelius in 1817. It is an important geogenic contaminant due to its ability to produce compounds like hydrogen selenide, aluminum sesquioxides, and cadmium selenide that

are extremely toxic to humans. Mobility of selenium and its complexes in groundwater governs by the temperature, moisture, concentration, climate, microbial activity, and organic matter content of the geological formations.

Major concern with the selenium is its ability to accumulate in the food chain as different compound. Exposure to selenium contaminated water in humans is responsible for loss of keratin protein, progressive deterioration of health, nausea, headache, and staining of teeth and nails with brittleness and longitudinal streaks. Techniques used for selenium remediation include ion exchange, activated alumina (AA), reverse osmosis (RO), and distillation.

2.3 Industrial Pollution

Apart from the geogenic processes occurring in the subsurface, industrial effluents are major source of groundwater pollution. Effluents from the factories whether in the form of chemical waste, solid waste, or in other toxic and hazardous form when reach the groundwater, exacerbated and aggravated the groundwater pollution. Industries are primarily related to the point source groundwater pollution due to mismanagement of their waste discharged either directly or indirectly to the groundwater. Fate and transport of these discharged effluents determine the extent and severity of groundwater contamination caused. They are usually more toxic than geogenic contaminant and have a long lasting effect on groundwater. There are numerous incidents of groundwater pollution by industries found all over the world listed in Table 2.2. Industrial pollutants include a wide variety ranging from heavy metals to complex biochemical compounds.

2.3.1 Lead (Pb)

It is a soft, malleable but denser metal having relatively low melting point. It is sparingly soluble in water and has the ability to combine with chloride, hydroxyl, and organics to form complexes. Tendency to form complexes increases the lead mobility in the subsurface. This increased mobility elevates its concentration in the groundwater. Lead contamination of groundwater due to industrial activities has been reported in many parts of the world.

It is a non-putrescible contaminant that is hard to remediate completely. It can inhibit the action of bodily enzymes resulting in potential threat to human and animal race. It may also affect the vegetation and aquatic life nearby the contaminated site. The existence and transport of lead depends on process like adsorption, dissociation, absorption along with various complex chemical and biological reactions.

Table 2.2 Recent studies emphasizing the presence of industrial pollutants in groundwater

S. no.	Reference	Study area	Contaminants and there source	Highlights
1	Miglietta et al. (2017)	Salento (Southern Italy)	Mercury (Hg), vanadium (V) from the industries located nearby (Cutrofino and Galatina)	Climatic characteristics and human activities involving the extensive use of water resources influence the level of groundwater contamination, leading to reduced water availability and to progressive deterioration of its quality
2	Wu and Sun (2016)	Guanzhong Plain, mid-West China	Nitrate from a fertilizer industry name Shanhua	The study concluded that the over 60% of groundwater samples are not fit for drinking, and total hardness, nitrate, nitrite, TDS, and fluoride are the main contaminants degrading its quality for drinking purpose. Spatial variability of pollutants indicates the groundwater pollution by some anthropogenic point source
3	Li et al. (2016)	The Hutuo River plain, China	Iron, manganese, and other organic contaminants like CCl ₄ industrial sewage discharge, landfills, and mining	The study revealed that 21.5% of the groundwater samples collected are exceeding the Class III water standard, and these are concentrated in areas receiving industrial sewage discharge, mining water, or susceptible to landfill leakage
4	Kumar et al. (2016)	Coimbatore, Tamil Nadu, India	Mercury and arsenic from Kurichi Industrial Cluster	The study used atomic absorption spectrophotometry (AAS) using Perkin Elmer AA 200 model to evaluate the levels of Hg, As, and Cd based on Indian Standards-3025

2.3.2 Mercury (Hg)

It is a transition or post-transition metal found in liquid state at room temperature. It is injurious, even lethal, to most of the living organisms. Its contact via contaminated groundwater can cause damage to respiratory, neural, and renal systems. The fate and transport of mercury is governed by various physio-chemical process like oxidation–reduction, precipitation–dissolution, aqueous complexation, and adsorption–desorption reactions at soil–air–groundwater interface.

2.3.3 Organics Pollutants

They are the most common and deadliest pollutants released into the groundwater majorly from petrochemical and automobiles industries. While some of them can degrade, most of the organic pollutants are either non-biodegradable or will take years to attenuate naturally. Groundwater primarily polluted by volatile organic compounds (VOCs) like aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylene) and chlorinated solvents (tetrachloroethylene (PCE), trichloroethylene (TCE), and vinyl chloride (VC)). Extent of contamination by such pollutants is governed by geological controls (i.e., intrinsic vulnerability), the degree of concealment of aquifer, the hydraulic properties of the overlying soil and underneath aquifer system. The Karstic aquifers are predominantly at risk from diffuse and point sources of these pollutant due to constrained natural attenuation in the vadose zone during recharge.

2.4 Countermeasures

Groundwater pollution is a serious concern and must be addressed adequately for sustainable developments. Most of the regulatory and governing agencies become active only after the area is being affected by groundwater pollution. Some of the precautions that must be adopted for the perseverance of groundwater resources are shown in Fig. 2.2.

Fig. 2.2 Precautionary measures must be adopted to obtain safe and sustainable groundwater



It must be collective efforts of all including politicians, industrialists, and other common peoples to protect the precious natural resource. Table 2.3 lists some case studies that depict the methods used for checking the status of groundwater pollution throughout the world. Steps listed in Fig. 2.2 can be further explained as:

1. *Sampling and monitoring*: The groundwater samples should be collected periodically for detection of any possible pollutants. The sampling locations should be spatially and temporally well distributed so that they can represent the quality of whole aquifer system.
2. *Awareness toward environment*: Awareness activities and programs should be planned to encourage environmental concern in people. The committee forming the laws and legislation for environmental components must comprise local residents of the concerned area.

Table 2.3 Case studies conducting to detect the groundwater pollution status worldwide

S. no.	Reference	Study area	Technique used	Key findings
1	Zhua et al. (2018)	Guangxi Province, China	CCME WQI and PLEIK (P: Protective cover; L: Land use; E: Epikarst development; I: Infiltration conditions; K: Karst development) method is used for hazard influence	A 36.35% and 49.73% of the groundwater samples in Guangxi and Luzhai, respectively, are contained hazardous levels of pollution. The study finds Karst area to be more vulnerable
2	Kumar et al. (2016)	Uttar Pradesh, India	The study performed the spatio-chemical assessment and multivariate statistics analysis of groundwater samples	The area is found to be polluted severely by both geogenic and industrial pollutant. The hazard quotient (HQ) value exceeded the safe limit of 1 which for As, B, Al, Cr, Mn, Cd, Pb, and U at few locations while hazard index (HI) > 5 was observed in about 30% of the samples which indicated potential health risk from these tubewells for the local population if the groundwater is consumed
3	Shrestha et al. (2016)	Katmandu, Nepal	GIS based DRASTIC and GRAM models are used for groundwater vulnerability assessment to nitrate pollution	More than half of the valley is vulnerable to the groundwater pollution and 87% of the subsurface basin are at moderate residual risk to nitrate pollution
4	Akinbile and YusoFf (2011)	Akure, Nigeria	Three dimensional, i.e., physical, chemical, and bacteriological analyses of groundwater samples	The groundwater in area I severely polluted by heavy metals and pathogens. Physical water quality parameters are in recommended limits for most of the samples

3. *Integrated waste management approaches*: Sewage mismanagement, industrial effluents, and leachates from solid waste are primarily responsible for groundwater pollution. An integrated waste management approach can lead the world toward the goal of sustainable development.
4. *Effective legislations*: The world needs more effective and strict laws governing the groundwater use and safeguarding it from pollutants. These laws can be drafted and implemented on a national or even local scale but will be more effective if they have international binding.

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