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REVIEW

Recent Advances in Groundwater Vulnerability and Risk Assessment Using Hydrogeochemical Parameters

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ABSTRACT

Groundwater is critical for supplying drinking water to billions of people worldwide. However, their excessive permeability makes them more vulnerable to retaining and spreading contamination. Assessing groundwater vulnerability is crucial for sustainable management, as it aids in reducing the risks associated with contamination of this valuable resource. As a result, the primary aim of this paper is to critically review and synthesize recent advances in groundwater vulnerability and risk assessment using hydrogeochemical parameters. A summary of groundwater contamination, sources, and consequences is presented. Information on hydrogeochemical factors and groundwater vulnerability is summarised. A review of the most commonly used groundwater vulnerability assessment methods is covered. It also covers the assessment of groundwater vulnerability using hydrogeochemical parameters and statistical approaches. Furthermore, these approaches are supported by global case studies. Finally, the limitations, conclusion, and future recommendations are presented. It can be concluded that integrating hydrogeochemical parameters with groundwater vulnerability models is an effective method for assessing the risk of groundwater contamination and developing management plans. Researchers in the fields of health, earth sciences, environmental studies, and water sciences will find this comprehensive review to be a valuable reference,

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as it offers an in-depth understanding of the current knowledge on the integration of hydrogeochemical parameters in groundwater vulnerability and risk assessment studies.

Keywords: Water Resources; Pollution; Groundwater Vulnerability; Risk Assessment; Logistic and Linear Regression; Chemical Parameters

1. Introduction

Water resources are essential to maintaining the world economy, which is currently expanding quickly [1]. In order to provide drinking water to billions of people worldwide, groundwater is essential [2]. Groundwater is crucial for economic growth because of its great percentage, low pollution sensitivity, and enormous storage capacity [3]. It is essential to human existence; without it, life on Earth would not exist [4]. However, in this new era, groundwater pollution is caused by rapid development, population growth, urbanisation, expanding industrial sectors, massive fertiliser applications in irrigation, insufficient sewage systems, urban constructions, and animal and human waste [5–7]. The aquifer's vulnerability to such pollution is related directly to the hydraulic aquifer properties overburden and is significantly influenced by the characteristics of contaminant attenuation. It is also determined by the degree and extent of interactions between soil/aquifer characteristics and pollutants [8]. The sustainability of groundwater for irrigation, industrial processes, livestock, human consumption, and other uses is largely determined by its chemical composition [4].

The extent to which the water's physicochemical characteristics are altered influences not just the degradation of its quality, but it also poses a health threat to humans [9]. Risk assessment for groundwater contamination can explain the presence and distribution of risk, which aids in the development of pertinent policies in regions where possible pollution sources pose a threat [10]. Additionally, the probability of groundwater contamination due to specific concentrations of contaminants introduced into the ground surface can be used to express pollution risk [11]. It is considered a continuation of the assessment of groundwater's vulnerability [10]. Evaluating groundwater's vulnerability is a basic component of effective groundwater management [1]. The term "groundwater vulnerability" describes how sensitive groundwater is to shifts in both natural and human-induced factors. It illustrates how resilient the groundwater ecosystem is [12]. Depending on the type of contamination, groundwater may be intrinsically or specifically vulnerable. Hydrogeological factors determine intrinsic vulnerability, which allows contaminants to enter the groundwater and spread once they reach the surface [13]. The term "specific vulnerability" describes water's susceptibility to a group of pollutants or specific pollutants due to the characteristics of the contaminant, the attenuation process, and the transport [14]. To evaluate the risks and vulnerabilities of groundwater and to minimise the use of contaminated groundwater, different techniques have been established [15]. These consist of models that consider the physical, biological, and chemical processes in the unsaturated zones, as well as statistical techniques and indexing methods [16].

To estimate groundwater risk and vulnerability to pollution, the methods of index and overlay, namely: DRASTIC, GOD, AVI, SINTACS, and GALDIT, are frequently used [13,17]. These methods require the assessment of factors which are directly linked to the inherent characteristics of the aquifer system, including (i) aquifer media, (ii) net recharge, (iii) the water table depth, (iv) morphology, (v) aquifer thickness, and vi) vadose zone depuration capacity [18,19]. A robust and consistent model of vulnerability known as DRASTIC has been used all over the world to assess aquifer vulnerability to contamination and map an area's risky areas [19–23]. While most extant works on groundwater vulnerability rely on traditional vulnerability assessment methodologies, few studies have been undertaken that include hydrogeochemical characteristics [3,6,11]. By including hydrogeochemical characteristics into vulnerability assessment, conventional methodologies can be modified to provide a more full and precise risk estimate. These studies rely on identifying specific hydrogeochemical parameters, namely EC, Depth, pH, Salinity, As, F^-, NO_3^-, PO_4^{2-}, Na^+, Ca^{2+}, SO_4^{2-}, Mg^{2+}, HCO_3^-, Cl^-, and K^+, that influence contamination risk. The vulnerability of groundwater resources is then modelled and mapped using these parameters, which aids in comprehending and reducing possible pollution risks [1,3,24].

Therefore, incorporating hydrogeochemical parameters into groundwater vulnerability assessments is key as it enhances our understanding of contamination risks and supports the development of effective management strategies [25]. Predicting pollution risks, ensuring sustainable groundwater management, and preventing contamination are vital, especially in arid and semi-arid regions where rainfall is scarce and irregular. As groundwater serves as the key water source in these areas, safeguarding it against pollution and quality deterioration is indispensable [16].

Given this context, the primary aim of this paper is to critically review and synthesize recent advances in groundwater vulnerability and risk assessment using hydrogeochemical parameters. To achieve the aim of the study, the paper provides a review of groundwater contamination, sources, and consequences. The data on hydrogeochemical factors and groundwater vulnerability are summarised. A review of frequently utilized groundwater vulnerability assessment methods is presented. The assessment of groundwater vulnerability utilizing hydrogeochemical parameters and statistical methods is discussed. Furthermore, these approaches are supported by international case studies. Finally, limitations, conclusions, and future recommendations are presented. Understanding the quality of groundwater and the factors that influence it is essential for effective management and ensuring the long-term sustainability of this vital resource across various applications. Researchers in the fields of health, earth sciences, environmental studies, and water sciences will find this comprehensive review to be a valuable reference, as it offers an in-depth understanding of the current knowledge on the integration of hydrogeochemical parameters in groundwater vulnerability and risk assessment studies. Furthermore, this research serves as a foundation for future research into groundwater quality and vulnerability around the world.

1.1. Review Methodology

The primary aim of this paper is to critically review and synthesize recent advances in groundwater vulnerability and risk assessment using hydrogeochemical parameters. To achieve this aim, a variety of sources were consulted, specifically original research articles, editorial articles, review papers, scientific reports, and book chapters. These articles were retrieved from major international scientific databases such as Web of Science, Scopus, ScienceDirect, Directory of Open Access Journals, Google Scholar, ProQuest, SpringerLink, and Institute of Electrical and Electronics Engineers. The majority of the information came from studies focusing on groundwater vulnerability assessment. Research involving hydrochemistry and hydrogeochemistry was also taken into account. To locate relevant materials, search terms such as physicochemical parameters, groundwater vulnerability, risk assessment, water resources, pollution, logistic, and linear regression, as well as groundwater contamination were used. In addition, the words such as GIS, DRASTIC, GOD, AVI, SINTACS, and GALDIT were also considered. Only articles published in English were reviewed. This included papers published from 1987 to 2025.

2. Groundwater Contamination, Sources and Risks

The world's population depends heavily on groundwater sources for industrial, agricultural, and residential purposes. In areas that are arid as well as semi-arid with minimal surface and precipitation water, it is a valuable resource [26]. Providing a renewable and safe supply of groundwater for various uses is a critical driver of sustainable development in any country. However, human-caused activities and natural events present considerable hazards to groundwater quality [27]. Many pollutants in the groundwater are of geogenic nature, coming from the breakdown of natural deposits of minerals inside the Earth's crust [28]. However, the world's population growth, mining, urbanisation, industrialisation, and agricultural production—especially in countries with fast economic development—may also introduce them into groundwater [27]. These activities may cause groundwater contamination by chemical pollutants, which has been a common theme reported in groundwater over the last decades [29].

Groundwater pollution occurs when contaminants are released into the environment and enter the groundwater. It is described as the introduction of unwanted materials into groundwater resulting from human activity [27]. Radioactive, chemical, and biological contaminants are the three main categories into which the majority of the unwanted substances found in groundwater can be broadly divided [30]. These contaminants (chemicals) such as nitrogen (nitrate, nitrite, and ammonia nitrogen), anions and oxyanions (F^-, SO_4, and Cl^-, Ca^{2+} and Mg^{2+}), and toxic metals and metalloids

(Zn, Pb, Hg, Cr, Cd, Se, Fe, and As) pose a risk health of humans, long-term socioeconomic progress, and ecological services[31,32]. Since groundwater is in the geological strata's subsurface and has a long residence period, repairing is difficult and costly once it is contaminated[33]. The purification of mechanisms naturally in polluted groundwater may take many years, even after the cause of the pollution has been eliminated[34].

Contamination of groundwater is a worldwide problem that has a major health impact on humans as well as ecological services[27]. High concentrations of metals and metalloids can cause serious poisoning, organ damage, developmental problems, cancer risks, and neurological, gastrointestinal, and respiratory disorders, even though some of these chemical elements are necessary micronutrients in smaller amounts[27,35]. Furthermore, the land quality and forests can also be severely affected by the contaminated groundwater. It may result in contaminated soil and deteriorated land quality. The surface water quality can deteriorate due to groundwater contaminants being carried by surface water-groundwater interactions[36,37]. For economic development that is sustainable, a balance must be struck between human demand and the rate at which natural resources are replenished[26]. On the other hand, persistent groundwater contamination may result in less freshwater available, upsetting the supply and demand balance and triggering social unrest and even war[38]. As groundwater contamination affects both the environment and society, cooperation between social and natural scientists is necessary[27].

3. Hydrogeochemical Factors and Groundwater Vulnerability

Understanding how hydrogeochemical factors impact water quality and resource availability is essential because they have a significant impact on groundwater vulnerability. Geological formations, water-rock interactions, human activity, and climate change are some of these variables that can change the chemical composition and cause contamination. For efficient groundwater management and protection, it is essential to comprehend these relationships[6,39,40].

Geological Influence: The chemistry of groundwater can be greatly influenced by the kind of rocks present in an aquifer. For instance, silicate rocks contribute to other ions and trace elements, whereas carbonate rocks dissolve and increase the concentrations of bicarbonate ions, calcium, and magnesium. Because they can control groundwater distribution and possibly concentrate pollutants, geological features like faults and fractures are also significant. Furthermore, the rate at which the contaminants can get to the water table is dependent on an aquifer's permeability, porosity, and depth[41].

Water-Rock Interaction: Water chemistry can change as a result of minerals from rocks and sediments being dissolved by groundwater. On the other hand, minerals may separate from the solution and form scales or alter the composition. High levels of toxic elements are transferred to water and soil (ground and surface water) by water-rock interaction processes[42]. Furthermore, ions on mineral surfaces can exchange with cations and anions in groundwater, changing the chemical composition. During processes involving water-rock interaction, variations in water geochemistry may result from the distinct geochemical behaviour of various elements[43]. Numerous geochemical processes, namely: oxidation, reduction, ion exchange, competitive adsorption, weathering, and dissolution, occur during water–rock interaction[44].

Anthropogenic Activities: The hydro-geochemical behaviour of groundwater can also be significantly influenced by anthropogenic activities like urbanisation, agriculture, industry, and mining[45]. Vulnerability of groundwater aquifer and contamination threats among the anthropogenic environment are increased by the complex interactions between the hydrological system's natural mechanisms and physical land surface changes, human-caused discharge of waste, and the manipulation of water resources[46]. The vulnerability of the systems groundwater is also increased by physical landscape changes, such as topography changes, man-made bodies of water, river channelling, construction, sealing of the surface, and variations of surface ruggedness[26]. As a result of contamination and depletion, they greatly increase the vulnerability of groundwater. They have the potential to increase extraction rates or introduce contaminants (such as metals, nutrients, salts, and pesticides) into groundwater aquifers[47].

Climate Change: By changing precipitation patterns, temperatures increase, and the frequency of severe weather events increases, making groundwater more vulnerable.

These modifications affect groundwater quality, recharge, and levels, increasing its vulnerability to contamination, depletion, and scarcity. Droughts and floods can also alter the quality of water and possibly introduce pollutants [48].

The removal of the source cannot improve groundwater quality once it has been adversely impacted by the presence of pollutants [6]. This is because contaminants in groundwater can linger for a very long time, even after the pollution source has been eliminated. Thus, careful monitoring is essential to managing groundwater quality and, consequently, to maintaining both human health and healthy aquatic ecosystems [4,49,50].

4. Groundwater Vulnerability Assessment Approaches

Numerous methods for assessing aquifer vulnerability have been created worldwide. They encompass statistical techniques that use variables related to contaminant concentration or probability, index methods that weight various criteria influencing vulnerability, and biological, chemical, and physical processes considered by models in the saturated zone [16].

4.1. Groundwater Vulnerability and Contamination Risk Assessment Methods

Process-based, parametric, sensitivity, statistical, index/overlay, and hydrogeological complex and setting techniques are some of the techniques that were established for groundwater vulnerability evaluation [51–53]. Among these methods, the index and overlay methods, namely DRASTIC, GOD, AVI, SINTACS, and GALDIT, are commonly applied to estimate groundwater risk and vulnerability to pollution [17,18]. Therefore, this subsection provides a detailed description of these commonly used vulnerability and risk assessment methods.

4.1.1. Overlay/Index Methods

These methods are relatively easy to use by combining different maps that show the depth to the water table, soil, and geology. They then map the physical and man-made characteristics of the area by giving each feature a numerical rating [51]. A composite sensitivity or vulnerability score is produced by combining these ratings [54]. DRASTIC, GOD, AVI, SINTACS, and GALDIT are some of the overlay/index techniques [52,55,56].

DRASTIC Method

It is the most common overlay and indexing technique globally [13]. Aller et al. [57] developed it for regional vulnerability assessments. It uses established hydrogeological parameters to evaluate the possible pollution of a given area. Three primary parts make up this model: parameter weights, rating system, and hydrogeological parameters [58]. The abbreviation DRASTIC refers to seven hydrogeological factors of the model: depth to water (D), net recharge (R), aquifer media (A), soil media (S), topography (T), impact of the vadose zone (I), and hydraulic conductivity (C) [53]. A scale of 1 to 10 is used to rate each factor, where 1 denotes the least vulnerability and 10 the greatest. Furthermore, relative weights are assigned to these hydrogeological factors on a scale of 1 to 5, with 5 being the most significant and 1 being the least significant [13]. The vulnerability index is computed by the application of a linear equation to weights and ratings of every parameter, as indicated in Equation (1) [57]:

$$DR_i = D_w D_r + R_w R_r + A_r A_w + S_r S_w + T_r T_w + I_w I_r + C_w C_r \quad (1)$$

where DRi represents the DRASTIC vulnerability index, D, R, A, S, T, I, and Cs represent the model's seven parameters; w represents the allocated weight of the DRASTIC parameter; and r represents the allocated rate for the particular DRASTIC parameter [53]. Its advantages include the ability to evaluate a zone based on its current conditions without the need for site-specific, comprehensive contamination data. This provides a basis for evaluating the susceptibility of groundwater sources to contamination, centred on hydrogeological factors, and an economical way to identify areas that may necessitate additional research. Despite its benefits and popularity, the DRASTIC vulnerability mapping technique has several drawbacks. Its main flaw is its particular nature, which raises questions about why some factors were chosen while other were excluded [59]. The DRASTIC had been modified to include risk and contamination in its index. This resulted in a series of modified DRASTIC indexes that are now used around the world. A few of the modifications include application to investigate the effect of acid mine drainage (AMD) [60], addition of contaminant originating from land use impact [61], and modification to the Pit

Groundwater Vulnerability to Pollution Index (PGVPI)[62].

GOD Method

It was suggested by Foster[63]. It considers the groundwater occurrence type (G) (none, confined, unconfined), the lithology that lies on top of it (O) (loam, gravel, sandstone, limestone), and the groundwater table depth (D). God has a score between 0 and 1. The three factors are multiplied to calculate the overall value of vulnerability assessment, which ranges from negligible (0.0) to extreme (1.0). The GOD method's primary advantage is that it applies to all aquifer types, except for karst regions. Another issue with using this technique in a karst environment is the distinct features of epikarst and vertical shafts. Other disadvantages include an overestimation of factor D; i.e., a depth of 100 meters below the water table is classified as moderately vulnerable (0.4)[52].

AVI Method

Van Stempvoort et al.[64] developed the Aquifer Vulnerability Index (AVI) as an additional method for evaluating aquifer vulnerabilities. AVI's methodological strength is based on vadose zone classification, which has been recognized as a crucial parameter in vulnerability assessment of the aquifer[65]. It is closely linked to the physical characteristics of the vadose zone[52]. Vulnerability of the aquifer is calculated by AVI using hydraulic resistance (c), which is a ratio of the estimated hydraulic conductivity (K) of each sedimentary unit above the topmost aquifer (d) to the thickness of each sedimentary unit. The c is computed by Equation (2):

$$c = \sum_{i=1}^{n} \frac{d_i}{k_i} \tag{2}$$

where sedimentary units above the aquifer are represented by *n,* the vadose zone's thickness is represented by d_i; the hydraulic conductivity of each protective layer is represented by K_i, the unit of length/time is K; and the travel time with dimension in seconds is c. Hydraulic resistance c connotes an inverse indicator of vulnerability. This represents the downward flow of water via the shielding strata. This is a rough estimate of water's vertical travel time through unsaturated layers. It is imperative to consider that AVI does not take into account noteworthy parameters that control travel time, such as hydraulic diffusion and gradient, which is one of the most significant drawbacks of the method of AVI. The AVI method is not considered a complete vulnerability method. Other limitations include the c is hydraulic resistance of water, which is not the only factor repelling water flow, and the method is overly simplified[52]. According to Connell and Daele[66], the method of AVI is among the best and may be the best fit for a vulnerability assessment of a large regional-scale, even though many methods take into account the processes taking place in the vadose zone more precisely.

SINTACS Method

The SINTACS method is a variant of the DRASTIC method that was designed in the 1990s to tackle hydrogeological differences[53]. It belongs to the class of system models of point count, like SINTACS, where every element is given an additional weight and a score to modify its analytic importance. Environmental factors like substantial dispersion from surface water to groundwater or pervasive contamination sources affect this weight[67]. This method identifies several key vulnerability parameters, including water depth (S), effective infiltration (I), unsaturated zone (N), soil media (T), aquifer media (A), hydraulic conductivity (C), and topographic slope (S)[68]. The SINTACS framework is more multifaceted than the DRASTIC model owing to the various methods for evaluating and weighting its parameters. SINTACS meticulously allocates rates and weights to account for all ecological aspects linked with the model's seven variables, which differ based on local hydrogeological state. As a result, SINTACS offers extra flexibility in parameter scoring and weighting than the DRASTIC model. Equation (3) is utilised to estimate the SINTACS vulnerability index (SIv), which involves adding the ratings for each of the seven parameters and their corresponding weights. P_i = a rating for the i^{th} parameter; W_j =a weight of the j^{th} weight classification. It is worth noting that the greater the SI_v value, the greater the vulnerability[69].

$$SI_v = \sum_{i=1}^{7} (P_i W_j) \tag{3}$$

GALDIT Method

Chachadi and Lobo-Ferreira[70] developed this open-ended additive model with six parameters comprising aquifer type: unconfined, confined, or leaky confined (G); aquifer hydraulic conductivity (A); depth to the groundwater level relative to sea level (L); distance from the shore (D), effect of current seawater intrusion in the area (I), and thickness of the aquifer (T). According to Mirzavand et al.[71], its constituents are quantifiable parameters for which data is accessible from numerous sources. Based on their importance in connection to seawater intrusion, each of the six indicators is given a set weight. Using the formula given in Equation (4), the GALDIT Index is computed by estimating the values for each indicator and their summation. W_i and R_i are the weight and rating of the i^{th} indicators, respectively[72].

$$GLADIT - Index = \frac{\sum_{i=1}^{6} W_i R_i}{\sum_{i=1}^{6} W_i} \quad (4)$$

Numerous scholars have applied these methods to determine the groundwater's contamination risk. In order to increase the rating system's efficacy, some researchers have also made improvements to it[42,73]. A case in point, Sujitha et al.[72] evaluated aquifer vulnerability in Gao State, India, using the GALDIT method. They observed that the northern region was more vulnerable to contamination than the southern region, and they discovered moderate to low levels of pollution. Using the DRASTIC index, Arya et al.[20] assessed the semi-arid Vattamalaikarai River Basin's groundwater vulnerability to contamination. The area was separated into "high," "moderate," and "low" groundwater contamination risk zones using the vulnerability map. The areas of "high" vulnerability were linked to the shallow and pervious aquifer formations, while most of the basin was at moderate risk for pollution. Aboulouafa et al.[56] used remote sensing and GIS, together with the DRASTIC and SINTACS methods in Morocco's Berrechid basin. A sensitivity analysis showed that, according to the DRASTIC method, "topography," "aquifer media," and "hydraulic conductivity" were the main factors influencing the region's highest risk of groundwater contamination, even though the maps created by the two approaches were almost identical. Two factors that indicated a higher risk of contamination for the SINTACS method were "depth to water level" (S) and "aquifer media." Additionally, DRASTIC, a robust and standardised vulnerability model, has been used globally to map the hazardous zones in specific areas and assess aquifer vulnerability to pollution[19,20,22,74] (**Table 1**).

Table 1. Application of groundwater vulnerability and risk assessment methods.

Studies	Method	Research Results	Author
Regional Aquifer Vulnerability and Pollution Sensitivity Analysis of DRASTIC Application to Dahomey Basin of Nigeria	DRASTIC	In the basin, 21% was classified as high-vulnerability and at risk of pollution, 61% as moderate vulnerability, and 18% as low vulnerability.	Oke[13]
Aquifer vulnerability valorization via DRASTIC index-based assessment within litho-facies of a coastal environment	DRASTIC	The method showed that the aquifer indicated moderate to high vulnerability to contamination.	Udosen et al.[19]
Groundwater vulnerability to pollution in the semi-arid Vattamalaikarai River Basin of South India through DRASTIC index evaluation	DRASTIC	The study area was divided into zones of 'high', 'moderate', and 'low' groundwater pollution risks.	Arya et al.[20]
SINTACS and DRASTIC Models for Groundwater Vulnerability Assessment and Mapping using a GIS and Remote Sensing Techniques: a Case Study on Berrechid Plain	SINTACS and DRASTIC	The two models showed a low to average vulnerability. However, by overlaying the map of distribution of Nitrate on the two maps, we find that the SINTACS model gives the best result with two classes of vulnerability (low and average).	Aboulouafa et al.[56]
DRASTIC: a standardized system for evaluating groundwater pollution potential using hydrogeologic settings	DRASTIC	The result illustrated four vulnerability classes based on DRASTIC models, including very low (34%), low (13%), moderate (48%), and high vulnerability (5%).	Aller et al.[57]
Vulnerability mapping of shallow groundwater aquifer using the SINTACS model in the Jordan Valley area, Jordan	SINTACS	The SINTACS vulnerability map of the study area indicated that the highest potential sites for contamination are along the area between Er Ramah and the Kafrein area.	Kuisi et al.[67]
Saltwater intrusion vulnerability assessment using the AHP-GALDIT model in the Kashan plain aquifer as a critical aquifer in a semi-arid region	AHP-GALDIT	Based on this method, the area was rated as 16.16, 25.51, 21.26, and 36.05% which denote high, average, low, and very low vulnerability, respectively.	Mirzavand et al.[71]

Table 1. *Cont.*

Studies	Method	Research Results	Author
Assessment of Aquifer Vulnerability Using GALDIT Model — A Case Study	GALDIT	The results obtained by the GALDIT model showed that about 42% of the wells in the study area were of low vulnerability and 58% of the wells were moderately vulnerable to seawater intrusion.	Sujitha et al.[72]
Modification of the GALDIT framework using statistical and entropy models to assess coastal aquifer vulnerability	GALDIT	The study concluded that the proposed GALDIT framework showed a more accurate estimation of vulnerability distribution in coastal aquifers.	Bordbar et al.[73]

4.2. Hydrogeochemical Parameters for Modelling Groundwater Vulnerability

Hydrogeochemical parameters play a crucial role in vulnerability assessment by providing information on the chemical composition of the groundwater. Water chemistry, aquifer characteristics, and the relationship between groundwater and geological formations are examples of hydrogeochemical parameters that are essential for vulnerability of the groundwater modelling. These parameters, including Depth, pH, EC, Salinity, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, HCO_3^{-}, NO_3^{-}, SO_4^{2-}, PO_4^{2-}, F^{-}, As, and TDS, can be used to identify groundwater vulnerability for modelling[1,24]. They are crucial for assessing the groundwater's quality and vulnerability since they offer concrete proof of past and present contamination[75,76]. Chemical parameter data display the concentration of the actual pollutant as well as its spatial distribution, in contrast to physical parameters that indicate potential vulnerability[77]. They can also be used to comprehend hydrogeological processes, find possible sources of pollution, and evaluate the general condition of the water resource[78]. While high levels of arsenic indicate geogenic contamination, high levels of nitrate are typically associated with agricultural runoff[79]. The presence of several contaminants suggests a mixed source of pollution, necessitating integrated management techniques[80]. Consequently, data on hydrogeochemical parameters are crucial for improving and confirming the vulnerability models[81]. These variables are frequently combined with other elements, such as soil composition, aquifer characteristics, and land use, to produce vulnerability maps or indices that aid in determining the likelihood of groundwater contamination[1,25]. They support risk maps for the emergence of contamination and water quality indices[82]. This is particularly crucial for making well-informed decisions. They provide early warning signals for intervention and help identify new threats. However, this calls for trend analysis and consistent observation. To evaluate and map groundwater vulnerability, these parameters are frequently combined with other modelling approaches, including statistical analysis and index-based approaches[83].

Many studies have integrated hydrogeochemical parameters with some of the vulnerability techniques. For example, in the basin of Bangladesh, studies have found widespread contamination of arsenic, which highlighted the role of natural geological processes in determining groundwater vulnerability. To identify the zones at high risk, researchers utilized an integrated approach of GIS-based mapping and field sampling[82]. In semi-arid areas of Iran, techniques that involve multivariate statistics have been used for groundwater vulnerability evaluation. By integrating chemical parameters like sulfates and fluoride with DRASTIC, the study demonstrated improved predictive power and model accuracy[84]. In Nigeria's Basement Complex Area, shallow groundwater was also hydro-geochemically characterised and its vulnerability evaluated. The use of NPK fertiliser for agricultural purposes in the region was associated with high K concentrations, according to the study. Additionally, the DRASTIC model showed that, given the current environmental circumstances, the area's groundwater is less susceptible to contamination[39]. Fifteen hydro-chemical data points were used for modelling in the Holocene multi-aquifers of the Ganges delta in Bangladesh. The vulnerability map's spatial distribution shows that, in terms of As and F^{-} F-F-concentrations, some areas were extremely vulnerable[2]. The Guanzhong Basin in China was assessed for intrinsic vulnerability using a modified DRATICL model. The model results were validated using hydrogeochemical parameters, including Fe, Cl^{-}, SO_4^{-}, F^{-}, COD, NO_3^{-}, NO_2^{-}, and TDS. The region had both high pollution loading and high vulnerability[85]. The aquifer vulnerability index method, combined with chemical parameters such as pH, EC, COD, BOD5, Ca, Mg, K, Na, SO4, Cl, Pb, Cu, Cd, Zn, Cr, Ni, and Fe, was used for groundwater modelling in the Niger

Delta, Nigeria. The study concluded that the location around the dumpsite showed low groundwater vulnerability [6]. The DRASTIC model was also used to analyze aquifer vulnerability and identify the hydrogeological conditions in Khyber Pakhtunkhwa, Pakistan. Vulnerability index concentrations showed 54.01% for high vulnerability, and concentration of Nitrate above 10 ppm, representing some anthropogenic influence [50]. In India, nitrate concentration was used to validate the DRASTIC and modified DRASTIC methods for assessing groundwater vulnerability. About 29.98% of the region is in a very high vulnerability zone, based on data on groundwater vulnerability to pollution. The amount of nitrate in the groundwater further supported these findings [86]. The utilization of hydrogeochemical parameters in vulnerability mapping has the potential to assist in policy development and land use planning. Moreover, it emphasizes the importance of monitoring systems that are integrated [85].

4.3. Statistical Approach for Modelling Groundwater Vulnerability

Data and statistical techniques are used in a statistical approach for modelling the vulnerability of the groundwater in order to study how susceptible groundwater resources are to contamination. When media data (e.g., land use, hydrogeological data, and soil properties) are connected to groundwater quality data, they offer a practical way to evaluate aquifer vulnerability. They frequently concentrate on the connections between pollution levels and environmental factors. Simple graphic statistics of the contaminants' concentrations or more intricate deteriorating analyses that consider the impacts of multiple descriptive variables are examples of these techniques [87]. In most rigorous statistical analyses, including logistic regression, additional data and information are usually included as possible sources of contamination, as well as the factors influencing the intrinsic susceptibility of resources. These strategies provide an alternative to conventional index-based techniques, enabling a more sophisticated comprehension of vulnerability grounded in anthropogenic influences and observed data. To improve or validate their findings, statistical methods can be combined with other vulnerability assessment approaches like the DRASTIC or process-based models [88]. Common statistical techniques used in groundwater vulnerability assessment:

Logistic Regression: Though it can estimate the possibility of pollutant occurrence rather than concentration, it is conceptually comparable to multiple linear regression (i.e., it determines whether something is true or false instead of forecasting something continuous) [89]. Logistic regression is a valuable method used to determine the probability of a categorical outcome based on input variables, making it useful across many fields. A popular statistical technique in groundwater vulnerability studies is logistic regression, which is particularly useful for forecasting the possibility of groundwater contamination as a categorical result (e.g., "vulnerable" vs. "not vulnerable"). It is perfect for risk classification tasks because, unlike linear regression, it models binary or categorical outcomes. It is used to categorise regions according to a range of hydrogeological and environmental factors into high-risk or low-risk zones for groundwater contamination. For instance, a logistic model may use predictors such as proximity to agricultural areas, type of land use, and the depth of the water table to determine whether a location is "vulnerable" or "not vulnerable" to nitrate contamination. In groundwater vulnerability studies, logistic regression is a useful and efficient technique for categorical risk prediction. It provides unambiguous insights into the likelihood and causes of contamination, facilitating good decision-making for the management and protection of water resources. Its simplicity, interpretability, and applicability to binary classification problems are its main advantages [87].

Multiple Linear Regression: Multiple linear regression is a statistical technique used to analyze the relationship of a single dependent variable and two or more independent variables, enabling predictions based on several influencing factors. Its primary aim is to represent the linear connection between the independent (explanatory) variables and the dependent (response) variable. When a plane is fitted to the data, it can predict a pollutant's level and assess the relationships between one dependent variable and various independent factors. A basic statistical technique that is frequently applied in environmental sciences, such as groundwater vulnerability studies, is multiple linear regression [89]. It aids in comprehending and measuring the relationship between several independent variables (such as depth to the water table, land use, and soil type) and a dependent variable (such as the level of contamination). By simulating the correlation between influencing parameters and vulnerability scores (or contamination risk levels), it can be utilised to create vulnerability indices or classifications. For instance, by combining factors like recharge rate, aquifer type, and proximity to pollution sources, it can be used to estimate a vulnerability index. Multiple Linear Regression's ease of use, interpretability, and capacity to measure correlations between numerous variables make it an invaluable instrument in groundwater vulnerability studies. It is still a popular and reliable method for risk assessment, factor analysis, and prediction in groundwater research, even though it might not be able to capture complex nonlinear interactions like sophisticated machine learning models [87].

Bayesian Belief Networks (BBNs): It is an artificial intelligence also known as neural networks [89]. These are probabilistic graphical models that depict both provisionally independent and provisionally dependent relationships of random variables. They are made up of directed edges and nodes. They permit concluding observations. Because they can handle uncertainty, incorporate expert knowledge, and model intricate, probabilistic relationships between variables, it has grown in popularity as a tool in vulnerability studies of groundwater. To determine how susceptible groundwater is to contamination, BBNs combine a number of hydrogeological, environmental, and land-use factors. By producing probabilistic maps that highlight high-risk areas, these models assist policymakers in setting priorities for protection and monitoring initiatives. It provides a strong and adaptable framework for comprehending and controlling groundwater vulnerability, particularly when there are many interrelated variables and uncertainty. Their application promotes more knowledgeable, open, and flexible water resource management and increases the validity of assessments [90,91].

Fuzzy Logic: It is an artificial intelligence method. Its foundation is the theory of fuzzy sets, which develops its logic as a foundation for inference rules by using the entire range of real numbers between zero and one (i.e., false and true). Because fuzzy logic can deal with imprecision, ambiguity, and uncertainty (all of which are prevalent in environmental systems and data), it is frequently used in groundwater vulnerability studies. Vulnerability maps that highlight regions with a higher risk of contamination are created using fuzzy logic. It uses fuzzy membership functions to represent the influence of several hydrogeological factors (such as recharge rate, soil type, and depth to water table). It can be used to create fuzzy vulnerability indices that evaluate groundwater vulnerability more flexibly than conventional models, such as Fuzzy-DRASTIC or Fuzzy-SINTACS [92].

Neuro-Fuzzy: This approach, known as the neuro-fuzzy model, combines two neural network and fuzzy logic techniques to support the development of a fuzzy system by using heuristic learning strategies based on neural network theory. Neuro-fuzzy systems combine fuzzy logic's reasoning and uncertainty-handling powers with artificial neural networks' capacity for learning. This hybrid approach is especially useful for modelling complex, uncertain, and nonlinear environmental systems in groundwater vulnerability studies. Detailed maps demonstrating the spatial distribution of vulnerability within a region are produced using neuro-fuzzy models. These models can handle the ambiguity present in natural systems while learning patterns from environmental and historical data. For instance, areas with a high risk of groundwater contamination can be predicted using a neuro-fuzzy model trained with information on land use, aquifer characteristics, rainfall, and contamination incidents [93].

Random Forest (RF): It is a supervised machine learning algorithm that utilises decision trees as base learners. Groundwater vulnerability studies frequently employ random forest, a potent ensemble machine learning algorithm, because of its high prediction accuracy, capacity to handle large datasets, and ability to model nonlinear relationships. By learning from a variety of environmental and hydrogeological factors, including soil type, depth to the water table, land use, recharge rate, and pollution levels, they are widely used to create spatial vulnerability maps. Areas can be accurately classified as low, medium, or high vulnerability zones using an RF model that has been trained on known contamination cases and associated input features [94].

Many studies have found that statistical methods provide a feasible way to assess aquifer vulnerability. For example, Tesoriero and Voss [95] utilised logistic regression to determine the aquifer's susceptibility and groundwater vulnerability to pollution in Washington, United States of America. Moreover, logistic regression was also used to evaluate groundwater vulnerability to heavy metals [96] and nitrate [97,98] in the United States of America. Multiple linear regression has been applied to evaluate groundwater vulnerability to nitrate in the United States of America [99] and arsenic concentration in Portugal [100]. A systematic review study by Fannakh and Farsang [88] reported that logistic regression and multiple linear regression are frequently used statistical techniques in the assessment of vulnerability. In Ardabil, Iran, the evaluation of groundwater vulnerability to nitrate was performed using DRASTIC indices combined with fuzzy logic. In this study, the estimated DRASTIC vulnerability and nitrate-N values improved significantly by fuzzy logic models[101]. In the Illinois River Watershed, United States of America,[93] predicted groundwater vulnerability using integrated GIS-based neuro-fuzzy techniques. The developed model has the potential to facilitate groundwater vulnerability modelling at a regional scale, as validated by the model using nitrate-N concentration data. The random forest is a data-driven technique that has recently become more significant in applications involving water resources[102,103]. Additionally, the Vega de Granada aquifer in southern Spain has been subjected to intrinsic and specific vulnerability assessments using random forest[102]. Groundwater vulnerability assessment, hydrogeology, and environmental sciences have all successfully used artificial neural network models to predict risk and hazard. For instance, Sirat[104] evaluated the level of pesticide contamination in the US Mid-continent's groundwater by applying artificial neural networks to data from 1302 wells of residential and rural hydraulic systems.

5. Challenges and Limitations in Groundwater Vulnerability and Risk Assessment Using Hydrogeochemical Parameters

A comprehensive framework for identifying contamination risks and implementing sustainable water management practices is provided by incorporating hydrogeochemical parameters into groundwater vulnerability and risk assessment studies. However, there are a number of significant obstacles to overcome, such as inconsistent and limited data availability, mismatches in spatial and temporal scales, and substantial uncertainties in parameter interpretation and model assumptions[11,13,18]. The intricacy of groundwater systems, in addition to the high expense and logistical challenges of thorough hydrogeochemical monitoring, frequently restricts the precision and regional applicability of models[52]. Additionally, in many areas, data on groundwater quality (such as EC, Depth, pH, Salinity, As, F^-, $NO_3{}^-$, $PO_4{}^{2-}$, Na^+, Ca^{2+}, $SO_4{}^{2-}$, Mg^{2+}, $HCO_3{}^-$, Cl^-, K^+, and nitrate is frequently unavailable, inconsistent, or out-of-date. Because of the computational needs and lack of established methodology, integrating chemical and physical groundwater processes necessitates complex, multidisciplinary approaches that are not always practical. These drawbacks emphasize how groundwater risk assessments require better data gathering, model calibration, and interdisciplinary cooperation[8,52,85].

6. Conclusion

The primary aim of this paper was to critically review and synthesize recent advances in groundwater vulnerability and risk assessment using hydrogeochemical parameters. The study findings showed that although there are some challenges and limitations, groundwater vulnerability assessment utilizing hydrogeochemical parameters gives a broad framework for identifying contamination risks and implementing sustainable water management practices. It also showed that understanding the hydrogeochemical methods that influence the chemistry of the groundwater is essential for effective groundwater resource management. The study also showed that groundwater vulnerability assessment utilizing hydrogeochemical parameters is useful in identifying pollutants and highlighting processes and pathways that affect groundwater quality. It can be concluded that, by combining these parameters with vulnerability models, the accuracy of risk assessments can be greatly improved. Moreover, integrating hydrogeochemical parameters with groundwater vulnerability models is an effective method for assessing the risk of groundwater contamination and for developing management plans. It offers a more complete understanding of groundwater vulnerability, resulting in better protection of this valuable resource. Researchers in the fields of health, earth sciences, environmental studies, and water sciences will find this comprehensive review to be a valuable reference, as it offers an in-depth understanding of the current knowledge on the integration of hydrogeochemical parameters in groundwater vulnerability and risk assessment studies. It is advised that researchers at universities, government agencies, businesses, and government decision-makers work closely together to address groundwater contamination because it is a worldwide problem. Governments, especially those in developing economies, must invest in and promote groundwater science research and training. It should also restrict future land development, drilling production, industrial effluent discharge, and the construction of high-loading factories in "double high" areas. The establishment and enhancement of vulnerability assessment methods built on statistical analysis and machine learning should be the main focus of future research.

Author Contributions

Conceptualization, I.M.M., S.A.O., L.E., and I.M.; methodology, I.M.M., S.A.O., L.E., and I.M.; formal analysis, I.M.M., S.A.O., L.E., and I.M.; investigation, I.M.M., S.A.O., L.E., and I.M.; data curation, I.M.M., S.A.O., L.E., and I.M.; writing—original draft preparation, I.M.M. and I.M.; supervision, S.A.O. and L.E.; writing—review and editing, I.M.M., S.A.O., and L.E., I.M. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

All the data generated and analysed during the current study are available in the manuscripts.

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Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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