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Review

A Review of the Publications on Carbon Isotopes in Groundwater and Rainwater

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Abstract: The terrestrial components of the hydrological cycle include rainwater, surface water, and groundwater. Carbon (C) isotopes allow hydrologists to pinpoint the age of groundwater, track its flow rate, and identify the sources and processes. This research summarizes previous investigations conducted on the isotopes of groundwater and precipitation. The Scopus database contains works from authors from fifty nations, who have conducted research integrating C isotopes in groundwater and precipitation. The review shows that there have been few C isotope investigations on carbon storage and sequestration, as well as on $\delta^{13}C$ of precipitation in arid regions. An integrated e-DNA investigation on the process of C isotope fractionation in diverse environments, as well as research on ^{13}C of precipitation in arid regions before and after dust storms, is required to elucidate the relative contributions of biogenic, geogenic, and anthropogenic sources. However, carbon isotope fingerprints that are unique to individual compounds, such as those of fugitive gases, need sophisticated analytical equipment in order to be investigated, limiting this type of study to nations with robust scientific infrastructures and well-trained manpower. The International Atomic Energy Agency (IAEA) has been instrumental in this effort by providing collaborative research and analytical support, resulting in the development of a network for isotope data generation.

Keywords: carbon dioxide; sources of carbon; carbon isotopes; groundwater; rainwater

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1. Introduction

The United Nations' (UN) Intergovernmental Panel on Climate Change (IPCC) predicted a global surface temperature rise of 2.6 to 4.8 °C by the year 2100. Carbon dioxide (CO_2) is a greenhouse gas that contributes to global warming and climatic shifts because of its ability to trap heat [1,2]. Excessive emissions of carbon dioxide into the atmosphere have exacerbated the greenhouse effect, accelerating climate change on a global scale. Thus, it has become crucial to identify the CO_2 levels, their sources, and origins in order to address the dynamics of CO_2 emission sources and sinks [3]. The over-exploitation of the Earth's natural resources and the release of excess carbon dioxide into the atmosphere, alongside other environmental threats, both contribute to the rising global average temperature [4].

The sources of carbon may vary according to their Land use and landcover, such as forests, agricultural practices, or industrial emissions [5]. Different natural sources of carbon include atmospheric CO_2, carbonate minerals, organic matter, dissolved inorganic carbon (DIC), weathering of carbonate rocks, respiration and decomposition of plant roots, forest fires, and emissions from volcanic eruptions [6–11] In addition, other contributors like mantle gases could also be considered CO_2 sources [12]. Furthermore, anthropogenic sources such as the combustion/burning of fossil fuels, the destruction of forests/deforestation, and the manufacture of cement all contribute to the atmospheric addition of carbon dioxide. Moreover, CO_2 can be produced from our daily activities such as agricultural practices, transportation, industrial goods, and chemical and petroleum production are also significant contributors [13–19]. Studies also have indicated that oil and gas fields (depleted or witnessing increased oil recovery), immovable coal beds, and deep saline aquifers are examples of potential geological formations that hold CO_2 [20].

Plastics/microplastics pollution and degradation are a growing concern for global greenhouse emissions (GHEs), and they contribute to the carbon cycle, which is currently being underestimated and ignored [21]. Plastics are a part of the carbon cycle since all fossil carbon plastic is in the form of polymer carbon [22,23]. Plastics pollution and its transport into the terrestrial environment, including aquatic ecosystems, are poorly understood on a global scale. Plastics account for nearly 6% of global oil consumption, and it is evident that plastic production for transportation and waste disposal contributes to GHEs. So, plastics and GHEs are highly interconnected and the flow of plastics and their degradation products into the environment is very complex [23,24]. In addition, oil and gas production industries contain around 4% of plastics as raw materials [25], and plastic extraction contributes to carbon emissions, thus impacting climate change.

Moreover, to mitigate microplastics, recycling of plastics, incineration, and landfills are used to manage and reduce usage, but they play a vital role in greenhouse emissions. If the emissions from plastics continue at the same rate by 2050, carbon emissions from plastics will increase to 309 million tons [26]. The carbon footprint of 1 ton of recycled plastic from cradle to grave contains about 1538 tons of CO_2 emissions [27]. Furthermore, 1 ton of plastic packaging waste contains about 79% combustible carbon, which produces 2.9 tons of CO_2 when incinerated or burnt in the open air [28]. Plastics that reaches landfills may also release some fraction of carbon to the atmosphere in the form of CO_2 and methane [24]. As carbon moves through the carbon cycle by various processes, the plastic cycle also transports carbon from one reservoir to another.

Understanding the precipitation and hydrogeological properties of an aquifer system can aid in identifying probable paths for CO_2 migration and entry into groundwater. It is to be noted that there have been several studies focusing on the carbon isotopic application in groundwater and rainwater individually, but there are very few studies addressing these two components together. As a result, a review of the organic and inorganic carbon sources in various components of the hydrosphere is required to gain a better understanding of climate change, carbon sequestration, and future carbon capture and storage. The current review focuses on the sources and distribution of carbon in these important components of the hydrological cycle (rainwater and groundwater). Though the studies on water focus on the development and management of resources by addressing the United Nations Sustainable Development Goal (SDG) 6, carbon studies establish a link between different SDGs like life on land (SDG 15), life below water (SDG 14), and climate action (SDG 13). The important United Nations Sustainable Development Goals (UNSDGs) 3, 6, and 14 include ensuring healthy lives and promote well-being for all at all ages, ensure access to water and sanitation for all, and conserving and sustainably using the oceans, seas and marine resources, respectively. The UN goals are interrelated, and achieving Goal 3, a healthy life, is dependent on the amount of carbon released from different sources. As a result, developing a framework to define and quantify plastic or microplastic complexes in dynamic systems is critical research required to decrease carbon emissions, which might pave the way for policymakers and decision-makers to provide solutions to achieve the UNSDGs. Hence, the current review focuses on the carbon isotopes of rainwater and groundwater, their scope and status in terms of journals, authors, and regional links, prominent contributors, and the future road ahead.

2. Classification of Carbon

Though carbon is often categorized as organic and inorganic, it is referred to in a descriptive framework by rainbow colors depending on its characteristics, function, and location at various stages in the carbon cycle (Figure S1). Purple, blue, teal and green describe carbon that is captured and stored in air or industrial emissions [29], ocean plants and sediments [30], freshwater and wetlands [31], and terrestrial plants [32], respectively. In contrast, black, gray, brown, and red are carbon released through the combustion of fossil fuels [33], industrial emissions [34], organic matter combustion [35], and biological particles on snow [36], respectively.

3. Presence of Different Carbon Forms in the Aquatic System

The main drivers of CO_2 enrichment in aquatic systems include respiration, which is fueled by human and natural organic matter inputs, groundwater discharge, terrestrial surface water runoff, and precipitation of carbonate or silicate minerals [37]. Since groundwater often has significantly higher concentrations of dissolved species than surface water, even modest volumes of dissolved species discharging into surface waterbodies may have a significant impact on aquatic biogeochemical cycles. Additionally, due to the high density of CO_2 ($\approx 1.87\ \mathrm{kg/m^3}$) and water solubility at the relatively high pressures in deeper aquifers, carbon dioxide is a feasible option for disposal in saline aquifers [20]. The solubility of CO_2 in shallow aquifers is often expressed as the pressure of carbon dioxide ($_{P}CO_2$) and may range between (log $_{P}CO_2$) -4 and $+1$ (in bars), which is the widest range anticipated under hydrostatic circumstances down to depths of 100 m. The following simple process in Equation (1) shows how dissolving CO_2 in water might result in a pH drop [20].

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3{}^- \tag{1}$$

However, there is an equilibrium between atmospheric CO_2 and groundwater recharged through precipitation. As groundwater moves through the unsaturated zone, concentrations of CO_2 are generally ten to one hundred times higher than atmospheric CO_2 due to soil microbiological activities [3]. Calcite ($CaCO_3$) is a common mineral found in many typical sedimentary aquifer systems consisting of sand, gravel, clay, sandstone, conglomerates, shales, and carbonates. The mineral framework combines with the H^+ ion to produce bicarbonate and calcium (Ca^{2+}) ions, as in Equation (2) [3]:

$$H^+ + CaCO_3 \rightarrow HCO_3{}^- + Ca^{2+} \tag{2}$$

As a result, half of the carbon mass in bicarbonate ions comes from soil and air gases (CO_2), while the other half comes from the solid aquifer structure ($CaCO_3$). The physico-chemical characteristics of groundwater are mostly determined by the chemical composition of the surrounding rock and sediment, as well as the interactions between soil in the unsaturated zone and infiltrating surface water. Consequently, soil respiration also enriches groundwater CO_2 [37].

The atmospheric CO_2 dissolution in rainwater is based on the prevailing physico-chemical conditions in the atmosphere. Thus, dissolved CO_2 changes the atmospheric CO_2 concentration. Drastic expansion in urbanization, populations, oil-based industries, the terrestrial environment, and the open sea leads to variation in land use. Because of the shift in land use, CO_2 levels in the atmosphere have fluctuated, reflecting changes in rainfall patterns. Warmer temperatures caused by CO_2 emissions increase evapotranspiration and result in an imbalanced hydrological cycle. For these reasons, studies on the carbon cycle and build up of carbon stock have shown that both have accelerated [38–40] in the recent years.

Furthermore, there is a significant risk that microplastics and other plastic degradation products will infiltrate from landfills into aquifers [24]. Laboratory experimental studies have shown that polystyrene could be largely photochemically converted into dissolved organic carbon and CO_2 over decadal and centennial periods [41]. So, it is apparent that plastics or microplastics degradation through landfills increases the carbon content through different pathways in the groundwater. Then, to add to these processes, through ocean and atmospheric exchange, plastics may become suspended and affect the climate.

4. Carbon Isotopes

Though there are different techniques used to address climate change in line with the fluctuation of carbon in the hydrological components, isotopes play a very significant role. Environmental tracers, such as carbon isotopes, and their applications in subsurface hydrology were discussed by previous authors [42]. The stable carbon isotopes carbon-12 ($\delta^{12}C$) and carbon-13 ($\delta^{13}C$) and the radiocarbon isotope carbon-14 (^{14}C) have been widely used as tracers to determine the origin, age, and flow of groundwater. Stable carbon isotopes are also used to monitor the degradation of organic pollutants in groundwater [43,44] and evaluate the efficiency of remediation strategies [45]. Moreover, carbon isotopes reveal valuable information regarding microbial activity [46] and biogeochemical processes in groundwater systems. Isotopic measurements have been used for determining both organic and inorganic carbon sources in the terrestrial environment, as illustrated by the literature review (Figures 1 and 2).

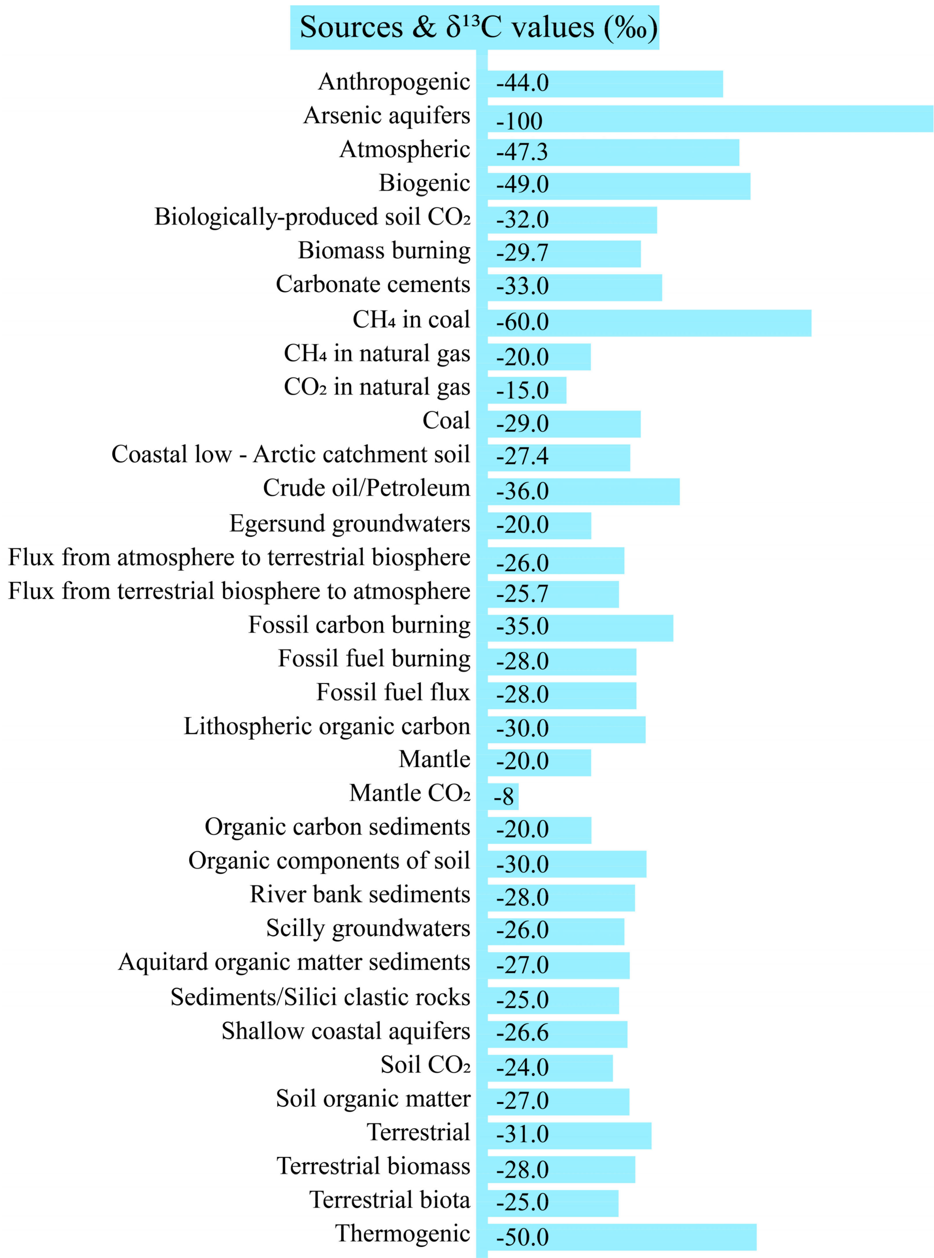

Figure 1. Carbon-13 isotopic values with respect to different sources of carbon in the environment [47–55].

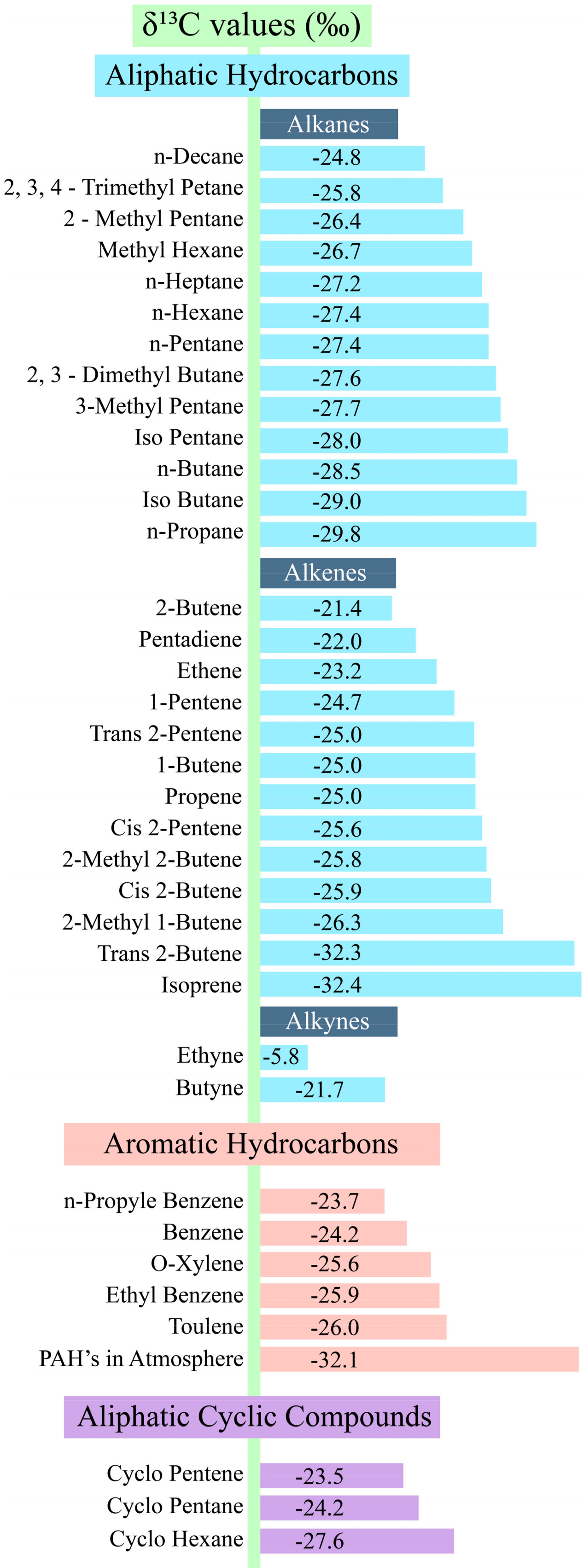

Figure 2. Carbon-13 isotopic values of different forms of organic carbon compounds represented in different colors (data source [56–59]).

Several studies have used carbon isotopes in groundwater investigations, significantly advancing our knowledge of groundwater dynamics and contamination processes. Carbon isotope measurement is a powerful tool for studying the CO_2 impact on aquatic and hydrogeological systems. The isotopic investigations are also used in carbon cycle and flux studies, as well as in chemical weathering, degassing from thermal and cold springs, and geochemical trapping in CO_2 injection for carbon capture and storage studies [60]. Chlorinated benzenes are the intermediates used in synthesizing pesticides, plastics, dyes, drugs, etc., which leach into the groundwater and undergo aerobic or anaerobic degradation. The lesser carbon isotope fractionation values can identify in situ degradation of these compounds in an aquifer matrix with a great extent of biodegradation.

Conversely, high carbon isotope shifts of chlorinated benzenes in contaminated groundwater indicate that their biodegradation is controlled by anaerobic reductive dechlorination [61]. Research shows that dissolved organic carbon (DOC) degradation contributes to groundwater with low depleted values, which is the difference between dissolved organic carbon of carbon-13 (δ^{13}C-DOC) and dissolved inorganic carbon of carbon-13 (δ^{13}C-DIC). However, groundwater migration was also inferred to be facilitated by the DIC concentrations [62].

Radioactive carbon-14 can provide significant information about the age and time of residency in the aquifer [63–70]. Researchers use the isotopic composition of DIC to estimate the fraction of young carbon that has been in the aquifer for a long time and the old carbon that has just infiltrated. Since various carbon sources have unique isotopic signatures, it is possible to identify the source of carbon in groundwater by using δ^{13}C signatures. The values of δ^{13}C in organic matter, carbonate minerals, and atmospheric CO_2 can vary significantly. Carbon-13 also plays a crucial role in assessing the fate and transport of contaminants in groundwater [71,72]. Moreover, studies also used δ^{13}C to investigate microbial activities and biogeochemical processes in groundwater systems as well as their contributions to the carbon cycle by measuring the carbon isotope composition of the microbial byproducts [73,74].

Applications of rainwater carbon isotopes are mainly focused on understanding various atmospheric and hydrological processes. Carbon isotopes in rainwater have been used in a number of studies to explore a variety of carbon sources and to study their fluctuation with time [75,76]. The rainwater isotopic composition of δ^{13}C and ^{14}C provides valuable information about the cycling of carbon and the contributions from different sources (atmospheric CO_2, fossil fuel emissions, and biogenic processes) in the atmosphere [75,77,78]. In this regard, the relative contribution of fossil fuel emissions to the atmosphere can be estimated by analyzing the carbon isotopic composition of the rainwater [79,80].

Comparative analysis of CO_2 concentrations in groundwater samples from different locations can help to identify anomalies or potential sources [81]. Isotopic analysis of carbon isotopes can provide insights into the origin of CO_2 in groundwater and rainwater. Different sources of CO_2 have distinctive isotopic signatures, allowing researchers to differentiate between natural sources and anthropogenic sources. Detailed investigations of groundwater flow patterns, geologic structures, and hydraulic properties can provide clues about the potential sources of CO_2, such as nearby CO_2 storage sites, geologic faults, or natural CO_2-rich formations [82].

5. Analysis of Scopus Database on Carbon Isotopes in Groundwater and Rainwater

This bibliometric study was performed with data retrieved from the Scopus database using the keywords (groundwater, carbon, isotopes, rain, water). The database was compiled in the form of a comma-separated value (CSV) file based on 132 articles. The file was checked for duplicate publications, and similar words were modified, for example, "ground water" and "groundwater", "aquifer" and "aquifers", "carbon isotope" and "carbon isotopes", etc. The publications were analyzed in different categories: author citation, country, and co-occurrence of keywords, using VOSviewer software (version 1.6.19) to generate network-based visualization maps [83]. A minimum occurrence of 15 was considered for keywords used in the retrieved database, which resulted in 26 frequently used keywords. Co-authorship analysis, depending on the number of citations (minimum number of citations = 0), resulted in a total of 598 depicting linkages between only 45 authors. Meanwhile, the number of documents by country (minimum number of documents = 3) resulted in a total of 50 countries, though only 18 countries were connected to each other. The current analysis considers, the first author affiliations for the number of publications by a country, which resulted in 35 countries.

The interlinkages of the keywords along with their chronological occurrences are reflected in Figure 3, indicating that the earlier studies focused more on recharge, tritium, and precipitation. Later studies related to groundwater, hydrochemistry, stable isotopes of oxygen and hydrogen, and carbon isotopes were linked to the chemical composition, the groundwater flow, and analytical precision. Subsequently, more articles on surface water–groundwater interaction, water quality, and their relation to geochemical processes like weathering, dissolution, and the availability of fresh groundwater resources were published. Furthermore, studies on specific isotopes of C, such as $\delta^{13}C$ and ^{14}C, along with their significance in each environment, like surface water, groundwater, and precipitation, evolved. Keyword associations showed that more recently, the isotope studies focused on seasonal variations and environmental impacts on river systems. It should not be forgotten that newly emerging keywords with fewer occurrences will not be represented in the diagram. Overall, it could be inferred that the carbon isotopes in groundwater were initially assessed for groundwater chemistry, recharge, and groundwater flow, reflecting the age of the water. Later, they were used to characterize the source, followed by unraveling the geochemical processes. Recently, more studies have evolved with finger printing on the type of isotope and environmental monitoring. The thickness of the linkage lines reveals strong associations, and particularly strong linkages can be observed between precipitation, groundwater, carbon isotopes, hydrochemistry, recharge, and aquifers.

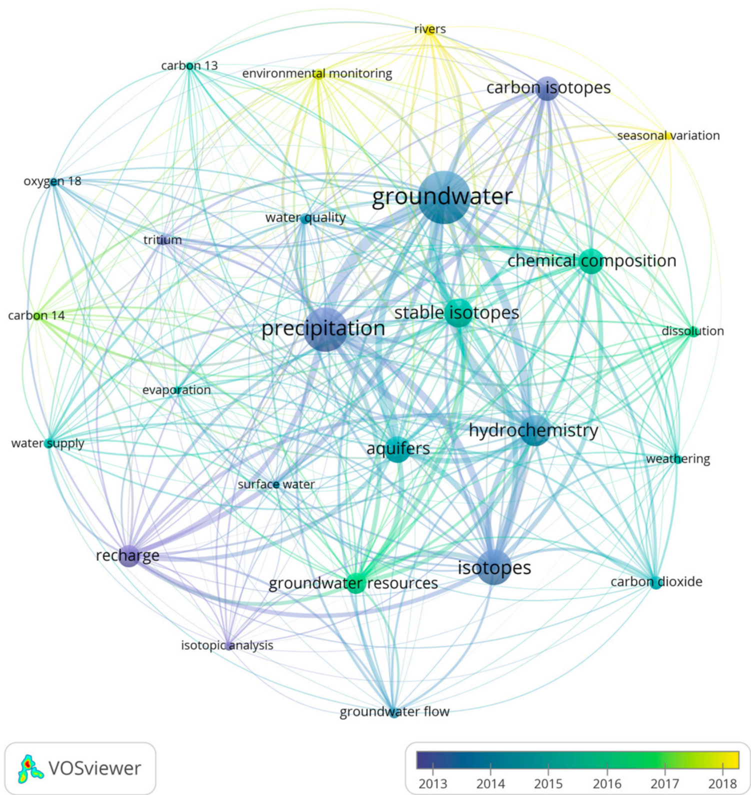

Figure 3. Author keywords interlinkages from Scopus literature search for carbon isotope studies integrating groundwater and rainwater based on 133 articles. The color shades reflect the chronology of the keywords used. The size of the bubble is proportionate to the number of occurrences.

Though there are studies comparing other geochemical parameters [84], pCO_2 values [85], OC in groundwater [86–88], sediments in coastal aquifers [89], and studies on compound-specific isotopes still needs acceleration. The database revealed 598 authors and co-authors related to these publications. The grouping of publications (Figure 4) based on authors showed that of 45 interlinked authors, Cendon D.I. and Meredith K. formed the major group, followed by Pigios J., though all these authors have collaborative publications. Cendon D.I. developed publications with two individuals (Group A and Group B) and one collaborative group with Pegois J. (Group C-a). Similarly, Meredith K. published with Group C-b and Group D. Groups C-a and C-b are linked by Baker A. Group D has developed an internal collaborative publication group E, which teamed up with the authors Humpherys, Grice, Sacco, Blyth, Kuhl, Smith, and Mazumder for their earlier publications. Recently, new authors to the team were Laini, Cooper, Campbell, Allard, Mousavi-Dermahalleh, White, Middleton, Hua, Griebler, and Grierson. Following on from Cendon, Pigois, and Meredith, the greatest numbers of publications were then from Sacco, Grice, Humphreys, Blyth, and Baker.

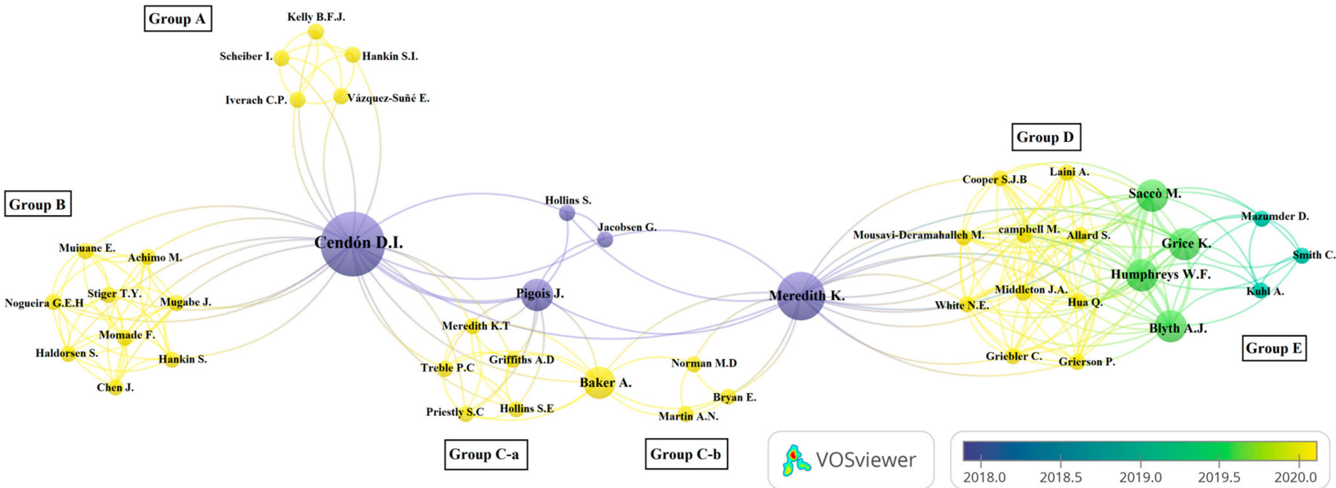

Figure 4. Author linkages were derived based on the literature obtained from the Scopus database. The color reflects the chronology of publications.

As mentioned before, there were articles published from 50 different nations, 18 of which demonstrated international collaboration (Figure 5). According to both the total number of papers and the relationships between countries, the United States, the United Kingdom, and Australia were the first to publish, followed by South Africa, Sweden, Switzerland, Taiwan, and Tunisia. The recent publications were from Austria, China, India, and New Zealand. The availability of analytical facilities, the interaction between the countries, and other technical knowledge affect the frequency of collaborations and the corresponding citations. The number of projects conducted in tandem with American institutions has increased. The collaborations were observed to be with Australia, China, France, Germany, India, Spain, Switzerland, Taiwan, and the United Kingdom. Furthermore, Australia has developed collaborative research on C isotopes with Austria, Canada, China, France, Germany, New Zealand, South Africa, Spain, Sweden, the United Kingdom, and the United States. It is also interesting to notice that France and the United Kingdom have collaborated with seven countries, while Germany and Spain have worked with eight. Meanwhile, Canada, and Switzerland have worked with four other countries to publish articles on C isotopes in groundwater and rainwater. In addition, authors from Austria, India, Israel, New Zealand, and Taiwan have worked together on papers with researchers from three additional nations. South Africa was observed to have joint publications with two countries (Australia and Israel). Argentina, Sweden, and Tunisia had collaborative publications with only one country. The countries' articles without collaborations are not presented.

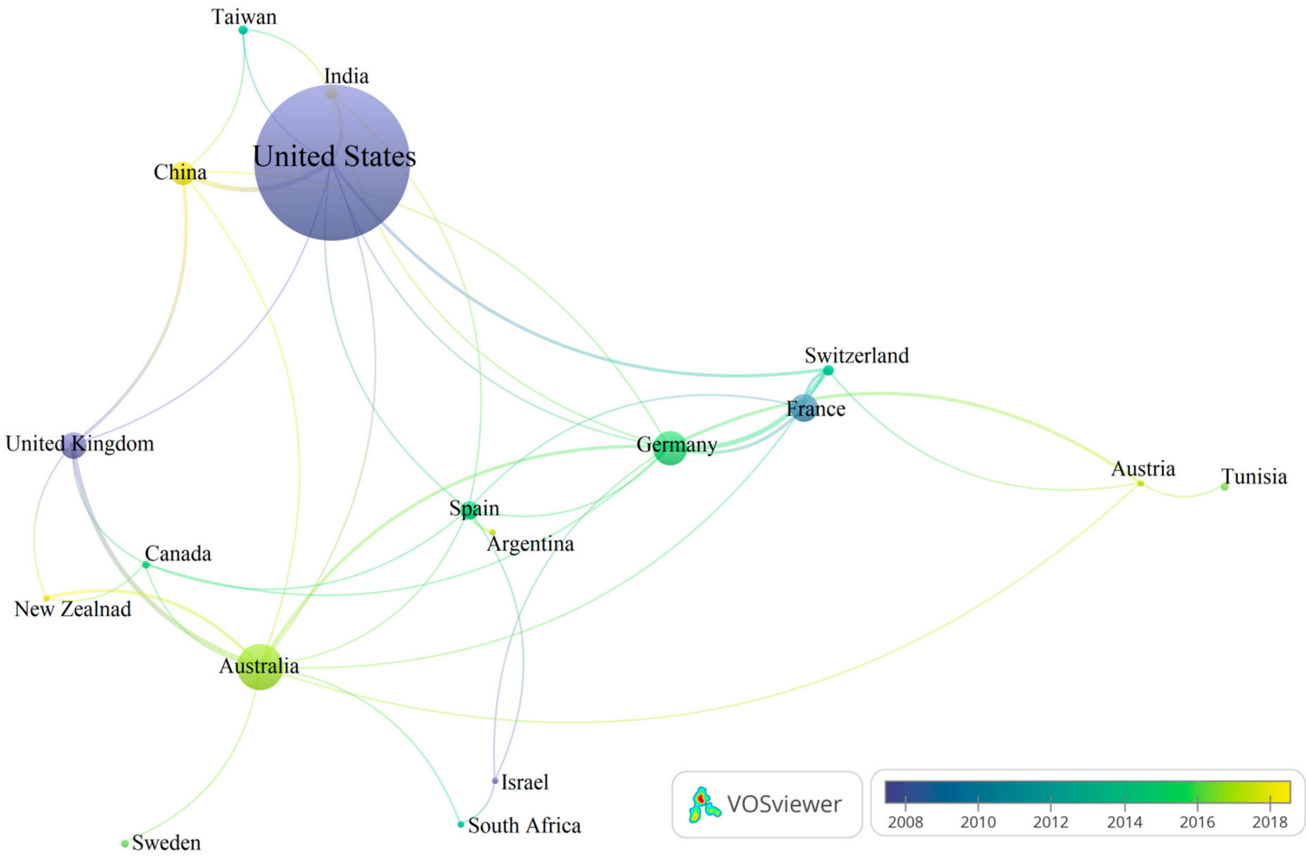

Figure 5. Representation of the number of articles published from different countries on carbon isotopes, integrating rainwater and groundwater, based on the corresponding author affiliations and the co-author linkages. The color indicates the chronology of publications, and the size of the circles represents the number of citations.

Published work on carbon isotopes combining the assessment of these two hydrological components was first initiated by the United Kingdom in 1975, followed by France, Israel, and South Africa in 1984, 1990, and 1993, respectively (Figure 6). The United States addressed this issue with carbon isotopes initially in 1996; since then, there have been frequent publications, with a maximum of four publications in 2018 and three in 2006 and 2004. During the year 2001, Japan attempted to correlate these components of hydrological systems with C isotopes; later, Australia did the same during the year 2002, and Germany and Switzerland during the year 2005. Niger, Sweden, and Taiwan initiated their publications during the year 2006 in the stated topic of study, followed by Austria, China, and the Ivory Coast in the year 2008. Denmark and Ethiopia had their initial carbon studies on precipitation and its linkage to groundwater reported in 2010, followed by Bangladesh in 2011 and Kuwait in 2012, and India, Norway, Thailand, and Tunisia initiated studies in 2013. Argentina followed in 2014; then, Egypt, Spain, and Sri Lanka published articles in this regard in 2015, followed by Brazil and Portugal in 2017, Belgium in 2018, Costa Rica and the Czech Republic in 2020, and New Zealand in 2022. Though published works on carbon isotopes of these two components were initiated during 1975, acceleration was observed after 2002, then in 2012, and recently, after 2015, with an average of nine publications per year (Figure 7).

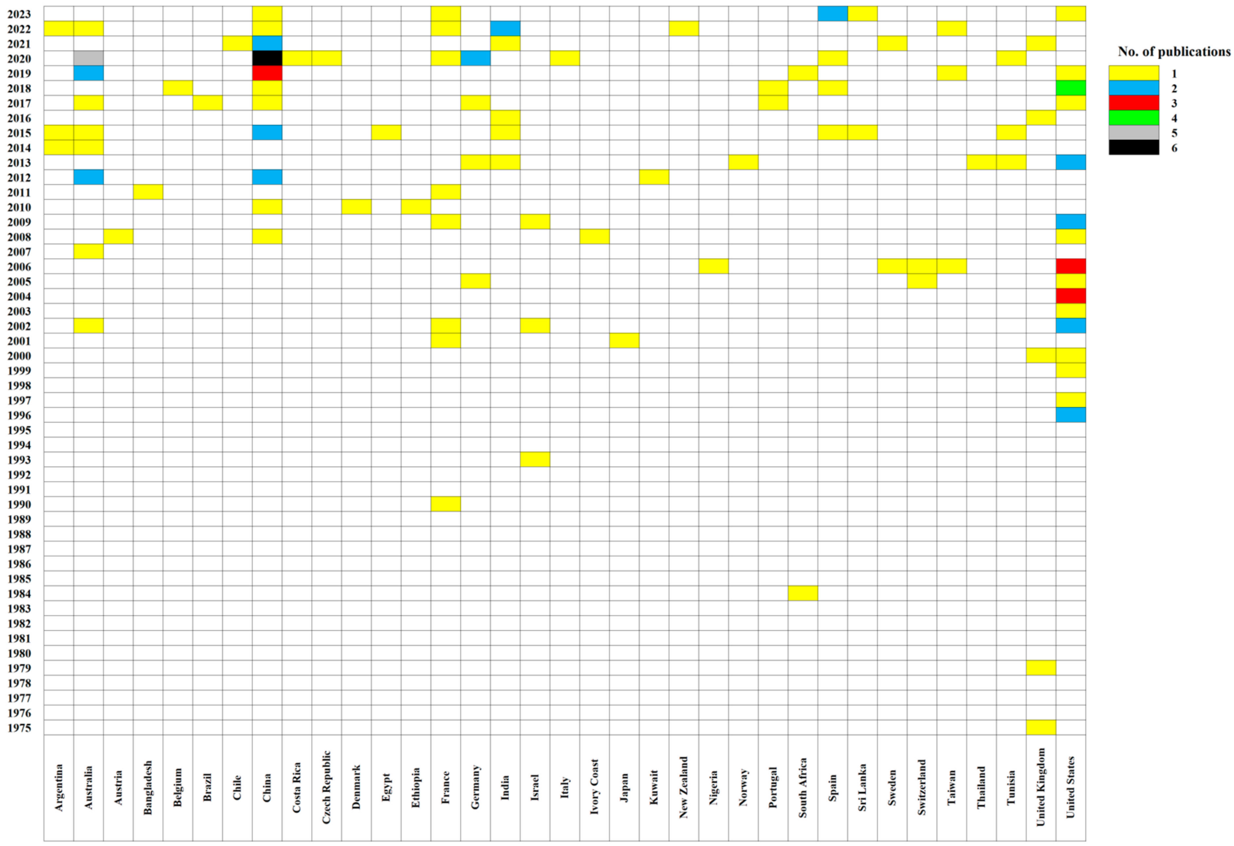

Figure 6. Number of publications on carbon isotopes integrating rainwater and groundwater from different countries based on the affiliations of the corresponding author.

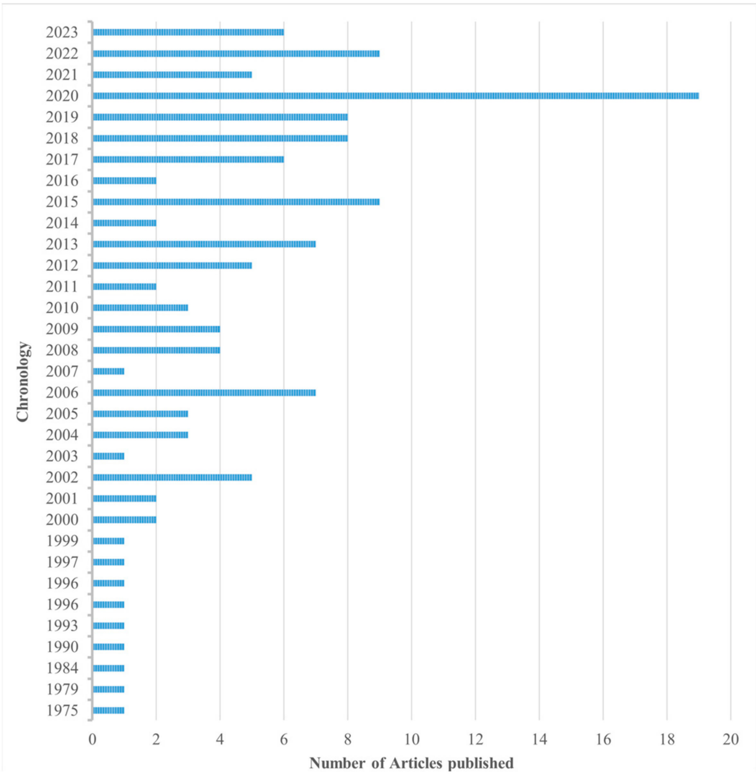

Figure 7. The increase in the number of articles published on carbon isotopes integrating rainwater and groundwater since its first report in 1975.

There were sixty journal articles, two book chapters, and one symposium proceeding found (Figure 8). *Science of Total Environment* has published the highest number of articles (23), especially during 2020 and 2022. The *Journal of Hydrology* has published thirteen articles since 1979. Seven articles are in *Applied Geochemistry* and five in *Environmental Earth Sciences Journal*. *Chemical Geology* and *Quaternary Science Reviews* have published four articles related to the topic of interest. Furthermore, *Environmental Science and Technology*, *Groundwater Isotopes in Environmental and Health Studies*, *Quaternary International*, and *Water Resources Research* have published three articles each so far. Similarly, two articles pertaining to these keywords were published in the *Bulletin of the Geological Society of America*, the *Journal of China University of Geosciences*, *Environmental Geology*, *Environmental Sciences and Pollution Research*, *Geochemistry*, *Geophysics*, *Geosystems*, *Hydrological Processes*, the *Journal of Radio Analytical and Nuclear Chemistry*, *Oecologia*, and *PLoS ONE*. The remaining forty journals listed had one publication each.

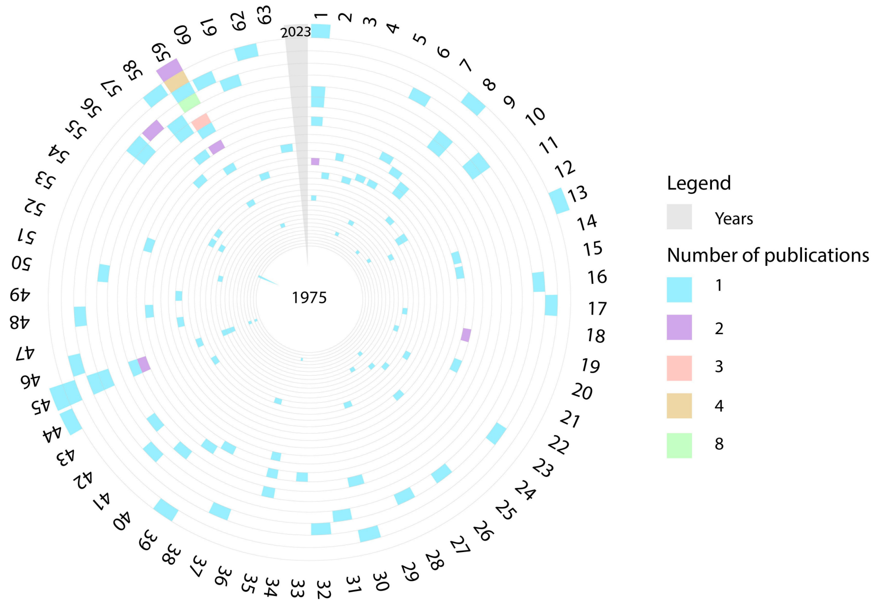

Figure 8. (1) *Applied Geochemistry*, (2) *Applied Groundwater Studies in Africa*, (3) *Applied Radiation and Isotopes*, (4) *Aquatic Geochemistry*, (5) *Bulletin of the Geological Society of America*, (6) *Chemical Geology*, (7) *Chinese Journal of Applied Ecology*, (8) *Environmental Earth Sciences*, (9) *Environmental Geology*, (10) *Environmental Science and Pollution Research*, (11) *Environmental Science and Technology*, (12) *Estuaries*, (13) *Exposure and Health*, (14) *Forest Ecology and Management*, (15) *Forest Research*, (16) *Frontiers in Ecology and Evolution*, (17) *Frontiers in Water*, (18) *Functional Ecology*, (19) *Geochemistry, Geophysics, Geosystems*, (20) *Geochronometria*, (21) *Geoderma*, (22) *Geological Quarterly*, (23) *Geothermics*, (24) *Global Change Biology*, (25) *Ground Water*, (26) *Groundwater for Sustainable Development*, (27) *Holocene*, (28) *Huanjing Kexue/Environmental Science*, (29) *Hydrogeology Journal*, (30) *Hydrological Processes*, (31) *Hydrological Sciences Journal*, (32) *International Journal of Environmental Research and Public Health*, (33) *International Journal of Environmental Science and Technology*, (34) *Isotope hydrology 1983. Proc. symposium, Vienna*, (35) *Isotopes in Environmental and Health Studies*, (36) *Isotopes in the Water Cycle: Past, Present and Future of a Developing Science*, (37) *Italian Journal of Groundwater*, (38) *Journal of Arid Environments*, (39) *Journal of China University of Geosciences*, (40) *Journal of Contaminant Hydrology*, (41) *Journal of Environmental Radioactivity*, (42) *Journal of Geophysical Research Atmospheres*, (43) *Journal of Geophysical Research: Biogeosciences*, (44) *Journal of Hazardous Materials*, (45) *Journal of Hydrology*, (46) *Journal of Hydrology: Regional Studies*, (47) *Journal of Paleolimnology*, (48) *Journal of Radioanalytical and Nuclear Chemistry*, (49) *Journal of Soils and Sediments*, (50) *Journal of Vegetation Science*, (51) *Journal of Water Science*, (52) *Marine Chemistry*, (53) *Nature*, (54) *Oecologia*, (55) *Perchlorate: Environmental Occurrence, Interactions and Treatment*, (56) *PLoS ONE*, (57) *Quaternary International*, (58) *Quaternary Science Reviews*, (59) *Science of the Total Environment*, (60) *Water (Switzerland)*, (61) *Water Resources Research*, (62) *Water Supply*, (63) *WIT Transactions on Ecology and the Environment*.

The frequency of publication with respect to journals was studied for different countries, and countries with more than three publications were considered for the discussion (Figure 9). The *Science of Total Environment* (4 articles), the *Journal of Hydrology* (4 articles), and *PLoS ONE* (2 articles) were the most common platforms for Australian publications. China had twenty-one publications, among which three publications were from the *Science of Total Environment*, two each were from *Applied Geochemistry*, the *Journal of China University of Geosciences*, and the *Journal of Hydrology*, and the remaining twelve articles pertaining to the selected keywords were in different journals. All publications from France were noted to be in different journals except for two in the *Journal of Hydrology*. Similarly, Germany has produced five publications on the subject, all of which appear in different journals. There were a total of six Indian publications, with two appearing in the *Science of Total Environment*. Out of a total of five Spanish publications, four were published in the *Science of Total Environment*. Similarly, among five publications from the United Kingdom, two were in the *Hydrological Processes* journal. Most of the United States publications were noted to be in different journals, and a maximum of two publications each were observed in *Applied Geochemistry*; *Bulletin of the Geological Society of America*; *Geochemistry, Geophysics, Geosystems*; *Ground Water Journal*; *Journal of Geophysical Research*; *Journal of Hydrology*; *Water Resources Research*; and *Oecologia*. It was noted that most of the publications related to the topics were observed in the *Science of Total Environment*, followed by the *Journal of Hydrology* and *Applied Geochemistry*.

Figure 9. Frequency of publications on carbon isotopes integrating rainwater and groundwater in a journal with respect to country.

The distribution of the publications with respect to isotopes of carbon in rainwater and groundwater showed that out of 132, the US topped the list with 27 publications, followed by China with 21 publications (Figure 10). Australia and France had fifteen and nine publications, respectively. India had six, followed by Germany, Spain, and the United Kingdom with five publications each. Argentina, Israel, Taiwan, and Tunisia had three publications each. Countries like Portugal, South Africa, Sri Lanka, Sweden, and Switzerland have two publications each. Other countries like Austria, Bangladesh, Belgium, Brazil, Chile, Costa Rica, the Czech Republic, Denmark, Egypt, Ethiopia, Italy, Ivory Coast, Japan, Kuwait, New Zealand, Nigeria, Norway, and Thailand had one publication each.

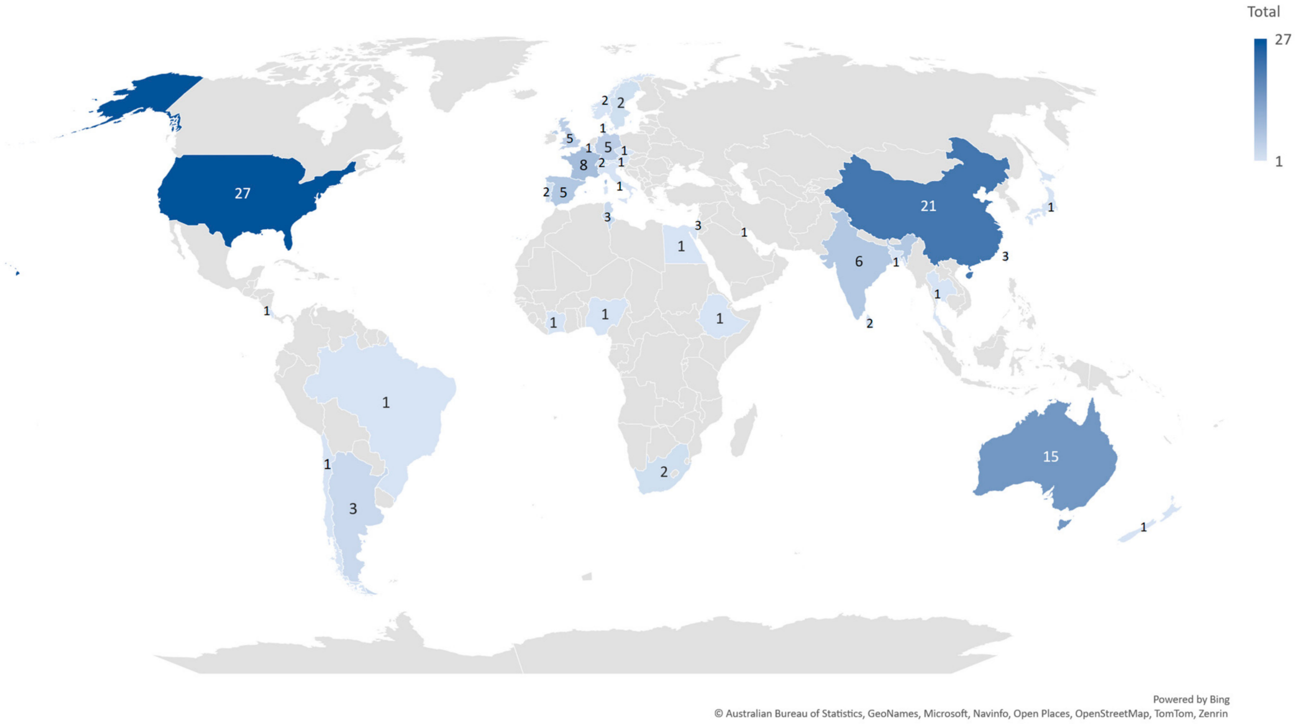

Figure 10. The number of publications on carbon isotopes, rainwater, and groundwater with respect to country.

Groundwater samples were analyzed for their radiocarbon dates using the ^{14}C isotope, particularly to ascertain the recharge rate and rate of flow. ^{13}C results have been utilized for adjustments and calibration in radiocarbon age model studies. Samples with ^{13}C levels were analyzed along with tritium isotopes to identify the sources and process of the recent recharge. Groundwater geochemical variations throughout its flow path were also studied using ^{13}C signatures; this included carbonate chemistry in groundwater that was controlled by rock–water interaction, anthropogenic sources, or natural biogenic processes. Additional attempts to trace the origins of atmospheric carbon using ^{13}C signals have been made in prior studies. Australian, Chinese, French, Italian, New Zealand, and American scientists conducted the majority of the research on atmospheric carbon signatures. These nations have also been pioneers in the study of numerous isotopes, associating DNA barcoding and environmental DNA with C isotopes and other stable isotopes, as well as hydrogeochemical parameters. The studies relating to advanced analytical processes and sampling for identifying specific processes were achieved only by countries with sophisticated infrastructural facilities, but other nations have conducted research on developing issues in tandem with these pioneers or in association with organizations like the International Atomic Energy Agency (IAEA).

It should be highlighted that publications were dependent on the pressing challenges of the locality, the analytical tools available, and the expertise of those tasked with interpreting the results. The International Atomic Energy Agency in Vienna, Austria (IAEA) has been instrumental in assisting its member states by assisting in analytical procurement activities, assisting with carbon isotope analysis of samples, and providing the requisite skills to interpret the data. In addition, regional cooperative initiatives have educated participants about carbon isotope science by giving them training with instruments and teaching them to analyze and interpret data. These efforts have aided the Asian member states (countries) in becoming more acquainted with the carbon isotopes of rain and groundwater. The Regional Cooperative Agreement (RCA) for research by the IAEA has brought together experts from multiple nations, resulting in a comprehensive and clear picture of the issue. The technological advancements in the field of isotope hydrology have been effectively addressed by the IAEA through the dissemination of information through executive meetings, sharing of knowledge through technical meetings, organizing regional training courses, providing expert missions to offer technical guidance and/or on-the-job training, and also by conducting regional-level executive management seminars to disseminate information and promote technology. Support from the IAEA allows countries without adequate capabilities for isotope analysis to have their samples analyzed by independent laboratories. Generally, the Regional Resource Unit (RRU) provides analysis of the stable isotopes of deuterium (^{2}H) and oxygen-18 (^{18}O) in water free of charge. This regional strategy facilitates technical cooperation between bewteen developing countries (TCDC) among RCA member nations allow for cost-effective resolution of regional issues shared by all members.

The use of nuclear technology to improve water quality and manage water resources is limited in several Asian nations due to a lack of resources and expertise. Assistance of IAEA has let these nations build up their own RCA infrastructure and research capacities for the future. Through mutually beneficial interactions, member states should grow closer and more familiar with one another. It has also been deduced that triangle Technical Cooperation (TC) programs and collaborative research initiatives are effective means of forging relationships. The first step in building international cooperation is to assess the various countries' requirements and resources. Opportunities for sharing technical inputs and expertise on the application of isotopic techniques, as well as introducing sustainability and capabilities at the regional and national levels, have been maximized through the IAEA initiative for regional cooperation. Since many of the RCA countries share similar local and transboundary water resource challenges, the RCA strategy has been useful in addressing these issues through the exchange of data, knowledge, and experience. This initiative has resulted in collaborative research between a few academic and research institutions.

There were some early publications on the topic of carbon isotopes in the integration of rainwater and groundwater, but this field only saw a significant uptick after 2012, when a regional cooperation project was launched (referred as RAS7022 by the IAEA) with a focus on using isotope techniques to study groundwater recharge and dynamics. Later, over the years 2016–2018 (referred to as RAS7030 by the IAEA), researchers focused on deep groundwater reserves. The increased publishing rate from Asia recently reflects the success of regional cooperation initiatives by providing member states with required analytical collaborations, data, and expertise on carbon isotopes connected to rainwater and groundwater. Apart from such initiatives to attain the UNSDGs, countries have also adopted studies to address climate change. In this regard, steps have been taken by countries to address carbon, especially in the atmosphere, rainwater, and groundwater in the carbon cycle. Still, significant research on carbon isotopes related to meso, micro, and nanoplastics is lacking.

6. Conclusions

Carbon dioxide is a greenhouse gas responsible for trapping heat and contributing to the greenhouse effect, which leads to global warming and climate change. Excessive usage of different sources of carbon threatens the Earth's atmosphere and causes a rise in temperature. Understanding the nature of carbon, its sources, types, and levels will help assess the impact of contamination in groundwater. Carbon isotope measurements are emerging techniques used to assess rainwater and groundwater quality. Since 1975, there has been a steady stream of publications on topics like precipitation and groundwater. In the present study, a literature review on carbon isotope studies from the Scopus database with important keywords provided significant insights into the status of the research in different countries, the publishing journals, and the years of significant publications. The study was based on data obtained from Scopus, and hence studies may have been missed that are not listed in the database, which could be considered as a limitation. Furthermore, the study also used keywords for filtering literature from the database, wherein certain similar words in different contexts could not have appeared in the list, for example, "aquifer" and "host rock matrix", "precipitation" and "rainwater", etc. Given the recent literature revealed few research outputs on carbon storage and sequestration with $\delta^{13}C$ isotopes, more efforts in this direction are required to address varied environments. Studies on $\delta^{13}C$ in rainwater prior to and after dust storms in arid regions and detailed studies comparing atmospheric CO_2 in different environments based on $\delta^{13}C$ values need to be future focuses. The role of carbon isotopes derived from plastics and their probability of interaction with the hydrosphere, or integrated study with other biogenic, geogenic, and anthropogenic sources, also warrant attention. The carbon isotope signatures of fugitive gases like methane and ethane (CH_4, C_2H_4) require specific analytical facilities, and such studies could be achieved only by countries with developed infrastructural facilities and with trained manpower. The study of carbon isotopes and their application is mainly limited by the availability of instruments and the cost of analysis. Hence, an increase in sophisticated facilities, especially compound-specific carbon isotope analysis in regional laboratories, promoting collaborative projects, and providing regional training courses on the analysis and interpretation of data would help to bring out valuable inferences from carbon isotopes around the globe. Research focused on carbon credits and future climate change solutions that consider the values of carbon isotopes will contribute to the SDGs set by the United Nations. In addition, the growth of analytical capabilities will spur on the creation of an extensive carbon database, which will form the basis for future machine learning (ML) and artificial intelligence (AI) studies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15193392/s1, Figure S1: USGS carbon classification in colors representing the different sources of carbon.

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