



Article

Groundwater Resources in the Main Ethiopian Rift Valley: An Overview for a Sustainable Development

Sabrina Maria Rita Bonetto , Chiara Caselle * , Domenico Antonio De Luca and Manuela Lasagna

Department of Earth Science, University of Turin, 10125 Turin, Italy; sabrina.bonetto@unito.it (S.M.R.B.); domenico.deluca@unito.it (D.A.D.L.); manuela.lasagna@unito.it (M.L.)

* Correspondence: chiara.caselle@unito.it

Abstract: In arid and semi-arid areas, human health and economic development depend on water availability, which can be greatly compromised by droughts. In some cases, the presence of natural contaminants may additionally reduce the availability of good quality water. This research analyzed the water resources and hydrochemical characteristics in a rural area of the central Main Ethiopian Rift Valley, particularly in the districts of Shashemene, Arsi Negelle, and Siraro. The study was developed using a census of the main water points (springs and wells) in the area and the sampling and physico-chemical analysis of the water, with particular regard to the fluoride concentration. In many cases, fluoride content exceeded the drinking water limits set by the World Health Organization, even in the absence of anthropogenic contamination. Two different aquifers were recognized: A shallow aquifer related to the eastern escarpment and highlands, and a deep aquifer in the lowland areas of the rift valley on the basis of compositional changes from Ca-Mg/HCO3 to Na-HCO3. The distribution of fluoride, as well as pH and EC values, showed a decrease from the center of the lowlands to the eastern highlands, with similar values closely aligned along an NNE/SSW trend. All these data contribute to creating awareness among and sharing information on the risks with rural communities and local governments to support the adequate use of the available water resources and to plan appropriate interventions to increase access to fresh water, aimed at the sustainable human and rural local development of the region.

Keywords: groundwater resources; fluoride; main Ethiopian Rift Valley



Citation: Bonetto, S.M.R.; Caselle, C.; De Luca, D.A.; Lasagna, M.
Groundwater Resources in the Main Ethiopian Rift Valley: An Overview for a Sustainable Development.

Sustainability 2021, 13, 1347.
https://doi.org/10.3390/su13031347

Academic Editor: Maurizio Tiepolo Received: 20 December 2020 Accepted: 25 January 2021 Published: 28 January 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

The regional planning and the management of natural resources require considering the interactions among human needs, ecosystem dynamics, and resource sustainability. Human needs and economic activities, such as industry, agriculture, and animal husbandry, require a continuous water supply. Over the past decades, water use has more than doubled [1], and the water demand will further increase due to a growing global human population. However, both the availability and the quality of water resources will be affected by socio-economic and technological developments, climate change and increasing climate extremes, such as droughts and floods, particularly in developing countries [2,3]. Demographic growth and unsustainable economic practices are affecting the water quantity and quality, making water an increasingly scarce and expensive resource, especially for the poor, the marginalized, and the vulnerable [4]. These factors will make it difficult to achieve the Sustainable Development Goal SDG 6 (one of the United Nations' Sustainable Development Goals (SDGs) for the year 2030), which requires sustainable management of clean accessible water for all. To achieve Goal 6, broad and in-depth knowledge of the global dynamics of water use and availability is necessary. Sustainable management of water resources for different uses will not only need to account for demand in water quantity, but also for water temperature, nutrient levels, and other pollutants [5].

The availability and quality of fresh water are particularly important in arid and hyper-arid environments, where groundwater plays an important role in supporting the

economy, being the main source of water [6,7]. In these environments, the geological setting commonly contains bedrock of crystalline rocks characterized by secondary porosity due to the presence of interconnected fractures, faults, and shear zones, which represent a favorable setting for hosting and channeling groundwater [8,9]. Therefore, groundwater flow and yield in these aquifers are strictly related to the presence of lineaments and structural features in the basement [10–12]. An additional supply of water is represented by loose deposits, such as fluvial or lacustrine deposits, that are randomly distributed on the surface [13].

The success of expensive drilling campaigns is influenced by the complexity of the geological, structural, and hydrogeological setting of many arid environments and by the lack of subsoil investigations [14]. More specifically, geological features greatly affect the yield and quality of groundwater resources. As a consequence, high concentrations of many chemical elements can occur naturally in groundwater due to the local geology and to water interactions with rocks. Several studies [15–19] have shown that water in areas with particular geological features did not meet established drinking water limits for the presence of natural geogenic contaminants without influence from anthropogenic causes.

This study focuses on the characteristics of groundwater quality in the Oromia Region of the south-center portion of the Main Ethiopian Rift (MER), which represents the northern sector of the East African Rift System. In this region, rocks are mostly volcanic, and volcanic activity is still ongoing. Only a few perennial streams are present at the surface and, despite the presence of many lakes, the water supply in the area mainly depends on rainfall because of the poor physical and chemical quality of surficial water. More specifically, due to the scarce data about water availability, the paper is mainly focused on groundwater quality in the study area.

Natural sources of elevated fluoride concentrations in groundwater and lakes in the MER have been reported in the scientific literature [20–23] and, therefore, water is not always suitable for human consumption. Indeed, prolonged ingestion of drinking water containing F^- ions that exceed the tolerance limits can cause dental and skeletal fluorosis, with negative effects on children and young people [24].

The concentration and mobilization of F^- ions and other elements in groundwater are dependent on the chemical and physical processes that occur between the water and the geological environment. The occurrence of F^- in water is generally associated with volcanic rocks, particularly in the high-temperature geothermal settings that are common at convergent plate boundaries, as well as in intraplate areas characterized by extensional tectonic activity, such as the African Rift [22].

The World Health Organization recommends a maximum concentration limit of 1.5 mg/L, in the case of hot water (above 25 °C), or in tropical countries where the daily intake of drinking water is high, the value decreases to 0.7 mg/L [25]. High concentrations of fluoride affect human health. Fluoride may give rise to mild dental fluorosis at concentrations between 0.9 and 1.2 mg/L in drinking water [26]. This is particularly true in warmer areas, where dental fluorosis occurs with lower concentrations in drinking water because of the greater amount of water consumed [27,28]. Fluoride can also have more serious effects on skeletal tissues (bones and teeth) with long-term ingestion, particularly if the drinking water contains 3–6 mg of fluoride per liter [28].

In reason of the reported presence of fluoride contaminations in surface and ground-water in neighboring areas, the present study aims to propose a census of wells and springs in the Oromia Region and qualitative analysis of the water resource available for the local communities, with particular attention to the presence and distribution of fluorides. The outcomes of the study may provide important elements for a thoughtful decision-making process aimed at the sustainable human and rural local development of the region. We focused, more specifically, on a countryside area of the West Arsi Zone (Oromia Region) in the rural district of Arsi Negelle, Shashamane, and Siraro. The area is characterized by flat land, and the economy is based upon the integration of smallholding agriculture and livestock. As a consequence, life in the community and rural activities are tightly con-

Sustainability **2021**, 13, 1347 3 of 15

nected to the water supply [29–32]. This rural area is very populated, but only 30% of the people have access to water, and rural communities are at greater risk from meteorological, hydrological, and agricultural drought [33,34]. The results of the geographical distribution and physico-chemical features of the water resource were interpreted and discussed on the basis of the geological setting of the area, creating a global picture of the water availability and quality.

2. Geological Setting

The study area is located in the central sector of the Main Ethiopian Rift Valley (MER). The MER is a NNE-SSW trending segment of the Rift Valley, and it is bordered by the Ethiopian Plateau to the west and the Somali Plateau to the east by means of evident fault slopes belonging to the main Rift Valley System Fault [35].

Lowlands (approximately 1600 m a.s.l.), transitional escarpments and highlands (approximately 2500 m a.s.l.) are the main geomorphologic environments of the MER. Many volcanic lakes are present in the lowlands. The lakes have had a recent evolution marked by transgressive and regressive phases, each phase followed by deposition of fluvio-lacustrine deposits.

The bedrock in the highlands consists predominantly of basic volcanic rocks (lava and ash, mainly of Tertiary age), whereas the bedrock in the lowlands consists mainly of acidic volcanic rocks (peralkaline silica-rich rhyolitic ignimbrites, including ash and pumice). Weathered and reworked volcanic rocks, silicic tephra, and small alluvial fans occur along the escarpments and the border of the highlands (Figure 1). Eluvial lateritic crusts are also present and consist of clay, silt, and fine sand [20,21].

The MER is geographically divided into three sectors: (i) NMER (northern MER), from the Afar depression to near Lake Koka; (ii) CMER (central MER), from Lake Koka to Lake Awasa through the lake region; and (iii) SMER (southern MER), from Lake Awasa to the broadly rifted zone of southern Ethiopia [36] (Figure 1).

The part of the Oromia Region is included in the CMER and is located in the Zway-Shala basin area. This sector is characterized by bedrock mainly consisting of volcanic products (pyroclastic rocks, rhyolites, tuffs, and basaltic lava flows), and volcano-lacustrine and fluvio-lacustrine deposits (clay, silt, sand, and gravel interbedded layers) [35,37–39]. In particular, the study area contains the Langano, Abijata, Awasa, and Shala Lakes, which are the remnants of a single wide ancient lake that extended to the area where upper Quaternary fluvio-lacustrine deposits are now observed [35]. Some lakes are connected by an ephemeral drainage system consisting of a few perennial streams and are closely linked with the groundwater system [40].

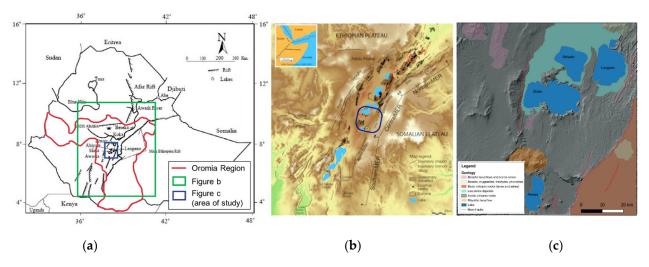


Figure 1. (a) Location of the Oromia Region, (b) sketch of the three geographic sectors of the Main Ethiopian Rift, in the blue square, the studied area (c) geological map of the study area (modified from [41]).

Sustainability **2021**, 13, 1347 4 of 15

The extensional tectonics are responsible for the presence of lineaments that are subparallel to the NE–SW-trending rift axis. In particular, at least three sets of faults have been recognized in the area: NNE–SSW, N–S, and NNW–SSE trending faults. The first two sets are dominant and extend for long distances, following the axis of a tectonically active fault system called the Wonji Fault Belt (WFB). In addition, E-W- to NW-SE-trending, cross-rift oblique-slip fault systems have been locally observed [38,39]. The marginal escarpments have well-defined, steep normal-fault scarps [40].

Older structural trends have been identified in the highlands, where faults with different orientations are reported [34,41].

Active faulting within the rift (i.e., Wonji Fault Belt) causes geothermal and fumarolic activity, and high-temperature thermal springs occur along the border of some lakes and in connection with scattered volcanic centers [21].

3. Hydrological Setting

Two major aquifer classes can be identified in the MER: (i) Extensive aquifers with intergranular permeability (unconsolidated sediment: alluvium, eluvium, colluvium, and lacustrine sediment), and (ii) extensively fractured and weathered volcanic rocks (basalts, rhyolites, trachytes, and ignimbrites) [42]. The latter shows variable transmissivity and different hydraulic conductivities in relation to both the degree of fracturing and weathering, and the presence of interbedded palaeosols and alluvial or pyroclastic deposits within the volcanic series [43].

In fractured volcanic rocks, the flow is predominantly fault-controlled and laterally discontinuous: The groundwater flows parallel and subparallel to the main trending faults, influencing the subsurface hydraulic connection among the rift lakes and the relationship between the river and groundwater. Local palaeochannels drive the groundwater flow (i.e., the palaeochannel along the Bulbula River, which connects the Ziway and Abiyata Lakes) [40,44].

Based on geological characteristics and structural settings, distinct hydrogeological systems are recognized in the highlands and lowlands [45]. Lowlands are characterized both by fractured basaltic and ignimbritic aquifers, which are mainly unconfined or semiconfined, and permeable alluvial and colluvial deposits or lacustrine deposits forming the main shallow aquifers. Conversely, in the highlands, alluvial deposits (in alluvial plains or strips along river courses) and weathered volcanic rocks (with limited interbedded alluvial gravels and sands) are present, forming multilayer confined, semi-confined, and unconfined aquifers.

In general, the main sources of recharge are rainfall and river channel losses [42]. The rate of recharge is strongly influenced by the distribution and amount of rainfall, the permeability of the rocks, the geomorphological setting, and the presence of surface water close to major unconfined and semi-confined aquifers. The main groundwater recharge occurs in the highlands and preferentially moves along the rift within the large regional faults parallel and subparallel to the axis of the rift. In most cases, the escarpments act as discharge areas, which is manifested by the occurrence of high-discharge and fault-controlled springs along them. The rift floor represents a regional discharge area, and indirect recharge from rivers and lakes occurs in the highly faulted area. Recharge and groundwater flow in the weathered upper zone of the highlands are the driving force for much of the hydrology of the Zway-Shala basin, rather than deep upwelling flow systems with long residence times. The sharp decrease in elevation favors fast drainage of the groundwater in the form of springs. The springs located along the steep boundary between the rift and escarpment have very high seasonal variations in discharge (Figure 2). The same situation exists in highland areas close to deeply incised and large river valleys [40].

Sustainability **2021**, *13*, 1347 5 of 15

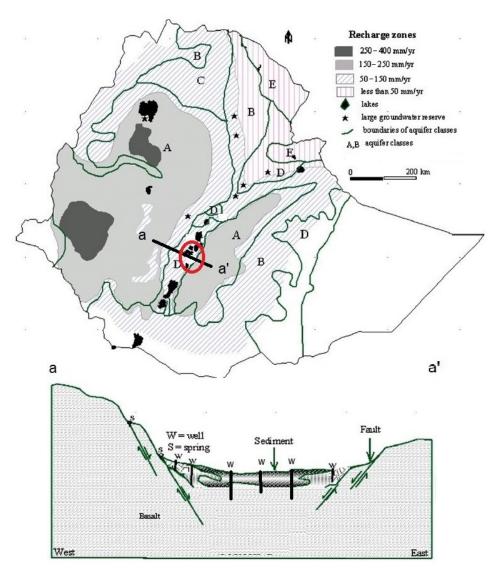


Figure 2. Map of groundwater recharge. A = widespread good quality groundwater at a relatively shallow depth (dominantly highland volcanic aquifers recharged by high rainfall). B = large groundwater reserve with fair to bad quality often localized in lower elevation areas (rift valley and volcanics in pediment covered with thick sediments and intermountain grabens), C = low to moderate groundwater reserve with fair quality (highland trap series volcanic aquifer with less sediment cover and recharge), D = low medium to high groundwater reserve in the volcanics and sediments recharged by rainfall and rivers in places with serious salinity problem, E = low groundwater reserve with moderate quality recharged by seasonal floods and streams. aa': Profile sketching the hydrogeological setting of the area (modified from [40]). The red circle shows the investigated area.

4. Materials and Methods

A field survey and groundwater sampling were performed in the districts of Shashemene, Arsi Negelle, and Siraro. The field work consisted of a census of the existing water points (wells and springs). The wells were classified into deeply drilled wells (ranging from 20 to 400 m deep) and shallow manually dug wells (up to 20 m deep).

The location of water points is reported in Figure 3. Corresponding to each water point, information about the location (geographic coordinates) and the water point features (depth, diameter, discharge) was collected. Moreover, a picture showing the conditions of the wells and springs was included. The data collection was realized with the support of the administrative staff of the Woredas and the cooperation of social promoters (LVIA).

Sustainability **2021**, 13, 1347 6 of 15

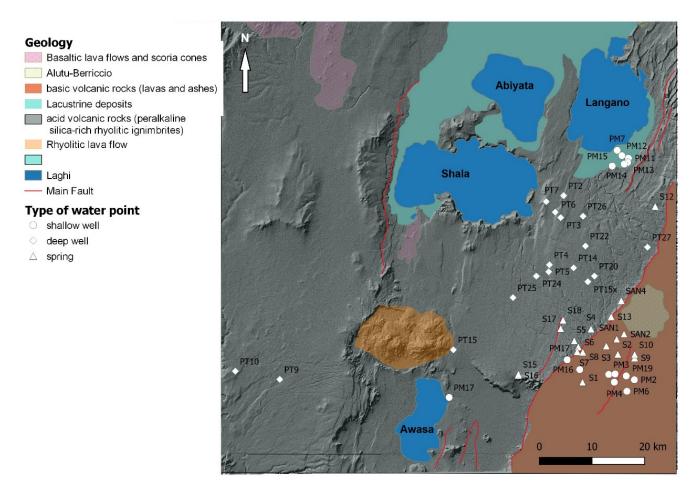


Figure 3. Types and Distribution of the Water Sampling Points in the Study Area.

To verify the groundwater quality, the following physical-chemical parameters (pH, electrical conductivity [EC], temperature, and fluoride concentration) were measured in situ with field instruments. The equipment for field measurements consisted of:

- handheld GPS instruments to locate points on a Landsat map through ArcPad,
- a portable fluoride meter (HI98402 by Hanna Instruments, USA) to measure the fluoride content in the water (ppm),
- a conductivity meter (HI99300 by Hanna Instruments, USA) to measure the water EC in the field ($\mu S/cm$),
- a freatimeter to measure the depth to groundwater in the wells;
- a litmus test for pH.

The collected field data were reported in a specific field card for each censused water point (Annex 1).

A total of 52 water points was sampled: 16 groundwater samples from shallow wells, 17 from deep wells, and 19 from springs. Groundwater from shallow wells was sampled using a polyvinyl chloride (PVC) bailer, 91 cm long and with a diameter of 4 cm. Bailer sampling techniques required a gentle lowering of the instrument into the water column of the well to reduce potential problems due to fluid turbulence and a proper transfer of water from the bottom of the bailer to sample containers. Bailers, when properly used, are an acceptable sampling tool [46,47]. Water sampling in deep wells was realized by means of pumps after at least five minutes of pumping, or until temperature and electrical conductivity EC remained stable, according to [48]. Sampling from springs was performed directly in correspondence with the water emergence from the soil. Groundwater was stored in 100-mL polyethylene bottles.

Sustainability **2021**, 13, 1347 7 of 15

Water analyses were carried out at the Hydrochemical Laboratory of the Department of Earth Sciences at the University of Turin. Major anions (Br, Cl, F, NO₂, NO₃, SO₄) were analyzed using ion chromatography. The concentrations of Ca, Mg, CO₃, and HCO₃ were measured by titration. Other ions were analyzed by spectrometry. Fluoride concentration was measured both in situ and in the laboratory.

The chemical analyses were followed by the ionic balance calculation. The level of error was calculated by using the following formula:

Error of ion balance = $((\Sigma cations - \Sigma anions)/(\Sigma cations + \Sigma anions)) \times 100$

An error of up to $\pm 5\%$ was considered as tolerable [49].

5. Results

The census of the water points in the Arsi Negele, Shashemene, and Siraro districts showed the presence of springs, shallow handmade wells, and deeply drilled wells, with a defined geographical distribution. Specifically, in this study we censused 16 shallow wells, primarily located along the eastern escarpment or along the highlands (PM in Annex 2), 30 deeply drilled wells, mainly located in the lowlands, (PT in Annex 2) and 21 springs, mainly located in the easternmost sector of the study area, particularly close to the eastern escarpment of the old caldera rift of Awasa Lake [50] (S or SAN in Annex 2). One of the censused springs (S15/c1) showed thermal physical-chemical features. Water in shallow wells may be contained in altered, highly fractured, or reworked volcanic rocks, residual soils or eluvial/colluvial deposits, while deep wells are mainly drilled in fractured volcanic rocks, intercepting water from the fractures.

The physical features of water (EC, pH, and temperature) showed an appreciable range of variability (Annex 2). The EC ranged from 57 to 1969 μ S/cm, with the lowest values measured in the springs (from 57 to 287 μ S/cm) and the highest values in the shallow and deep wells (from 109 to 1453 μ S/cm). The pH values ranged from 5.5 to 9 in wells and from 5.5 to 6 in springs, with the only exception of the thermal spring, which was strongly alkaline (pH = 8). The distribution of pH and EC showed a decrease from the center of the lowlands (western-central sector of the study area) to the eastern highlands, with similar values closely aligned along an NNE/SSW trend. The temperature ranged from 17.6 to 30 °C, with higher values in the deep wells (from 21 to 30 °C, 25.4 °C on average), and lower values in the shallow wells (from 17.6 to 24 °C, 20 °C on average) and in the springs (from 18.2 to 25 °C). The thermal spring reaches a temperature of 90 °C.

The results of the chemical analyses, reported in Annex 2 and summarized in Figures 4 and 5, identified different hydrochemical facies for the different kinds of well. In the springs and in the shallow wells, water samples can be described as both sodium bicarbonate and calcium bicarbonate, even if a higher concentration of HCO₃ was registered in the wells. In the deep wells, on the other hand, a prevalence of sodium bicarbonate facies was observed (with the only exception of p27/C1 well), suggesting the presence of a deep groundwater circulation influenced by ion exchange (i.e., Ca-Na ion exchange).

The Schoeller diagram (Figure 5) shows a similar trend for all of the samples, with the exception of the S15c/1 (i.e., thermal spring), which had high Na, Cl, and HCO₃ concentrations and very low Mg content.

In all the performed tests, the error of ion balance was inferior to $\pm 5\%$, and consequently, it was considered tolerable.

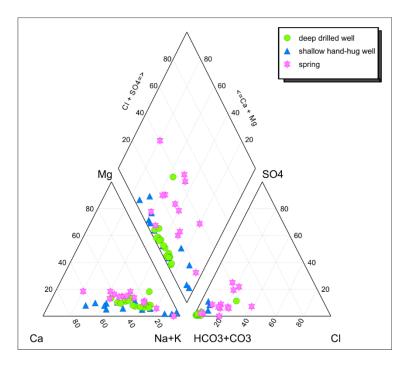


Figure 4. Piper classification diagram for different water types in the investigated area.

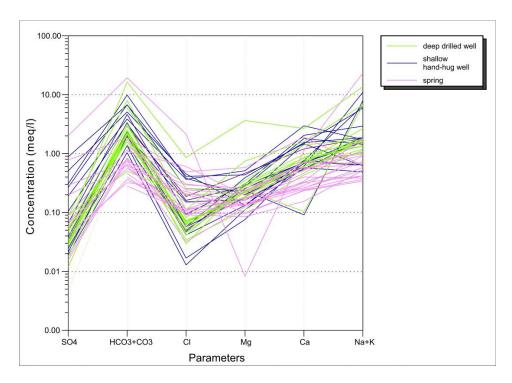


Figure 5. Schoeller classification diagram for different water types in the investigated area.

In the deep wells, despite the low concentrations of Ca and Mg, the concentration of F was usually high. Fluoride exceeding the WHO maximum acceptable concentration (1.5 mg/L) was highlighted in 25% of the samples (69% were from deeply drilled wells, 23% from shallow wells, and 8% from springs). More than 21% of the samples ranged between 0.7 and 1.5 mg/L in fluoride concentration (45% were from shallow wells and 55% from deeply drilled wells). A fluoride concentration between 1.5 and 4 mg/L was observed in the area south of Langano Lake (Arsi Negele District), whereas concentrations higher than 4 mg/L were mainly observed in the Awasa volcanic district, in the westernmost study area

(Siraro District), and southwest of Shala Lake, close to the old caldera rift [50]. The lowest values (less than 0.7 mg/L) were observed along the eastern escarpment and highlands, while the maximum concentrations were in the thermal spring of Awasa (S15/c1) and in the deep well PT15x/c1, located northeast of Awasa Lake, with values of 28.6 mg/L and 13.1 mg/L, respectively (Figure 6). However, with the exception of the thermal one, the censused springs generally showed low salinity and low fluoride concentration. The measured concentrations of fluoride describe a distribution similar to the one observed for pH and EC values, with a decrease from the center of the lowlands (western-central sector of the study area) to the eastern highlands, with similar values closely aligned along an NNE/SSW trend.

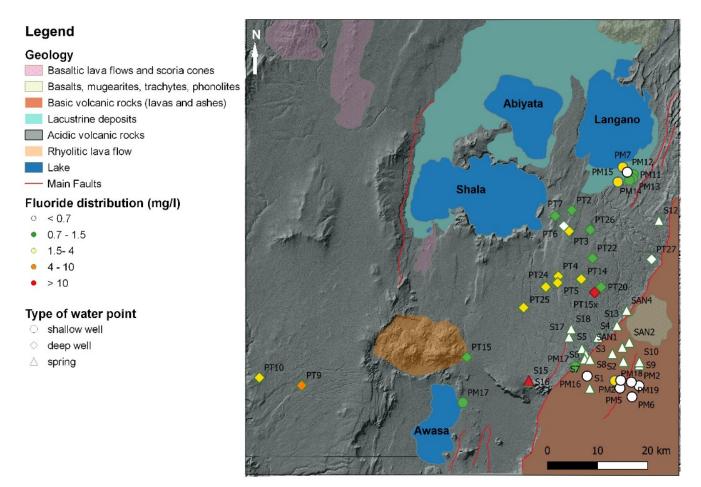


Figure 6. Geographical distribution of the fluoride values recorded in the investigated area.

The concentration of nitrates was usually below the drinking water standards (50 mg/L, [51]). Both hand-dug shallow wells and deep wells showed low nitrate concentrations, inferior to 15 mg/l (with the only exceptions of PM17/c4, having a nitrate level of 36.5 mg/L and PT27/c1, with a nitrate concentration of 45.6 mg/L). In the springs, on the other hand, the nitrate level was generally higher, often showing a concentration greater than 10 mg/L. However, only one of the springs (S16/c1) presented a nitrate concentration higher than the limits, equal to 70.1 mg/L.

6. Discussion

The geographical distribution of shallow and deep wells and springs in the Oromia region (Figures 3–6) suggests the presence of two different aquifers, respectively exploited with the different kinds of wells. The maps show, indeed, a preferential location of shallow manually-dug wells and cold springs in correspondence with the eastern escarpment and highlands, while the deep wells and the thermal springs are mainly located in the lowland

areas of the rift. The physical and chemical features of water support the hypothesis of two different water circuits, as also observed by Ayenew [40,45] and Rango et al. [21]. Water samples from the shallow wells and from the cold springs showed, indeed, lower temperatures (17 to 25 °C) and Ca–HCO $_3$ or Na–HCO $_3$ hydrochemical facies. In contrast, the hot spring and most of the groundwater samples in the rift displayed a Na–HCO $_3$ fingerprint, with Na and HCO $_3$ concentrations representing more than 80% of the ionic species in the solution. Consequently, it is possible to suggest a compositional change from Ca–Mg/HCO $_3$ to Na–HCO $_3$ along the path of groundwater flow from the highlands to the rift floor.

In accordance with the hydrogeological model proposed by [40], the shallow aquifer is hosted in altered rocks, residual soils, and fluvio-lacustrine deposits and is usually present in the uppermost tens of meters, where water flows in porous media. This aquifer is mainly located in the highland end-rift escarpments and appears more productive than those in the deep escarpments, with a decrease in permeability with the degree of alteration. In contrast, the deep aquifer of the lowlands is hosted in fractured volcanic bedrock where water is intercepted at different depths, generally hundreds of metres below the surface (up to 250–300 m). In the northern part of lowland areas, near to the lakes, however, additional shallow porous aquifers may be hosted in the fluvio-lacustrine deposits, as confirmed by the shallow wells PM7, PM11, PM13, PM15.

Data obtained from chemical analyses showed that the increase in Na observed in the deep aquifer affected the F concentration (Figure 7). Similarly, water with relatively low contents of Ca and Mg had a higher concentration of fluoride. High fluoride concentration values reflect a strong removal of Ca from the solution and a concurrent enrichment in Na. An increase in EC and temperature were also associated with the F concentration: The water temperature generally increased with the depth of the wells, as well as with the fluoride concentration (Figure 8).

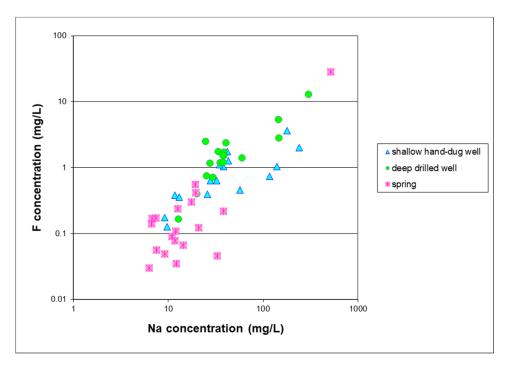


Figure 7. Scatter plot between sodium and fluoride (linear trend with equation y = 0.04x - 0.7 and $R^2 = 0.8$).

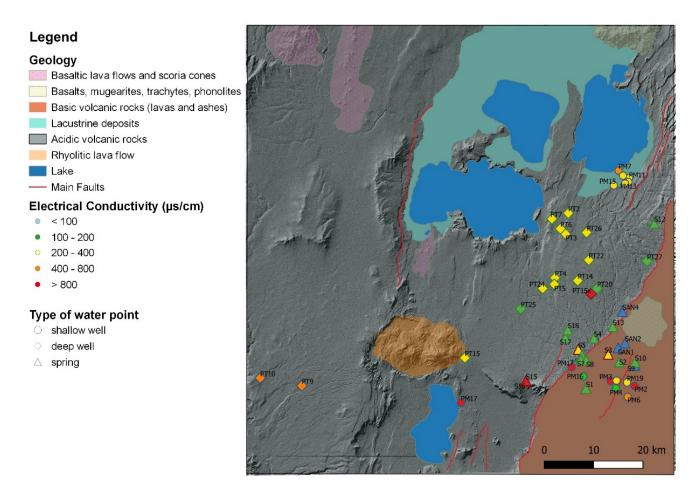


Figure 8. Geographical distribution of ce values recorded in the investigated area.

The decreasing trend of fluoride and pH and EC values from the center of the lowlands to the eastern highlands is consistent with the geological and structural framework of the area, in accordance with the type of bedrock, the distribution of surface deposits, and the orientation of the main faults (NNE/SSW to NE/SW trend).

For the springs, various hydrochemical features were recorded, suggesting two different origins, which are also reported in the literature. Springs can have a superficial flow circuit with low electrical conductivity and fluoride concentration, and relatively high nitrate levels, or a deep flow circuit of thermal water with high electrical conductivity, fluoride concentration, and temperature, and low nitrate levels. These data support an anthropic origin of nitrate concentration, probably due to the oxidation of nitrogenous waste products in human and animal excreta [52–54]. The discrimination between animal manure and domestic sewage was not possible using the current data. However, a groundwater isotopic analysis (i.e., using nitrate and boron isotopes) could be a valuable help to distinguish between these two nitrate sources and to implement management actions for groundwater protection [55,56].

The fluoride content has a geogenic origin, which is supported by the geological setting and the low anthropogenic pressure in the region, as well as by the low contents of nitrate and sulfate. During magmatic processes, fluoride does not easily fit into the crystal structure of minerals and is preferentially partitioned into melt, remaining in the residual magma until its crystallization. Consequently, fluoride is more concentrated in evolved sialic rocks, such as the bedrock of the lowland Oromia Region, rather than in primitive basic rocks (e.g., basalts) [22]. The increase in pH and temperature favors the interaction between sialic rock and water because they influence the reactions of dissolution and adsorption-desorption, which contribute to the mobility of the fluoride contained in the primary mineral phases (such as fluoride, apatite, amphibole, biotite, and volcanic glass) or

secondary minerals (such as Fe⁻, Al⁻ and Mn⁻ oxides and hydroxides, and clay minerals), particularly in arid or semi-arid climates [21,57,58].

Locally, the leaching of fluoride in groundwater is connected to the presence of active faults where the circulation of CO_2 enhances the dissolution process of silicates, oxides, and hydroxides [59]. In the study area, which is located in an active rift zone, similar conditions are common and can contribute to fluoride mobilization from rock and sediment into groundwater. The alignment of water points (springs and wells) with similar F^- ion concentrations along preferential NNE-SSW trends (consistent with the orientation of the main faults) highlights the possible tectonic contribution to the high content of fluorides in the groundwater.

7. Conclusions

In arid and semi-arid areas, human health and economic development depend on water availability, which can be strongly compromised by droughts [60]. Many people have no access to fresh water. Surface water and precipitation are insufficient, and in some cases, the quality of the water is compromised by natural contaminants.

The present research analyzed the physical and chemical characteristics of groundwater in a rural area of the central MER, particularly in the districts (Woredas) of Shashemene, Arsi Negelle, and Siraro, to create awareness of the availability, quality, and risks connected to water resource management. The study area is located in a symmetrical rift basin where groundwater flows from the highlands to the rift valley, across well-defined marginal faults that form escarpments, and into the fractured rift floor, which is dotted by volcanic cones. The study was developed using a census of the main water points (springs and wells) in the area with sampling and physical-chemical analysis of the water samples, with particular regard to the fluoride concentration. The hydrochemical analyses of the groundwater showed large variability in both geographical location and depth of the water points. Regarding the geographical distribution, most springs and shallow wells were located in relation to the eastern highland and at the bottom of the eastern plateau slopes. The deep-drilled wells were, instead, concentrated in the center lowlands of the rift valley. The depth of the groundwater surface varied within a wide range. The depth of the groundwater surface ranged from 250 to 300 m in the lowlands to a few meters in local shallow aquifers with scarce productivity, whereas, in most of the highland plains, the water depth did not exceed 50–60 m. Fluoride represents the main pollutant of groundwater. The highest fluoride contents were measured in the deep-drilled wells of the lowlands, which were related to the fractured aquifer, or in the thermal springs. Moreover, similar fluoride concentrations were primarily aligned in an NNE-SSW direction, similar to the orientation of the main fault systems of the MER. Low fluoride contents (<0.7 mg/L) were normally measured in connection with the shallow and porous aquifer of the highlands and eastern escarpment. Commonly, high fluoride concentrations were associated with Na-HCO3-type water. Two different origins were observed for the springs: A superficial flow circuit with low electrical conductivity and fluoride concentration and relatively high nitrate levels, or a deep flow circuit of thermal water with high electrical conductivity, fluoride concentration and temperature, and low nitrate levels.

The study describes the hydrogeological setting of the study area, providing a frame-work of the water-point distribution and water quality. The collected data provide information on the risks with rural communities and local governments. Moreover, these results can be useful to support the adequate use of the available water resources and to plan proper actions to increase access to fresh water (new water points, locations, expected depths of the water level, associated costs, etc.), aimed at the sustainable human and rural local development of the region.

Future studies in this region may include the measures of the static level of the water table in different periods of the year in order to evaluate the influence of the seasonality (i.e., dry season and rain season) on the water resource. In addition, quantitative analy-

sis through water flow measurements would be important to assess the real amount of available water in correspondence with the different types of wells.

Supplementary Materials: The following are available online at https://www.mdpi.com/2071-105 0/13/3/1347/s1.

Author Contributions: Conceptualization, S.M.R.B. and M.L.; methodology, S.M.R.B. and M.L.; software, M.L., C.C.; validation, S.M.R.B., M.L., D.A.D.L.; formal analysis, C.C.; data curation, C.C.; writing—original draft preparation, C.C., S.M.R.B., M.L.; writing—review and editing, C.C.; supervision, D.A.D.L.; project administration, S.M.R.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article or supplementary material.

Acknowledgments: The authors desire to thank LVIA Onlus for the useful contribution in the on-site activities.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Gleick, P.H. Water Use. Annu. Rev. Environ. Resour. 2003, 28, 275–314. [CrossRef]
- 2. Kundzewicz, Z.W.; Krysanova, V. Climate change and stream water quality in the multi-factor context. *Clim. Chang.* **2010**, *103*, 353–362. [CrossRef]
- 3. Lasagna, M.; Ducci, D.; Sellerino, M.; Mancini, S.; De Luca, D.A. Meteorological Variability and Groundwater Quality: Examples in Different Hydrogeological Settings. *Water* **2020**, *12*, 1297. [CrossRef]
- 4. Unesco. Available online: https://sustainabledevelopment.un.org/topics/waterandsanitation (accessed on 15 November 2020).
- 5. van Vliet, M.T.H.; Flörke, M.; Wada, Y. Quality matters for water scarcity. Nat. Geosci. 2017, 10, 800–802. [CrossRef]
- 6. Bechis, S.; Bonetto, S.; Bucci, A.; Canone, D.; Cristofori, E.; De Luca, D.A.; Demarchi, A.; Garnero, G.; Guerreschi, P.; Lasagna, M. Improving governance of access to water resources and their sustainable use in Hodh el Chargui communities (South East Mauritania). In Proceedings of the 20th EGU General Assembly 2018, Vienna, Austria, 4–13 April 2018; Volume 20. EGU2018-15888-1.
- 7. Datta, S.; Ajaz, A. Geospatial Data Assimilation and Mapping Groundwater Vulnerability in High Plains Aquifer Using DRASTIC Model. *Fundam. Appl. Agric.* **2019**, *4*, 933–942. [CrossRef]
- 8. Sultan, M.; Wagdy, A.; Manocha, N.; Sauck, W.; Gelil, K.A.; Youssef, A.; Becker, R.; Milewski, A.; El Alfy, Z.; Jones, C. An integrated approach for identifying aquifers in transcurrent fault systems: The Najd shear system of the Arabian Nubian shield. *J. Hydrol.* 2008, 349, 475–488. [CrossRef]
- 9. Tessema, A.; Mengistu, H.; Chirenje, E.; Abiye, T.A.; Demlie, M. The relationship between lineaments and borehole yield in North West Province, South Africa: Results from geophysical studies. *Hydrogeol. J.* **2011**, *20*, 351–368. [CrossRef]
- 10. Fernandes, A.J.; Rudolph, D.L. The influence of Cenozoic tectonics on the groundwater-production capacity of fractured zones: A case study in Sao Paulo, Brazil. *Hydrogeol. J.* **2001**, *9*, 151–167. [CrossRef]
- 11. Prabu, P.; Rajagopalan, B. Mapping of lineaments for groundwater targeting and sustainable water resource management in hard rock hydrogeological environment using RS-GIS. In *Climate Change and Regional/Local Responses*; Pallav, R., Ed.; InTech: London, UK, 2013; pp. 235–247.
- 12. Bonetto, S.M.R.; Facello, A.; Umili, G. The contribution of CurvaTool semi-automatic approach in structural and groundwater investigations. A case study in the Main Ethiopian Rift Valley. *Egypt. J. Remote Sens. Space Sci.* **2020**, 23, 97–111. [CrossRef]
- 13. Bonetto, S.; Facello, A.; Cristofori, E.I.; Camaro, W.; Demarchi, A. An Approach to Use Earth Observation Data as Support to Water Management Issues in the Ethiopian Rift. In *Climate Change Adaptation in Africa: Fostering Resilience and Capacity to Adapt. Climate Change Management*; Leal Filho, W., Belay, S., Kalangu, J., Means, W., Munishi, P., Musiyiwa, K., Eds.; Springer: Cham, Switzerland, 2016; pp. 357–374. [CrossRef]
- 14. Lasagna, M.; Bonetto, S.M.R.; Debernardi, L.; De Luca, D.A.; Semita, C.; Caselle, C. Groundwater Resources Assessment for Sustainable Development in South Sudan. *Sustainability* **2020**, *12*, 5580. [CrossRef]
- 15. Bretzler, A.; Johnson, C.A. The Geogenic Contamination Handbook: Addressing arsenic and fluoride in drinking water. *Appl. Geochem.* **2015**, *63*, 642–646. [CrossRef]
- 16. Nickson, R.; McArthur, J.M.; Ravenscroft, P.; Burgess, W.G.; Ahmed, K. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl. Geochem.* **2000**, *15*, 403–413. [CrossRef]

Sustainability **2021**, 13, 1347 14 of 15

17. Hussain, I.; Arif, M.; Hussain, J. Fluoride contamination in drinking water in rural habitations of Central Rajasthan, India. *Environ. Monit. Assess* **2011**, *184*, 5151–5158. [CrossRef] [PubMed]

- 18. Missimer, T.M.; Teaf, C.; Beeson, W.T.; Maliva, R.G.; Woolschlager, J.; Covert, D. Natural Background and Anthropogenic Arsenic Enrichment in Florida Soils, Surface Water, and Groundwater: A Review with a Discussion on Public Health Risk. *Int. J. Environ. Res. Public Health* 2018, 15, 2278. [CrossRef] [PubMed]
- 19. Alarcón-Herrera, M.T.; Martin-Alarcon, D.A.; Gutiérrez, M.; Reynoso-Cuevas, L.; Martín-Domínguez, A.; Olmos-Márquez, M.A.; Bundschuh, J. Co-occurrence, possible origin, and health-risk assessment of arsenic and fluoride in drinking water sources in Mexico: Geographical data visualization. *Sci. Total Environ.* **2020**, *698*, 134168. [CrossRef]
- 20. Ayenew, T. The distribution and hydrogeological controls of fluoride in the groundwater of central Ethiopian rift and adjacent highlands. *Environ. Earth Sci.* **2007**, *54*, 1313–1324. [CrossRef]
- 21. Rango, T.; Bianchini, G.; Beccaluva, L.; Tassinari, R. Geochemistry and water quality assessment of central Main Ethiopian Rift natural waters with emphasis on source and occurrence of fluoride and arsenic. *J. Afr. Earth Sci.* **2010**, *57*, 479–491. [CrossRef]
- 22. Bianchini, G.; Brombin, V.; Marchina, C.; Natali, C.; Godebo, T.R.; Rasini, A.; Salani, G.M. Origin of Fluoride and Arsenic in the Main Ethiopian Rift Waters. *Minerals* **2020**, *10*, 453. [CrossRef]
- 23. Bonetto, S.M.R.; De Luca, D.A.; Lasagna, M.; Lodi, R. Groundwater Distribution and Fluoride Content in the West Arsi Zone of the Oromia Region (Ethiopia). In *Engineering Geology for Society and Territory*; Springer: Cham, Switzerland, 2014; Volume 3, pp. 579–582.
- 24. Rango, T.; Bianchini, G.; Beccaluva, L.; Ayenew, T.; Colombani, N. Hydrogeochemical study in the Main Ethiopian Rift: New insights to the source and enrichment mechanism of fluoride. *Environ. Earth Sci.* **2009**, *58*, 109–118. [CrossRef]
- 25. WHO. Volume 1—Recommendations. Guidelines for Drinking Water Quality, 3rd ed.; WHO: Geneva, Switzerland, 2004.
- 26. Moulton, F.R. Fluorine and Dental Health; American Association for the Advancement of Science: Washington, DC, USA, 1942.
- 27. Environmental Protection Agency (EPA). Office of Drinking Water. Drinking Water Criteria Document on Fluoride; TR-823-5; US Environmental Protection Agency: Washington, DC, USA, 1985.
- 28. WHO. Fluorine and Fluorides; Environmental Health Criteria: Geneva, Switzerland, 1984; No. 36.
- 29. Bonetto, S.; Facello, A.; Camaro, W.; Cristofori, E.I.; Demarchi, A. An approach to integrate spatial and climatological data as support to drought monitoring and agricultural management problems in South Sudan. In Proceedings of the EGU General Assembly, Vienna, Austria, 17–22 April 2016; Volume 18. EGU2016-16952-2.
- 30. Dan-Badjo, A.T.; Diadie, H.O.; Bonetto, S.M.R.; Semita, C.; Cristofori, E.I.; Facello, A. Using Improved Varieties of Pearl Millet in Rainfed Agriculture in Response to Climate Change: A Case Study in the Tillabéri Region in Niger. In *Climate Change Research at Universities: Addressing the Mitigation and Adaptation Challenges*; Leal Filho, W., Ed.; Springer International Publishing: Cham, Switzerland, 2017; pp. 345–358.
- 31. Lasagna, M.; Dino, G.A.; Perotti, L.; Spadafora, F.; De Luca, D.A.; Yadji, G.; Dan-Badjo, A.T.; Moussa, I.; Harouna, M.; Konaté, M.; et al. Georesources and Environmental Problems in Niamey City (Niger): A Preliminary Sketch. *Energy Procedia* **2015**, 76, 67–76. [CrossRef]
- 32. Perotti, L.; Dino, G.A.; Lasagna, M.; Moussa, K.; Spadafora, F.; Yadji, G.; Dan-Badjo, A.T.; De Luca, D.A. Monitoring of Urban Growth and its Related Environmental Impacts: Niamey Case Study (Niger). *Energy Procedia* **2016**, *97*, 37–43. [CrossRef]
- 33. Demarchi, A.; Bechis, S.; Perott, L.; Garnero, G.; Isotta Cristofori, E.; Alunno, L.; Facello, A.; Semita, C.; Bonetto, S.; Guerreschi, P. An interdisciplinary approach to the analysis of agro pastoral resilience in the Hodh el Chargui region (Mauritania). In Proceedings of the 20th EGU General Assembly 2018, Vienna, Austria, 4–13 April 2018; Volume 20. EGU2018-15808-1.
- 34. Caselle, C.; Bonetto, S.M.R.; De Luca, D.A.; Lasagna, M.; Perotti, L.; Bucci, A.; Bechis, S. An Interdisciplinary Approach to the Sustainable Management of Territorial Resources in Hodh el Chargui, Mauritania. *Sustainability* **2020**, *12*, 5114. [CrossRef]
- 35. Benvenuti, M.; Carnicelli, S.; Belluomini, G.; Dainelli, N.; Di Grazia, S.; Ferrari, G.; Iasio, C.; Sagri, M.; Ventra, D.; Atnafu, B.; et al. The Ziway–Shala lake basin (main Ethiopian rift, Ethiopia): A revision of basin evolution with special reference to the Late Quaternary. *J. Afr. Earth Sci.* **2002**, 35, 247–269. [CrossRef]
- 36. Keranen, K.; Klemperer, S.L. Discontinuous and diachronous evolution of the Main Ethiopian Rift: Implications for develop-ment of continental rifts. *Earth Planet Sci. Lett.* **2008**, *265*, 96–111. [CrossRef]
- 37. Abebe, B.; Boccaletti, M.; Mazzuoli, R.; Bonini, M.; Tortorici, L.; Trua, T. *Geological Map of the Lake Ziway—Asela Region (Main Ethiopian Rift)*; 1:50000 scale; C.N.R., ARCA: Firenze, Italy, 1998.
- 38. Boccaletti, M.; Bonini, M.; Mazzuoli, R.; Trua, T. Pliocene-Quaternary volcanism and faulting in the northern Main Ethiopian Rift (with two geological maps at scale 1:50,000). *Acta Vulcanol.* **1999**, *11*, 83–97.
- 39. Abbate, E.; Bruni, P.; Sagri, M. Geology of Ethiopia: A Review and Geomorphological Perspectives. In *Landscapes and Landforms of Norway*; Billi, P., Ed.; Springer: Dordrecht, The Netherlands, 2015; pp. 33–64.
- 40. Ayenew, T.; Demlie, M.; Wohnlich, S. Hydrogeological framework and occurrence of groundwater in the Ethiopian aquifers. *J. Afr. Earth Sci.* **2008**, 52, 97–113. [CrossRef]
- 41. Dainelli, N.; Benvenuti, M.; Sagri, M. *Geological Map of the Ziway-Shala Lakes Basin*; 1:250,000. European Commission (EC), STD3 Project—Contract TS3—CT92-0076, 2001; Italian Ministry for University and Scientific and Technological Research (MURST) DB Map; Department of Earth Science, University of Florence: Firenze, Italy, 2001.
- 42. EIGS. Hydrogeological Map of Ethiopia; 1:2,000,000 scale; Ethiopian Institute of Geological Surveys: Addis Ababa, Ethiopia, 1993.

Sustainability **2021**, 13, 1347 15 of 15

43. Kebede, S.; Travi, Y.; Alemayehu, T.; Ayenew, T. Groundwater recharge, circulation and geochemical evolution in the source region of the Blue Nile River, Ethiopia. *Appl. Geochem.* **2005**, *20*, 1658–1676. [CrossRef]

- 44. Chernet, T.; Travi, Y. Preliminary observations concerning the genesis of high flouride contents in the Ethiopian Rift. In *Geoscientific Research in Northeast Africa*; Thorweiche, U., Schandlmeier, H., Eds.; Balkema: Rotterdam, The Netherlands, 1993; Volume 8, pp. 651–654.
- 45. Ayenew, T. Major ions composition of the groundwater and surface water systems and their geological and geochemical controls in the Ethiopian volcanic terrain. SINET Ethiop. J. Sci. 2006, 28, 171–188. [CrossRef]
- 46. Lee, W.E., III. A tale of two samplers-part I: A comparison of bailer and peristaltic pump groundwater sampling protocols. *Pollut. Eng.* **2002**, *34*, 4.
- 47. Lasagna, M.; De Luca, D.A. The use of multilevel sampling techniques for determining shallow aquifer nitrate profiles. *Environ. Sci. Pollut. Res.* **2016**, 23, 20431–20448. [CrossRef]
- 48. Yeskis, D.; Zavala, B. Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers. In *Ground Water Forum Issue Paper*, EPA; US EPA: Washington, DC, USA, 2002; EPA 542-S-02-001, 53p.
- 49. Appelo, C.; Postma, D. Geochemistry, Groundwater and Pollution; Balkema: Rotterdam, The Netherlands, 2004.
- 50. Boccaletti, M.; Getaneh, A.; Mazzuoli, R.; Tortorici, L.; Trua, T. Chemical variations in a bimodal magma system: The Plio-Quaternary volcanism in the Dera Nazret area (Main Ethiopian Rift, Ethiopia). *Afr. Geosci. Rev.* **1995**, *2*, 37–60.
- 51. WHO. Guidelines for Drinking-Water Quality, 4th ed.; WHO Library Cataloguing-in-Publication Data: Geneva, Switzerland, 2011.
- 52. WHO. Nitrate and Nitrite in Drinking-Water. Background Document for Development of WHO Guidelines for Drinking Water Quality. Available online: https://www.who.int/water_sanitation_health/dwq/chemicals/nitratenitrite2ndadd.pdf (accessed on 20 January 2021).
- 53. Martinelli, G.; Dadomo, A.; De Luca, D.; Mazzola, M.; Lasagna, M.; Pennisi, M.; Pilla, G.; Sacchi, E.; Saccon, P. Nitrate sources, accumulation and reduction in groundwater from Northern Italy: Insights provided by a nitrate and boron isotopic database. *Appl. Geochem.* **2018**, *91*, 23–35. [CrossRef]
- 54. Lasagna, M.; De Luca, D.A.; Franchino, E. Intrinsic groundwater vulnerability assessment: Issues, comparison of different methodologies and correlation with nitrate concentrations in NW Italy. *Environ. Earth Sci.* **2018**, 77, 277. [CrossRef]
- 55. Lasagna, M.; De Luca, D.A.; Franchino, E. The role of physical and biological processes in aquifers and their importance on groundwater vulnerability to nitrate pollution. *Environ. Earth Sci.* **2016**, *75*, 961. [CrossRef]
- 56. Lasagna, M.; De Luca, D.A. Evaluation of sources and fate of nitrates in the western Po plain groundwater (Italy) using nitrogen and boron isotopes. *Environ. Sci. Pollut. Res.* **2019**, *26*, 2089–2104. [CrossRef] [PubMed]
- 57. Amini, M.; Mueller, K.; Abbaspour, K.C.; Rosenberg, T.; Afyuni, M.; Møller, K.N.; Sarr, M.; Johnson, C.A. Statistical Modeling of Global Geogenic Fluoride Contamination in Groundwaters. *Environ. Sci. Technol.* **2008**, 42, 3662–3668. [CrossRef]
- 58. Belete, A.; Beccaluva, L.; Bianchini, G.; Colombani, N.; Fazzini, M.; Marchina, C.; Natali, C.; Rango, T. Water-rock intercation and lake hydrochemistry in the Main Ethiopian Rift. In *Landscape and Landforms of Ethiopia*; Paolo, B., Ed.; Springer: Berlin/Heidelberg, Germany, 2015; pp. 307–321.
- 59. Sracek, O.; Wanke, H.; Ndakunda, N.; Mihaljevic, M.; Buzek, F. Geochemistry and fluoride levels of geothermal springs in Namibia. *J. Geochem. Explor.* **2015**, *148*, 96–104. [CrossRef]
- 60. Caselle, C.; Lasagna, M.; Bonetto, S.M.R.; De Luca, D.A.; Bechis, S. Groundwater features in Hoedh el Chargui, Mauritania. *Acque Sotter. Ital. J. Groundw.* **2020**, *9*, 43–51. [CrossRef]