water

Review

Research Trends in Groundwater and Stable Isotopes

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Abstract: Groundwater is essential in the management of water resources globally. The water quality of aquifers is affected by climate change and population growth, aspects that can be addressed with stable isotope analysis. This study aims to carry out an analysis of the scientific information related to groundwater and stable isotopes (GSI) using scientific databases (Scopus and Web of Science) to evaluate the intellectual structure of the subject and the emerging research lines. The methodology includes: (i) topic search selection, (ii) tools in databases processing, (iii) bibliometric analysis, and (iv) review by clustering technique. The results showed that the scientific production of GSI can be addressed through three evolution periods: I (1969–1990), II (1991–2005), and III (2006–2021). Periods I and II did not significantly contribute to publications because, in the past, most of the student's thesis (M.Sc. and Ph.D) consisted of writing a report that summarizes their works. Therefore, the researcher was not obliged to publish their results in a professional journal. Finally, the third period showed exponential growth, representing 82.34% of the total publications in this theme because, in the last years, institutions require at least one scientific article depending on the country and university, in order to graduate with an M.Sc. and PhD. Finally, the contribution of this study is reflected in the recognition of new research lines and their applicability by the knowledge of recharge sources, environmental aspects, infiltration, knowledge of the aquifer-meteoric water system, and groundwater-superficial water interaction. These aspects offer the possibility of analyzing integrated water resources management at the watershed or river-aquifer systems level.

Keywords: coastal aquifer; environmental isotopes; intellectual structure; co-citation analysis

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1. Introduction

Groundwater is one of the most important resources in the freshwater supply to meet the needs of a region [1,2]. Globally, 2.5 billion people depend on groundwater supplies for their basic needs [3–5]. Groundwater and surface water constitute a complex cycle in the atmosphere, the earth's surface and the soil [6,7]. A challenge in the sustainable management of groundwater resources is the lack of comprehensive studies that involve the quantification of groundwater depletion and aquifer deterioration [8]. Identifying aquifer quality and vulnerability characteristics helps decision-makers manage groundwater resources and mitigate potential contamination pathways [9,10] where these ecological techniques of green filters exist [11–13].

The most crucial water problem facing the world is water scarcity, intensifying during the 21st century due to population and economic growth and the need to protect environmental assets [14–16]. The characterization of groundwater flow systems requires the identification of the dominant spatial and temporal patterns of their movement and flow scales [17–19].

The main processes that influence groundwater chemistry are salinization, precipitation, mineral dissolution, cation exchange and human activity [20]. Therefore, stable isotope data in water ($\delta^{18}O$ and $\delta^{2}H$) serve as markers to identify the different flow paths and origins of water [21]. Interactions between groundwater and surface water are complex because they are related to climate, landform, geology, and biotic factors [22,23]. Therefore, hydrogeochemical data and stable environmental isotopes are used to identify recharge sources and water-rock interactions in the direction of groundwater flow [24,25].

The relevance of the stable isotope technique resides in that the most commonly studied elements (H, C, O, and S) constitute the major components of Earth's reservoirs (water, air, lithosphere, and organic matter) [26,27]. For example, hydrogen and oxygen isotopic studies of natural waters have a distinct advantage over studies using other chemical indicators due to hydrogen and oxygen being the principal constituents of aqueous solutions [28].

As a consequence, applying stable isotopes in groundwater has multiple benefits. For example, a study in Japan used stable water isotopes ($\delta^{18}O$ and $\delta^{2}H$) and hydrochemical information to estimate groundwater recharge in a mountain-plain transition area [29]. In the Maheshwaram watershed in India, these isotopes were used to understand the dynamics of groundwater sources and flow paths in the watershed [30]. Complementarily, in the case of the Qaidam basin in China, the implementation of representative cations and anions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, $HCO_3{}^-$) and isotopes (^2H, ^{18}O, ^3H, ^{13}C and ^{14}C) improved the understanding of the origin, flow pattern, hydrochemical evolution, and control mechanisms of regional groundwater systems [31]. Finally, relationships between $\delta^{2}H$ and $\delta^{18}O$ values in precipitation and elevation represent helpful tools for evaluating groundwater recharge areas and flow paths [32].

Given that the importance of isotopic analyses in groundwater would complement a bibliometric study on this subject, groundwater and stable isotopes (GSI). Bibliometrics provides a clear and precise answer to a global analysis of a given country, journal or field of study [33–35]. In addition, these bibliometric studies allow for the exploring of the structure of scientific publications, collaboration patterns and outstanding areas of knowledge [36,37]. Various research fields have applied bibliometrics in the evaluation and prediction of scientific productivity, development and future trends [38–42].

This theme is of global interest for watershed management authorities and its inhabitants, whose main economic activities often depend on groundwater reserves. For this reason, some research questions have arisen about the relationship between stable isotopes and groundwater: what is the contribution of the theme (GSI) in scientific research, emerging methods and trends?; and, complementary to this, what are the most representative components of the intellectual structure and relationships of GSI (authors, documents, topics, countries and journals) and the topics associated with this structure?

Answering these research questions was purposed as an objective to carry out an analysis of the scientific information related to GSI using scientific databases (Scopus and WoS) to evaluate the intellectual structure of the subject and the emerging lines of research.

This work consists of five sections. The first contains an introduction to the applicability of stable isotope techniques in groundwater evaluation. Section 2 presents the methodology for the treatment and use of the data described in four phases (search and document selection, database treatment, bibliometric maps, and research trend analysis). Section 3 presents the intellectual structure of stable isotopes, groundwater and the analysis of publications related to the subject, according to their quantity and quality. Section 4 presents the discussion of the exposed analyses. Finally, Section 5 presents the main conclusions, findings and limitations of this study.

2. Materials and Methods

The methodology includes four research phases: (i) topic search selection, (ii) tools in databases processing, (iii) bibliometric analysis, and (iv) review by clustering technique (see Figure 1).

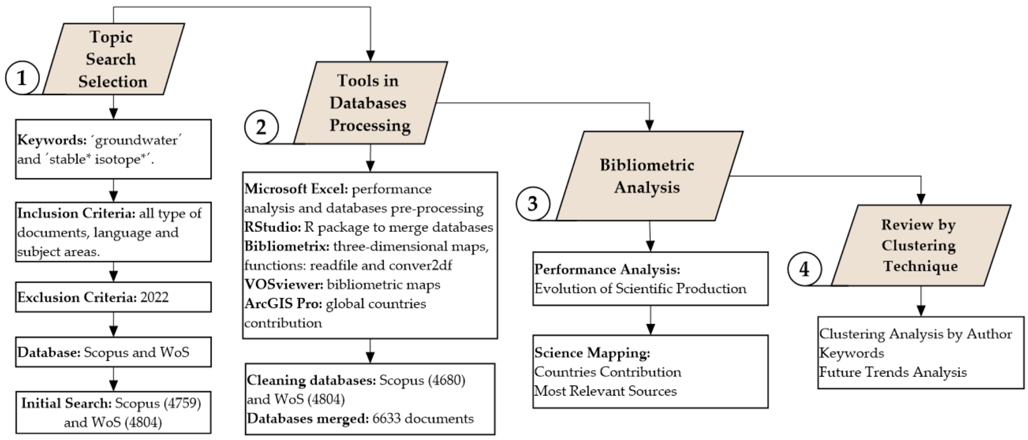

Figure 1. Methodological scheme applied to GSI.

2.1. Topic Search Selection

Bibliometric studies require the selection of a reliable database with quality information [35,43]. The databases of the Web of Science (WoS, launched by Clarivate Analytics, London, UK) and Scopus (developed by Elsevier, Amsterdam, The Netherlands) are the most widely used in bibliometrics [44]. The results (articles) and impacts (citations) of the countries obtained from these two databases are strongly correlated [45,46]. Therefore, both databases (WoS and Scopus) were used due to institutional access and significant journal coverage (20,346 journals in Scopus and 13,605 in WoS) [47].

Data collection was carried out in January 2022 using a series of descriptors related to the term groundwater, contained in the title, abstract and keywords, together with Boolean logic functions (AND, OR), which allowed the search to be carried out (see Table 1). A total of 9613 documents were obtained as a result of the initial search. The search terms selected were the following: groundwater and stable* isotope*.

Table 1. Topic Search of GSI.

Database	Initial Number of Documents	Topic Search
Scopus	4759	(TITLE-ABS-KEY (“groundwater”) AND TITLE-ABS-KEY (“stable* isotope*”)) AND (EXCLUDE (PUBYEAR, 2022))
WoS	4804	Topic: (“groundwater”) AND Topic: (“stable* isotope*”). Period Time: 1900–2021. Indexes: SCI-EXPANDED, SSCI, A&HCI, CPCI-S, CPCI-SSH, BKCI-S, BKCI-SSH, ESCI, CCR-EXPANDED, IC.

Prior to downloading the database, some inclusion and exclusion criteria were designated in selecting the documents obtained [48]. Considering all types of documents, languages, and subject areas was added as an inclusion criterion because it is a topic of great importance at the international level, pretending to know its trends and advances over time [49], excluding 2022 for the current year.

2.2. Tools in Database Treatment

The results obtained from the Scopus search were downloaded in BibTeX format and those of WoS in plaintext format for later treatment in RStudio. Both formats include bibliographic information, citations, abstracts, keywords, and references. However, Scopus and WoS differ in their download formats, scope terms, data volume, and coverage policies [50]. Therefore, the Bibliometrix library was used to unify these databases [51]. This library belongs to the statistical software RStudio, which is freely available [52,53]. The unification of Scopus and WoS allows for the deleting of duplicate documents and incomplete and erroneous items of the resulting 6633 documents. Five types of software were used in the analysis of the extracted data:

- Microsoft Excel: this software allows the analysis of scientific production through documents, languages, subject areas and journals [54–56].
- RStudio: this is an integrated development environment, launched in 2011 by Joseph J. Allaire, that belongs to R (free software) [52,53]. R version 4.0.5 was used for the big data processing and merging databases (Scopus and WoS). R was developed by Ross Ihaka y Robert Gentleman in Auckland, New Zealand. RStudio enabled automatic post-cleanup, preserving WoS files and removing duplicate Scopus documents [57].
- Bibliometrix: This is an RStudio package developed by Massimo Aria and Corrado Cuccurullo in University of Naples Federico I (Naples, Italy) [51]. This software processes the information by encoding it in RStudio [58] by using two functions: readfile and conver2df, to (i) load and convert data to UTF-8, and (ii) extract and create a data frame, respectively.
- VOSviewer: This is free software developed by the University of Leiden (Leiden, Netherlands), which allows the analysis of the intellectual structure of a knowledge field through the bibliometric maps construction [59,60]. This program has been widely used in different areas of knowledge [61–65].
- ArcGIS Pro: This is a Geographic Information Systems (GIS) software developed by Environmental Systems Research Institute (ESRI), in Redlands, California [66]. This software represents countries' contributions according to the number of publications worldwide and has been used in several bibliometric studies [35,42].

2.3. Bibliometric Analysis

Two main techniques are used in bibliometric analyses: performance analysis and science mapping [67,68]. Performance analysis encompasses the study of the structure of scientific publications, such as publication year, number of documents, citations, journals, countries, authors, and affiliations [69]. Otherwise, science mapping allows the graphical representation of research fields and subfields, observing their links [70]. In addition, these maps expose the relationships between some variables, such as co-occurrence with the author's keywords.

Bibliometrix software was used to generate some complementary bibliometric analyses, relating two or three variables of the intellectual and conceptual structure of the field of study. These analyses included Sankey Plot maps (Three-Fields Plot) which relate three variables: countries, authors, and keywords [71]. They also included the Thematic Evolution graph, which analyzes the evolution in periods of the subject of study [38].

2.4. Review by Clustering Technique

A literature review permits one to know the intellectual state of a topic [72,73]. It also collects data based on eligibility criteria, reduces biases and errors, and identifies possible gaps in research efforts [74,75]. The systematic analysis structure is based on keywords, literature, and the analysis of the results [76]. A literature review uses an algorithm that allows for the evaluating of the literature selection in a determinated field of study [77].

For the literature review in this work, we selected a sample of 20 documents per cluster, considering the most significant clusters of the 11 clusters obtained (clusters one to six) of the author keywords bibliometric map, according with the occurrence in the databases [78].

As a result, were reviewed a total of 120 publications. Furthermore, it was considered the most cited and relevant publications in the selected clusters, generating a table with the main topics related to the clusters selected and a description of the research trend lines in each cluster analyzed.

3. Results

3.1. Evolution of Scientific Production

The scientific production in the GSI line of research shows a growth in the interest in the topic of the academy (see Figure 2), presenting 5455 documents between the years 2006–2021, which represents 82.24% of the publications. The analysis of the results was divided into three periods: (i) constant (1969–1990), (ii) linear (1991–2005), and (iii) exponential (2006–2021). According to the mathematical form of growth, the periods of scientific production were selected.

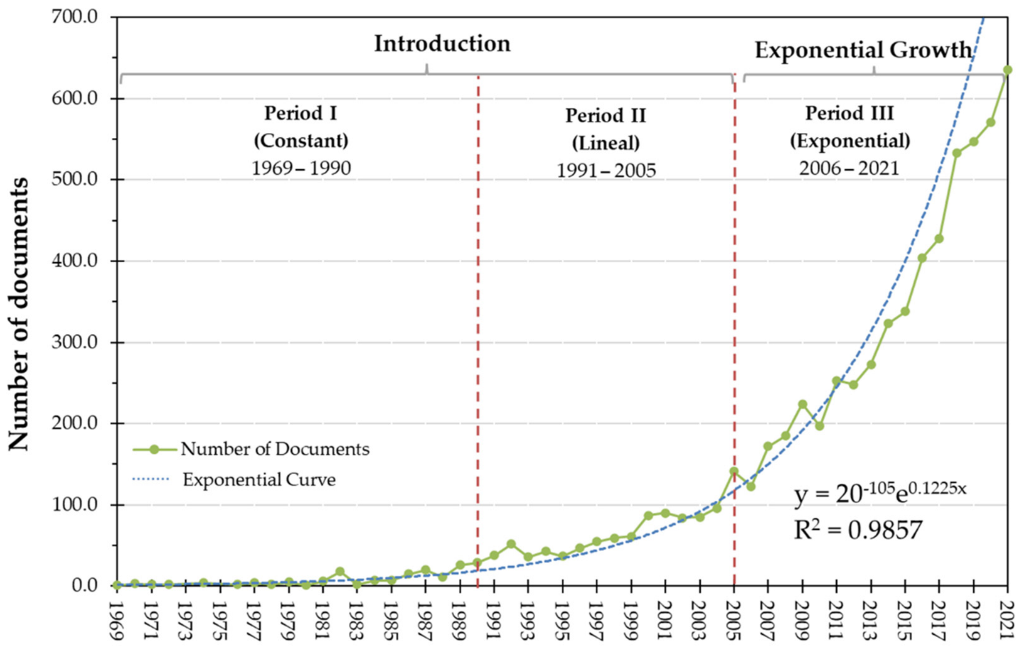

Figure 2. Scientific production of GSI.

Scientific production was evaluated using Price's law [79], which measures the increase in research in the field of study, showing exponential growth [80,81]. The entire production of the study field was estimated, and a growth model was generated (see Figure 2). The equation obtained ($y = 20^{-105}\ e^{0.1225x}$) has a value of $R^2 = 0.9857$, which verifies that the GSI is growing exponentially, demonstrating its interest in the academic world to be recognised as a field of study.

In determining the topics related to GSI in different subperiods, it was necessary to apply a matrix of co-words and grouping methods, thus exploring the evolution over time of this field of study [38]. For this analysis, a strategic diagram to show the themes with different Callon's centrality (x-axis) and density (y-axis) [38] was applied, as is shown in Figure 3a–c. Callon's centrality is an indicator of theme's importance across a full set of publications, while Callon's density is an indicator of the theme's development [82,83].

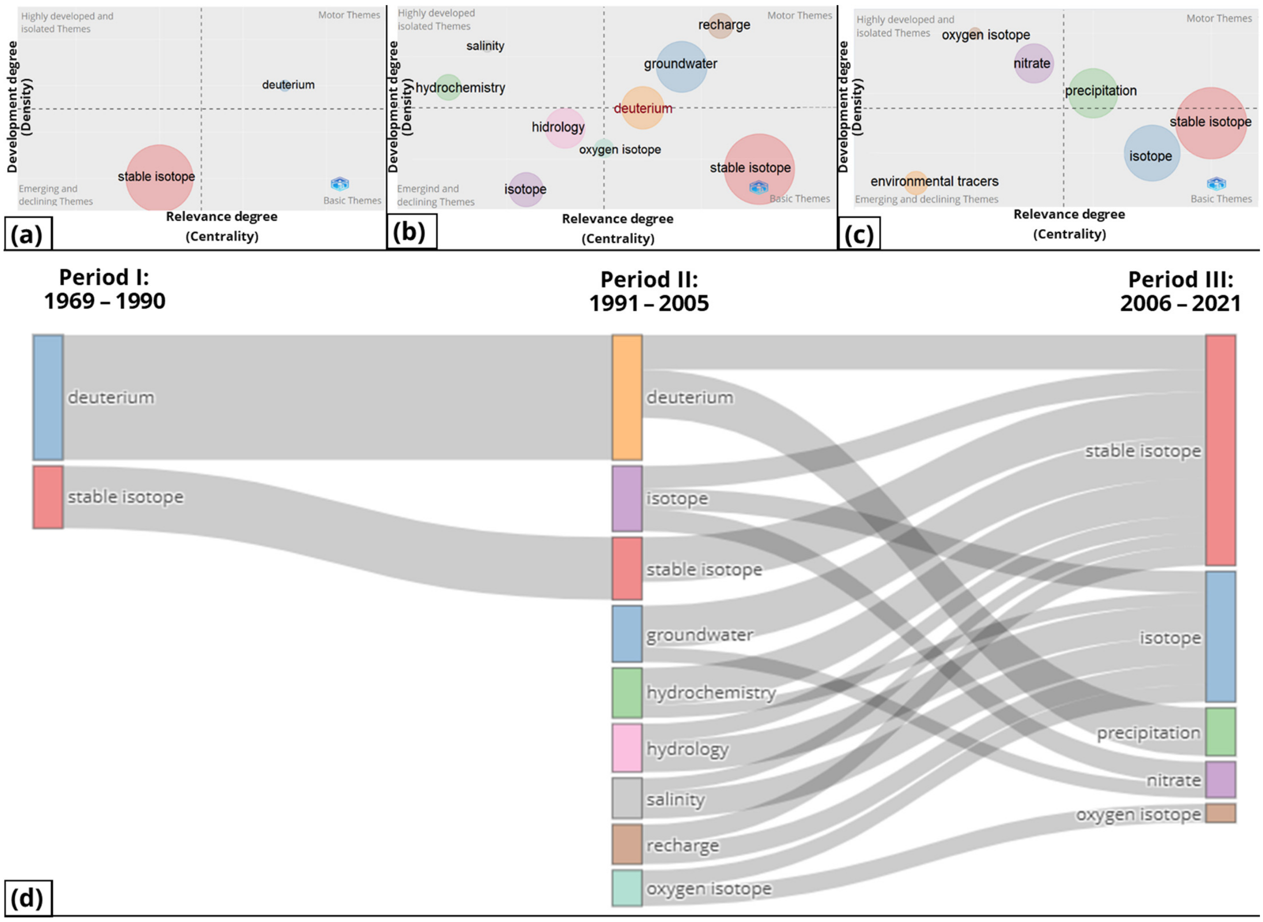

Figure 3. Thematic evolution of GSI in three periods. (**a**–**c**) Thematic maps (strategic diagrams). The circle size is proportional to the total frequency of terms in each theme. Each theme is labeled with the corresponding three most frequent keywords, and (**d**) Evolution map (Sankey graph), where the thickness of the edges is proportional to the inclusion index.

These graphs (Figure 3a–c) consist of four quadrants, whose location determines how developed or new the topic is, as described below:

Quadrant I (upper right): topics with high density and centrality are called motor themes, with strong links to other topics in other quadrants.

Quadrant II (upper left): themes of high density and low centrality, called developed and isolated themes.

Quadrant III (lower left): themes with low density and centrality, called emerging or declining themes.

Quadrant IV (lower right): themes of low density and high centrality, called basic and transversal themes, focusing on general questions that were transversal to the different research areas of a domain.

Period I (1969–1990): The growth in publications on GSI was reduced during these 21 years of scientific production, with only 167 publications, which represented 2.52% of the total publications on this subject. Deuterium has been identified as a motor theme as its discovery dates back to 1934 [84]. Stable isotopes became an emerging topic because these techniques are considered essential in groundwater systems' qualitative and quantitative evaluation [85–88]. The first publication related to the GSI was published in 1969, which produced 68 citations, where the isotopic composition of mineral water sources in the Jordan Rift Valley was analyzed [89]. The most cited publication (581) is that of Allan J.R. and Matthews R.K. [90], where variations in the carbon and oxygen isotopic composition of limestones generated during early freshwater diagenesis was analyzed. The second most cited publication is that of the authors Maoszewski P. and Zuber A [91]. Three new lumped parameter models were developed to interpret environmental radioisotope data in groundwater systems, resulting in 546 citations. Until 1990, the publications in the field of study focused on topics such as: (i) the isotopic composition of waters [92,93], (ii) carbonate diagenesis [94,95], and (iii) the use of stable isotope methods for groundwater studies [86–89]. These studies are considered the basis for applying stable isotope techniques for future research.

Period II (1991–2005): In this period there was notable growth in the number of publications on GSI. With this, their interest in the subject, with 1011 documents, represents 15.25% of the scientific production. After 21 years, stable isotopes went from being a driving theme to a transversal theme. Isotopes and hydrology appear as emerging topics. On the other hand, deuterium went from being an emerging theme to a theme in transition to becoming an engine theme. Similarly, the topics under development, aligned with the emerging topics, are hydrochemistry and salinity. Finally, recharge and groundwater have been established as motor themes, with a strong relationship with the themes of the other quadrants. The publication by the author Dawson [96] stands out, where the use of soil water and groundwater by trees and forests was investigated through measurements of transpiration rates using porometry, sap flow methods and the Bowen ratio method. In this period, publications on the following topics stand out: (i) arid region recharge [97–99], (ii) groundwater age through isotopes [100–102], (iii) denitrification [103–105], (iv) groundwater flow with stable water isotopes (δ^{18}O and δ^{2}H) [106–108], and (v) water movements through isotope analysis [109–112].

In the past (the first and second periods), most of the M.Sc. and Ph.D theses consisted of writing a report summarizing the work and its results. Therefore, the researcher was not obliged to publish the results of his career in a professional journal, decreasing the number of publications.

Period III (2006–2021): There is evidence of exponential growth in publications on GSI, with 5455 documents representing 82.24% of scientific production. In the last 15 years, the use of environmental tracers has become an emerging topic in studies related mainly to: (i) the solution of hydrological problems with environmental isotopes [113–116], (ii) groundwater salinization [117–119], (iii) the hydrochemical-isotopic characterisation of groundwater [120–122], and (iv) coastal aquifers recharge [123–125]. The topics under development are studies related to nitrates and oxygen isotopes. Also, the representative driving theme of this period is precipitation, which has evolved from previous themes such as recharge and groundwater. Finally, isotopes appear as cross-cutting themes that are not closely related to the rest of the emerging themes. However, the stable isotopes are specifically found in the transition zone from quadrant IV to I, which indicates that it could become the driving theme with the longest evolution time in the coming years (1969–2021).

This exponential increase in the number of articles is related to changes in university requirements for receiving M.Sc. and Ph.D degrees. In many universities, the research and its results are published in several professional articles, increasing the number of publications in this period. Another reason for this increase is the improvement in the sampling methods and measuring equipment that made it more accurate and easier to operate. Currently, the amounts of water required to perform chemical and isotopic analyses are very small. In parallel, software and data processing made it possible to increase the resolution of the statistical trend, with more variety of trends and more professional material that can be published. The most cited publication in this period was Mulholland et al.'s study [126], with 863 citations. These authors used stable nitrogen isotope tracers in 72 streams and eight regions, representing various biomes. It showed that total nitrate uptake is related to the ecosystem's photosynthesis. Finally, denitrification is linked with ecosystem respiration. The second most cited publication (699) was by Burgin and Hamilton [127], where the importance of alternative nitrate removal pathways was analyzed in aquatic ecosystems, including the application of stable isotopes and other tracer techniques.

3.2. Countries Contribution

Considering the authors' affiliation with the articles, the countries' contribution to this topic was included [128]. Furthermore, a bibliographic coupling analysis of countries was carried out to measure the references of publications in the database, particularly the countries involved [129]. VOSviewer was used for this analysis, and a threshold of at least five documents per country was set, with 78 countries reaching this threshold (see Figure 4). The colours distinguish them according to the number of publications on GSI, whereas the countries in white are those without publications on GSI. Finally, it was demonstrated that most of the publications were made in developed countries due to the rise and international importance of this topic.

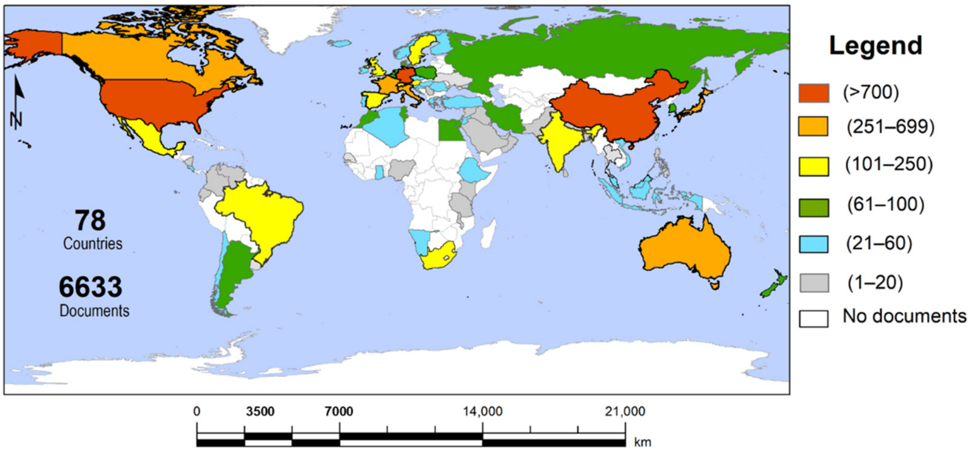

Figure 4. Countries contribution to GSI.

Additionally, an analysis of the scientific production by country was carried out, which presents a rule of association between three variables that determine the relationship of an investigation [51]. This analysis showed the author-country-keyword intersection with a limit of 10 variables per category (see Figure 5).

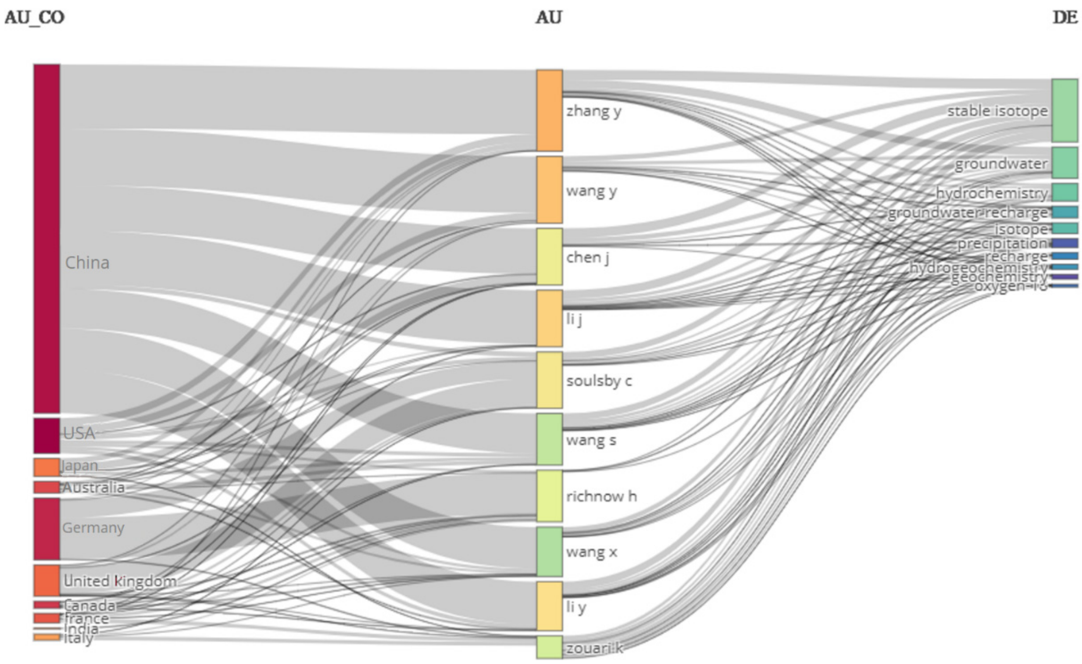

Figure 5. Author-Country-Keyword relation.

This study revealed the most relevant countries that contribute to scientific production (e.g., the USA, China and Germany), which coincides with the most cited authors and affiliations. For example, Zhang Y. (USA), Li J. (China), and Richnow H. (Germany) are authors who have published studies on topics related to the composition of stable isotopes in surface-groundwater and evidence of stable isotopes in groundwater salinization and its impact. Another reason for the large number of articles coming from these countries is that there are still many areas that have not yet been studied in detail, and thanks to the combination between many universities and students for the M.Sc. and PhD degrees, it can be documented as a new scientific production in GSI.

The following countries stand out among the 78 countries that have conducted scientific research on the GSI: China, the United States, Japan, Australia, and Germany, as shown in Table 2.

Table 2. Main Countries Collaboration about GSI.

R	Country	Publications	Cites	CCL	Main Topics	References
1	China	1180	15,784	73	Groundwater recharge Surface-groundwater interaction Hydrochemical evaluation	[130,131] [132,133] [134–136]
2	United States	1553	45,656	74	Isotope hydrology Stable isotopes in groundwater Groundwater recharge and flow characterization	[137–139] [114,140,141] [142,143]
3	Japan	312	4590	70	Groundwater nitrate contamination Groundwater characterization Residence times and flow paths	[144–147] [108,148–150] [151–153]
4	Australia	424	10,804	68	Stable isotopes in groundwater Groundwater quality Environmental isotopes in groundwater systems	[154–156] [156–159] [160]
5	Germany	788	17,521	74	Hydrogeochemical characterization Stable isotope in water resources Hydrological processes	[161,162] [163,164] [165,166]

Note: R: Ranking; CCL: Collaboration Countries Links.

3.3. Most Relevant Sources

This analysis generates a global vision of the disciplines that make up the intellectual structure of the subject under study [35]. A total of 1085 sources formed this field of study. Table 3 shows the top 10 journals with the highest number of publications, where the *Journal of Hydrology* has the highest number of contributions (494). In this journal, the most cited article (565) is by McGuire and McDonnell. The authors conducted a review study on lumped parameter transit time modelling for the watershed of water drainage to promote new advances in watershed hydrology [167]. The second and third positions correspond to the *Hydrogeology Journal* and *Applied Geochemistry* journals.

3.4. Review by Clustering Analysis

The keyword co-occurrence network analysis provides a network in which the terms that appear most frequently in the field of study are presented [35], related to GSI. The network helps explore themes (keywords), thematic groups (clusters), and existing research gaps [168,169].

Graphical and multidimensional representation of the author's keywords co-occurrence map was performed with VOSviewer [83,170]. A total of 9580 keywords were obtained, of which 340 have a co-occurrence of at least five incidents. For example, in Figure 6, 11 clusters, 340 nodes (keywords), 5356 links and a total link strength of 15,807 are shown. The mid-term is a stable isotope (cluster 4 in yellow) with 2056 occurrences and a relationship with 310 terms (topics).

Table 3. Main Information of the top 10 of the most relevant sources in GSI.

R	Journal	Country	SJR	ND	Main Publication Topics
1	Journal of Hydrology	Netherlands	1.68	494	Hydrological sciences, including water-based management and policy issues that affect economics and society.
2	Hydrogeology Journal	Germany	0.94	390	Integration of subsurface hydrology and geology, geochemistry, geophysics, geomorphology, and surface-water hydrology.
3	Applied Geochemistry	United Kingdom	1.02	278	Geochemistry, urban geochemistry, environment preservation, health, waste disposal, isotope geochemistry and geochemical processes.
4	Hydrological Processes	United Kingdom	1.22	266	Movement and storage of water, and water interaction with geological, biogeochemical, atmospheric and ecological systems.
5	Environmental Earth Sciences	Germany	0.64	253	Groundwater, soil contamination, waste management, environmental problems associated with transportation by land or water-geological processes.
6	Science of the Total Environment	Netherlands	1.8	226	Environmental topics including the atmosphere, hydrosphere, biosphere, lithosphere, and anthroposphere.
7	Water	Switzerland	0.72	127	Water resources management, water governance, hydrology and hydraulics, water scarcity, and flood risk.
8	Chemical Geology	Netherlands	1.54	126	Isotopic and elemental geochemistry, geochronology and cosmochemistry.
9	Water Resources Research	United States	1.86	126	Natural and water social sciences, water in the Earth's system, water resources research, water management, and water policy.
10	Isotopes in Environmental and Health Studies	United Kingdom	0.45	118	Natural isotope abundance, stable isotope tracer techniques, and isotope measurement methods.

Note: R: Ranking; SJR = SCImago Journal Rank; ND: Number of Documents.

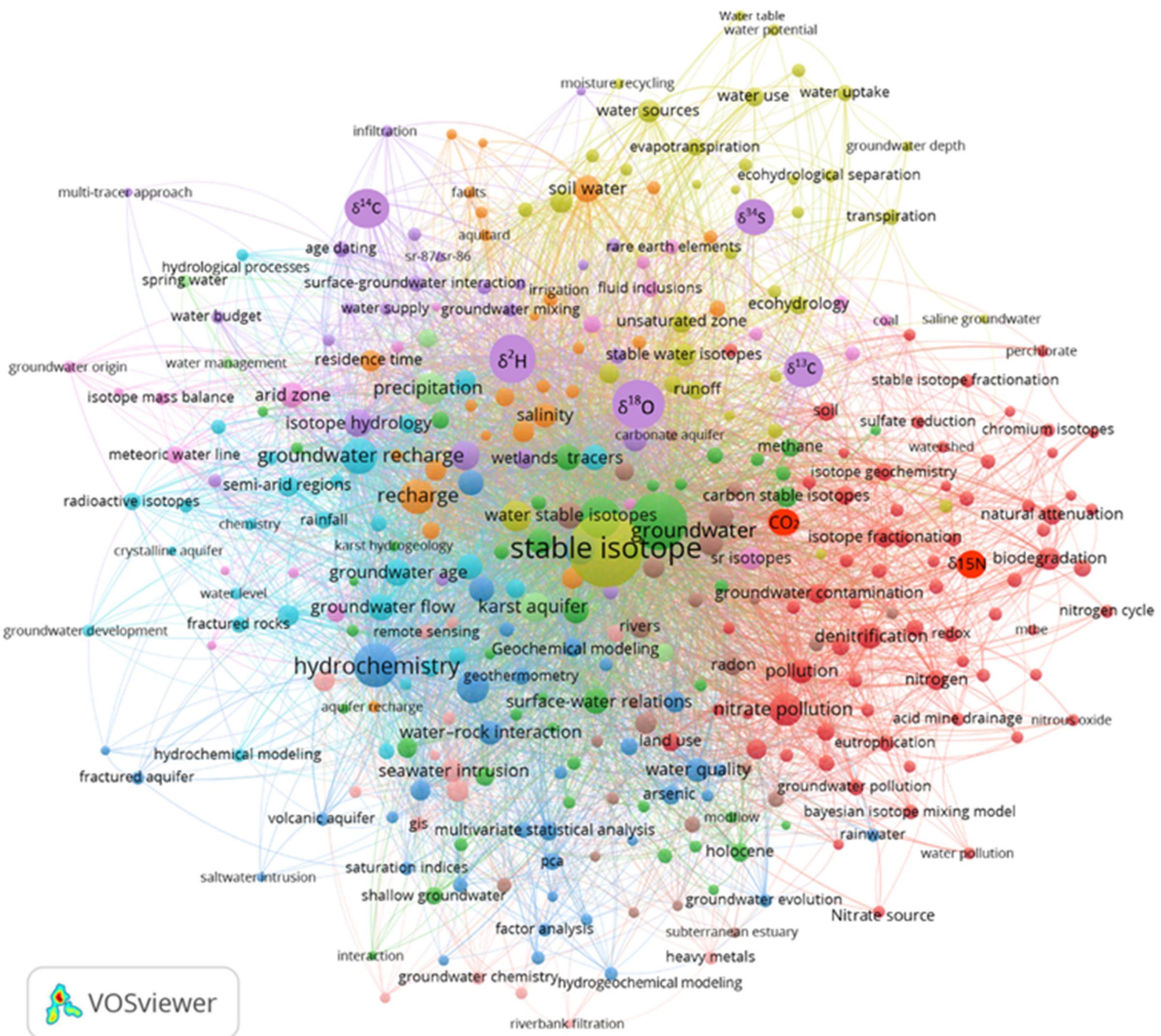

Figure 6. Co-occurrence of author keywords map in both databases (WoS y Scopus).

Table 4 summarizes the literature review conducted on the most relevant clusters (clusters from one to six with occurrence greater than 240) shown in Figure 6. This table includes the main topics emerging from each cluster.

Table 4. Keywords clusters about GSI.

Cluster	Cluster Name	Main Keywords Ocurrence	Topics	References
1 (72 nodes)	'Nitrate Pollution' (red)	Nitrate pollution (187) Denitrification (86) Pollution (71)	Groundwater and nitrate pollution interaction	[171,172]
			Flow dynamics	[173,174]
			Principal Component Analysis (PCA) application	[175,176]
2 (44 nodes)	'Groundwater and isotopes' (green)	Groundwater (941) Isotopes (341) Surface-water relations (88)	Groundwater flow in arid zones	[177–179]
			Surface-groundwater interaction	[177,180]
			Remote sensing in groundwater management	[181–183]
3 (37 nodes)	'Hydrochemistry' (blue)	Hydrochemistry (437) Hydrogeochemistry (164) Geochemistry (141)	Hydrochemical studies in surface-groundwater systems	[184–187]
			Groundwater modelling	[188–190]
4 (36 nodes)	'Stable and Environmental Isotopes' (yellow)	Stable isotope (2056) Environmental isotopes (135) Water sources (64)	Stable and environmental isotopes for understanding hydrological systems	[191–194]
			Recharge and contamination sources	[195–197]
5 (29 nodes)	'$\delta^{18}O$ and δ^2H stable isotopes' (violet)	$\delta^{18}O$ (376) δ^2H (276) δ^3H (127)	Stable Isotopes	[198–200]
			Environmental tracers in water quality	[201–203]
6 (28 nodes)	'Groundwater Recharge' (light blue)	Groundwater recharge (241) Groundwater age (102) Groundwater flow (89)	Groundwater recharge	[204,205]
			Groundwater flow	[206–208]
			Groundwater-surface water interaction	[209–211]
7 (27 nodes)	'Recharge' (orange)	Recharge (204) Soil water (89) Salinity (65)	Groundwater age	[212–214]
			Recharge sources	[206,215]
			Numerical modelling	[216,217]
			Aquifer recharge	[218,219]
			Environmental tracers	[203,220]
8 (25 nodes)	'Water Stable Isotopes' (brown)	Water stable isotopes (90) Hydrology (68) Water balance (66)	Groundwater-surface relation	[221–223]
			Groundwater quality	[215,224,225]
			Water age	[226,227]
			Groundwater salinity	[228,229]
9 (21 nodes)	'Arid zone' (violet)	Arid zone (78) Sr isotopes (61)	Arid zone hydrology	[230,231]
			Environmental tracers	[232,233]
			Groundwater processes	[234,235]
10 (15 nodes)	'Seawater Intrusion and coastal aquifers' (pink)	Seawater intrusion (63) Coastal aquifers (62)	Coastal aquifer salinization	[236–238]
			Groundwater modelling	[191,239,240]
			Groundwater exploitation	[241,242]
			Urban groundwater	[243–245]
			Hydrochemical processes	[246,247]
11 (6 nodes)	'Precipitation' (light green)	Precipitation (155) Karst aquifer (134)	Climate variability	[248,249]
			Water chemistry	[250–252]
			Groundwater infiltration	[253–255]

Cluster 1, called 'Nitrate Pollution', is the most extensive research area, and according to the co-occurrence of terms, it is considered the eighth most crucial research group (see Figure 6). In this cluster, research trends are mainly linked to: (i) groundwater nitrate pollution sources in the agricultural area, (ii) the application of nitrogen and oxygen isotopes to identify nitrate pollution in surface water, and (iii) agricultural and urban nitrate pollution.

Cluster 2 is called 'Groundwater and isotopes'. In this cluster, future lines of research will focus on: (i) water intrusion evidence from groundwater isotopes, (ii) groundwater isotopes and their implications for recharge sources, and (iii) the use of precipitation and groundwater isotopes to interpret regional hydrology.

Cluster 3 is called 'hydrochemistry' in this cluster, and trending publications are related to the following topics: (i) modelling of hydrochemistry evolution in aquifer systems, (ii) hydrological interaction between fresh-submarine groundwater discharge and coastal groundwater, (iii) identification of sources and groundwater recharge zones from hydrochemistry and stable isotopes, and (iv) tracing nitrate sources in urban waters using hydrochemistry and stable isotopes.

Cluster 4 is called 'stable and environmental isotopes'. Future lines of research associated with this topic include: (i) determining the origin of nitrate in watersheds using environmental isotopes, (ii) hydrochemical and environmental isotope analysis for characterizing a karst aquifer system, (iii) age and origin of groundwater, and (iv) hydrochemical tracers and environmental isotopes applied to conceptual modelling.

Cluster 5 is called 'δ^{18}O and δ^{2}H stable isotopes´. In this cluster, research trends are oriented towards: (i) improving the groundwater structural characterization, (ii) understanding evaporation moisture stress in arid areas, (iii) identifying groundwater recharge sources, (iv) tracing surface and groundwater flow systems, and (v) surface water-groundwater interaction.

Clusters 6 to 11 are smaller since they contain between 6 and 28 nodes (keywords), which represents a weaker relationship with the most representative clusters (1–5). These clusters comprise the following themes: 'Groundwater recharge' (cluster 6-light blue), 'Recharge' (cluster 7-orange), 'Water Stable Isotopes' (cluster 8-brown), 'Arid zone' (cluster 9-violet), 'Seawater Intrusion and coastal aquifers' (cluster 10-pink), and 'Precipitation' (cluster 11-light green).

3.5. Future Trend Analysis

This analysis presents the frequency of the main themes that allowed for the analysis of the selected field of study's evolution (see Figure 7). This section included keywords in at least three studies, placing the node with the highest frequency in the year.

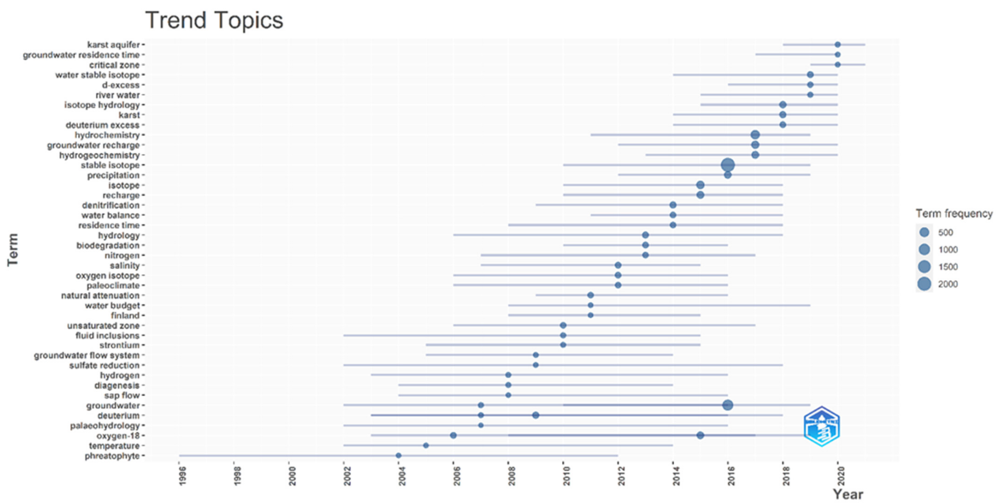

Figure 7. The trend of keywords by year of the GSI.

The most extended periods correspond to the phreatophyte (1969–2012), oxygen-18 (2003–2019), and groundwater (2002–2019) areas. In contrast, the shortest period is the critical zone (2019–2021). Additionally, the most frequent keywords are stable isotope (2012), groundwater (884), hydrochemistry (422), isotope (257), and groundwater recharge (218). Current trends are karst aquifer (21), groundwater residence time (14), and critical zone (14), which may serve as a basis for future research trends. For example, some publications identify karst recharge areas by applying isotopic and hydrogeological techniques [256,257]. They also identify the geochemical and isotopic variability in karst aquifers [258]. In addition, hydrochemical methods and stable/environmental isotopes characterize the interaction between karst water and surface water [259,260]. Finally, to develop a multicomponent reactive transport framework, the evolution of lithium isotope signatures in actively weathered drainage [261].

4. Discussion

The intellectual structure of GSI has had an evolution over 52 years thanks to the contribution of 78 countries through 13,867 authors, whose research has appeared in 6633 publications. These publications come from the Scopus and WoS databases, as they are considered relevant in the academic world [46,262]. These data reflect the relevance of the isotope issue in groundwater studies.

Stable isotope analytical methods were developed soon after the discovery of the isotopes. For example, deuterium (δ^2H) was discovered by Harold Urey in 1934 [84,263]. Early techniques were based on determining isotopic ratios by the densimetric, gravity, electric resistivity, and pycnometer methods. The development of a usable mass spectrometer in the late 1940s and early 1950s gave a vital impulse to use stable isotope techniques in scientific studies. Furthermore, in the 1970s and previous years, hydrochemical studies played a leading role in aquifer contamination analyses [264,265], and isotopic techniques have become essential tools in the qualitative and quantitative evaluation of surface-groundwater systems [85–88]. However, the early methods of stable isotope analysis up to the 1990s were generally complicated, time-consuming procedures with relatively low precision and accuracy [266,267]. Therefore, there is minimal amount of publications on GSI in scientific databases in the period I (1969–1990), as shown Figure 2.

In the second period of scientific production in GSI, stable isotopes have increasingly been used as environmental tracers [268]. One common application uses isotope mixing models to quantify source contributions to a mixture [269]. Isotopes are also implemented in models of groundwater origin, age and evaporation [100–102,270], recharge identification in arid regions [97,99], denitrification [103–105], groundwater flow [106–112], and nitrogen-stable isotopes in estuarine food webs as a record of increasing urbanization in coastal watersheds [271,272].

Interactions between groundwater and surface water play a fundamental role in the functioning of riparian ecosystems, and this has gained more attention in the last years (period III of Figure 2). In the context of sustainable watershed management, it is crucial to understand and quantify exchange processes between groundwater and surface water [273]. Numerous methods exist for parameter estimation and process identification in aquifers and surface waters, divided into two main methods: (i) based on Darcy´s law (e.g., piezometers, and pumping tests), and (ii) mass balance approaches (e.g., environmental tracers, monitoring wells) [274]. However, the transition zone has become a subject of significant research interest; thus, the need for appropriate methods applicable in this zone has evolved [275]. For regional research, large-scale techniques can be more suitable, whereas process studies may require measurements which enable high resolution. All methods have their limitations and uncertainties. However, a multi-scale approach combining multiple techniques can considerably reduce uncertainties and constrain estimates of fluxes between groundwater and surface water [274]. The isotopic techniques allow for the identifying of groundwater origin [276,277], age and direction of groundwater flow [278,279], and the surface water-groundwater interaction [280–282].

Hydrochemistry and stable isotopes are methodologies that complement each other and focus mainly on the analysis of recharge sources in surface-groundwater systems [176,183]. Environmental studies have been carried out mainly in China, the United States, Japan and Australia due to the high risk of erosion in delta areas, population growth and anthropogenic activity evidenced in changes in land use. Furthermore, several areas have not yet been studied in detail, combining many universities and students for the M.Sc. and Ph.D degrees and "virgin" research areas. For example, in the Badain Jaran desert in China, groundwater recharge sources have been determined using geochemical and isotopic techniques of environmental tracers (δ^{18}O and δ^2H) from the surface and groundwater [283]. In addition, there are applications of environmental tracers to hydrology in the arid zones of Australia, finding groundwater and using large floods for aquifer recharge [232]. In addition, the application of environmental tracers to investigate young groundwater systems provides the age of the groundwater and residence times [284].

The implementation of environmental isotopes of water has made it possible to identify the interaction of river-aquifer systems and recharge sources. Such is the case of the Sava river-Zagreb aquifer system in Croatia. In this study, the δ^2H and δ^{18}O values indicated a spatial variability of the influence of individual groundwater sources within the local rainfall-aquifer and river [285]. Furthermore, the impact of coal extraction in Raigarh District, India and its interaction with the Kelo River water and groundwater has been studied. They analyzed the interaction through water level monitoring, river flow measurements, stable isotopes, and groundwater flow modelling [286]. Finally, community participation is essential in water studies. It allowed for the achieving of sustainable development in some sectors [287–291].

5. Conclusions

This study allowed us to analyse the scientific information on Groundwater and Stable Isotopes (GSI). It was necessary to unify the two most used scientific databases in bibliometric studies (Scopus and WoS). Finally, an analysis of the evolution of the theme in these three periods and a trend topics map generated in Bibliometrix was carried out. These analyses determined the emerging lines of research about GSI in recent years (2017–2021), which are mainly related to karst aquifers, groundwater residence time and critical zones. The analysis of the intellectual structure of GSI included the review of 6633 publications, 78 countries, 1085 sources (journals, and books, among others) and 13,867 authors.

This study evaluated the evolution of scientific production for 52 years through the analysis of three periods: I (1969–1990), II (1991–2005), and III (2006–2021). Periods I and II did not significantly contribute to publications because, in the past, most of a student's thesis (M.Sc. and PhD) consisted of writing a report related to their results. Thus, the researcher was not obliged to publish their work in a professional journal. Additionally, in Latin America, universities did not require their research professors to publish publications indexed in Scopus or WoS; they were mostly published in local bibliographical information systems (e.g., Latindex), whose production is not reflected in the database of this study. However, the third period reached exponential growth, representing 82.34% of the total publications because, in recent years, institutions (depending on the country and university) require at least one scientific article to graduate as an M.Sc. or Ph.D.

The main limitation of this study was that some database documents published before 1990 did not include keywords. Therefore, some terms would be lost in the thematic evolution analysis from 1969 to 1995. This work represents a contribution to the academy by:

- Exposing the study techniques and methodologies that enrich scientific knowledge about GSI. For example, the combination of hydrochemical techniques and stable isotopes of water for the recharge source identification and contamination in surface water-groundwater systems, in addition to the environmental isotopes application for the hydrological systems understanding and water quality. Finally, in the generation of conceptual models of the river-aquifer interaction, we would include the modeling of hydrological processes at the level of watersheds, aquifers, infiltration, and urban groundwater systems.
- The analysis of the publications on GSI in the period 1969–2021 allowed us to know the main applications of stable isotopes in groundwater which contribute to the approach of the conditions and characteristics of conceptual models of river-aquifer systems at the watershed level. Stable isotopes also provide insight into groundwater flow dynamics, recharge sources' identification, meteoric waters and research related to karst aquifers. In addition, they help to identify possible sources of contamination. Finally, with the intervention of radioactive isotopes such as tritium (δ^3H), aquifer waters are dated, and residence times in groundwater are determined.
- Most research on GSI is conducted in China, the United States, Japan and Australia (see Table 2). It is because these countries presented a contribution from at least 65 countries, obtaining the most cited publications in the database, mainly on the following topics: residence times and flow paths of water, groundwater recharge

estimation, the occurrence of denitrification in shallow aquifers in agricultural areas, spatio-temporal evolution in stable isotopes in precipitation, and groundwater salinization. Moreover, in China, there are publications related to groundwater pollution, hydrogeochemistry characterization in arid, semi-arid zones, and human impacts on karst groundwater contamination. In the United States, there are publications about isotopic variation in groundwater; in Japan, there is research on aquifer interaction through hydrochemistry; in Australia, there is research about palaeohydrology and the investigation of groundwater/surface-water interactions. It highlighted the value of scientific databases that show relevant information contributing to integrated water resources management.

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