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Investigating Nitrate with Other Constituents in Groundwater in Two Contrasting Tropical Highland Watersheds

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Abstract: Nitrate is globally the most widespread and widely studied groundwater contaminant. However, few studies have been conducted in sub-Saharan Africa, where the leaching potential is enhanced during the rainy monsoon phase. The few monitoring studies found concentrations over drinking water standards of 10 mg N-NO_3^- L^{-1} in the groundwater, the primary water supply in rural communities. Studies on nitrate movement are limited to the volcanic Ethiopian highlands. Therefore, this study aimed to evaluate the transport and fate of nitrate in groundwater and identify processes that control the concentrations. Water table height, nitrate, chloride, ammonium, reduced iron, and three other groundwater constituents were determined monthly in the groundwater in over 30 wells in two contrasting volcanic watersheds over two years in the Ethiopian highlands. The first watershed was Dangishta, with lava intrusion dikes that blocked the subsurface flow in the valley bottom. The water table remained within 3 m of the surface. The second watershed without volcanic barriers was Robit Bata. The water table dropped rapidly within three months of the end of the rain phase and disappeared except near faults. The average nitrate concentration in both watersheds was between 4 and 5 mg N-NO_3^- L^{-1}. Hydrogeology influenced the transport and fate of nitrogen. In Dangishta, water was blocked by volcanic lava intrusion dikes, and residence time in the aquifer was larger than in Robit Bata. Consequently, nitrate remained high (in several wells, 10 mg N-NO_3^- L^{-1}) and decreased slowly due to denitrification. In Robit Bata, the water residence time was lower, and peak concentrations were only observed in the month after fertilizer application; otherwise, it was near an average of 4 mg N-NO_3^- L^{-1}. Nitrate concentrations were predicted using a multiple linear regression model. Hydrology explained the nitrate concentrations in Robit Bata. In Dangishta, biogeochemistry was also significant.

Keywords: Ethiopia; groundwater; highlands; nitrate; Sub-Saharan Africa; volcanic

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1. Introduction

Nitrate is the most extensive groundwater contaminant globally [1–3]. Diffuse sources such as excess nitrogen fertilizer in intensively cropped land and urban areas without sanitation facilities are significant sources of nitrate [4–7]. Shallow aquifers are often the only safe drinking water source for rural communities [8,9]. For instance, more than 90% of the public drinking water in Ethiopia is supplied from groundwater wells [10], most of which are shallow [11]. High nitrate concentration in drinking water causes diseases such as thyroid and methemoglobinemia in infants [1,12]. The World Health Organization [13] has established 10 mg N-NO_3^- L^{-1} as a maximum allowable level of concentration for drinking water.

Nitrate concentration in groundwater has been well studied in the past 100 years. A search with "groundwater and nitrate" resulted in 12,500 citations in the Science Citation Index. However, only 1% of these studies were conducted in Africa and less than 0.1% in Ethiopia. These studies in Ethiopia were mainly focused on the evaluation of concentration levels in groundwater [14–17]. Only one study looked at the mechanisms of nitrate transport in groundwater [8]. Thus, despite the overabundance of global studies on nitrate pollution in groundwater, investigations on nitrate transport and its fate in groundwater are still needed in sub-Saharan Africa and Ethiopia because of the complex hydrologic pathways in volcanic soils. Moreover, nitrate leaching is faster in the sub-humid and humid tropical monsoon climate than in temperate climates because of more than 1200 mm of rainfall within four to five months [18]. On the other hand, the temperature is higher in the tropics, and watersheds are wetter, with many valley bottoms being saturated, enhancing denitrification and lowering nitrate concentrations.

The hydrology in the Ethiopian highlands is affected by the volcanic past. Despite their loam or clay texture, volcanic soils have high infiltration rates that, in many cases, are greater than 100 mm h^{-1} [19,20]. Only when the soils are saturated does overland flow occur. In addition, water transport through fissures and faults, and blockage by volcanic dikes, in Ethiopia's volcanic landscape significantly affect hydrology [14]. Subsurface water transfer between watersheds and basins is commonplace [21,22]. Additionally, land-use alteration due to agricultural practice for many years has modified the hydrology [23].

To feed the increasing population in sub-Sahara Africa, nitrogen fertilizer use increased by 6 Gg over the last 20 years to intensify agriculture [24]. In Ethiopia, nitrogen fertilizer use increased twofold within the past two decades, and the current input is 43 kg N ha^{-1} [25]. Therefore, to understand the dangers of groundwater pollution in the highlands with a monsoon climate such as Ethiopia, this study aims to contribute to understanding the transport and fate of nitrate in the volcanic soils and groundwater systems in the sub-humid and humid tropical highlands with a monsoon climate. To meet the objective, groundwater nitrate concentration and other geological, hydrological, and chemical parameters were evaluated in two geologically contrasting watersheds over two years. The watersheds were different in hydrogeology, farming practices, and extent of irrigation.

2. Materials and Methods

2.1. Description of the Two Watersheds

The 57 km^2 Dangishta and 9 km^2 Robit Bata watersheds are part of the Lake Tana basin in the headwaters of the Blue Nile. The Dangishta watershed is south of Lake Tana in the upper Gilgel Abay catchment. Robit Bata is at the southeastern edge of Lake Tana (Figure 1). Dangishta has a tropical highland monsoon climate rain phase between May and October. Over the past ten years, the annual average rainfall in Dangishta was 1745 mm a^{-1}, with temperatures varying between 10 °C and 25 °C. In Robit Bata, the average annual rainfall was 1420 mm a^{-1}, of which most falls between June and September. The temperature was between 11 °C and 27 °C.

Quaternary olivine volcanic rock is the geologic unit in the Dangishta watershed. The unit consists of porphyritic basalts, basaltic breccias, minor tuff, and scoriaceous lava flows with young cinder cones and vesicular basalts [26]. The transmissivity of Quaternary basalts is high and ranges from 100 to 200 m^2 day^{-1} [27]. Quaternary lacustrine and alluvial deposits are found in the lower part of the Robit Bata watershed, where the aquifer was located. Transmissivity of the Quaternary alluvial sediment is around 700 m^2 day^{-1} [27].

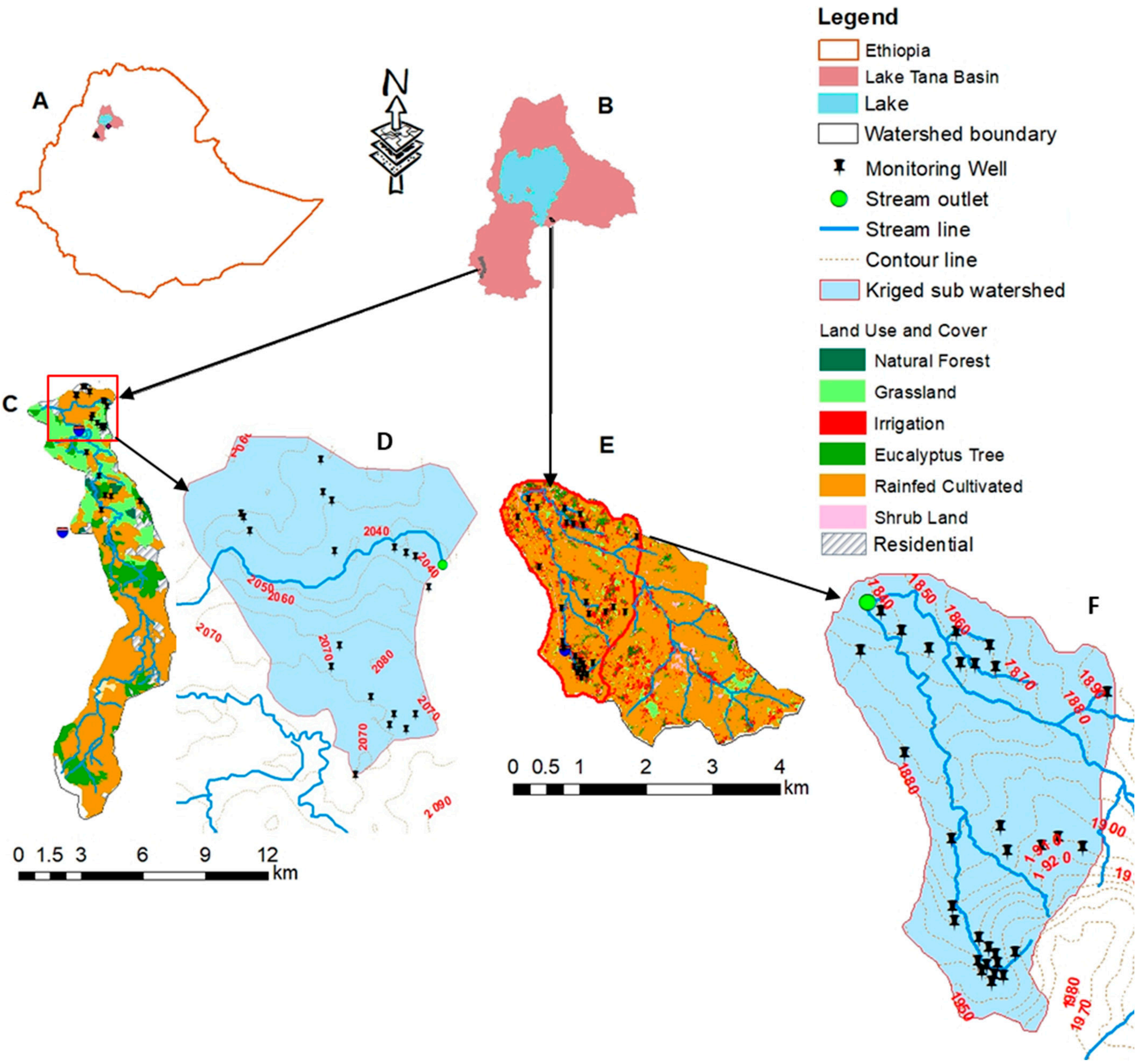

Figure 1. Location of Dangishta and Robit Bata watersheds in Lake Tana basin. (**A**) Lake Tana basin and (**B**) Lake Tana basin with Dangishta and Robit Bata watershed. Land-use maps, monitoring wells, and rain gauges for (**C**) Dangishta and (**E**) Robit Bata watersheds. (**D**) The topographic map of Dangishta and (**F**) Robit Bata, the area used for nitrate kriging.

In Dangishta, the surface soil consists of Regosols, Alisols, Nitosols, and Vertisols [19]. The soil depth varies from 4 to 21 m (Figure 2C), with the deepest soils in the uplands. In Robit Bata, the upper part of the watershed is severely degraded (Figure 2D), with shallow Eutric Cambisols and Luvisols soils over bedrock [28]. Deep Alisols are underlain by a conductive regolith layer above the bedrock in the mid and lower portion of the watershed (Figure 2E,F).

Figure 2. Maps and photos depicting features in the Dangishta and Robit Bata watersheds: (**A**) map of Dangishta showing seasonally saturated floodplain (taken from Google Earth image on 6 June 2018); yellow line is the boundary of the floodplain, and arrows indicate surface water flow directions; (**B**) photo taken in the rain phase of 2021 that shows subsurface flow is surfaced and appears as springs in a floodplain in Dangishta; (**C**) riverbank in Dangishta shows that the valley bottom has deep soils (except for areas with volcanic dikes); (**D**) a thin weathered topsoil with gravel at steeply sloping areas in Robit Bata; (**E**) excavated well materials from a 12 m deep hand-dug well; and (**F**) photograph of bedrock geology with visible outcrops in riverbeds of Robit Bata. (**C**–**E**) were photographed in 2018 and (**F**) in 2017.

The volcanic surface soils are highly conductive. In both watersheds, the infiltration rate exceeded the rainfall intensity less than 2.5% of the time [19,20]. Otherwise, the two watersheds are hydrologically different. In Dangishta, 87% of the area is underlain by the aquifer [29,30]. About 90% of the excess rainfall flows laterally through fissures and faults to the main watercourse. It is forced to the surface by volcanic dikes nearly perpendicular to the stream and appears as springs in the valley bottom (Figure 2B). It results in a grass-covered floodplain with a high groundwater table and is unsuitable as cropland (Figure 2A). A hillslope aquifer underlies Robit Bata's middle and lower portion of the watershed. The upper part with thin soils becomes saturated during rainfall, generating saturation excess overland flow. Unlike Dangishta, interflow does not resurface but directly discharges to the stream. Hence, a minimum grassland along the creeks periodically saturates, as seen in Figure 2F.

Rainfed cultivated land is practiced on 65% of the land in Dangishta and 74% in Robit Bata. The combined acreage of grassland and eucalyptus is 32% of the land in Dangishta but under 10% in Robit Bata [29]. Thirteen percent of the land is irrigated in Robit Bata during the dry monsoon phase. Irrigation in Dangishta is negligible at less than 1%.

Crop and livestock-integrated agriculture practices are followed [31,32]. Cereal crops, including 'tef' (*Eragrostis tef*), maize (*Zea mays*), millet (*Eleusine coracana*), and barley (*Hordeum vulgare*) are grown on rainfed land. Khat, a mild narcotic perennial small bush, is irrigated during the dry phase in Robit Bata [33]. According to the local agricultural office, livestock densities are 975 animal units per square kilometer in Robit Bata and 1500 in Dangishta.

Fertilizer use in the two watersheds was documented in 2017 by the Bahir Dar University in collaboration with Feed the Future Innovation Lab for Small-Scale Irrigation (ILSSI). The results are summarized in Table 1. Di-ammonium phosphate (DAP), urea, and organic compost fertilizers were applied in split doses. The first application consisting of DAP and compost occurred when crops were planted at the beginning of the rainy phase in May or early June in Dangishta and the end of June in Robit Bata. The second application of urea was in July in both watersheds. In Robit Bata, urea was applied to irrigated khat in the dry phase from November to March.

Table 1. Summary of fertilizers used and average N and P application rate in Dangishta and Robit Bata.

Fertilizers	Ingredients	Application Rate (kg N or P ha^{-1})						National-Level Application (CSA 2021)	
		Dangishta		Robit Bata					
		Rainfed		Rainfed		Irrigation			
		N	P	N	P	N	P	N	P
UREA $CO(NH_2)_2$	N.P.K (46:0:0)	48	0	45	0	5	0		
DAP $(NH_4)_2HPO_4$	18% N, and 20% P	24	27	23	25	2	3		
Compost	1.8% N, 0.25% P	3	0.4	1	0.1	22	3		
Total	Total applied (kg ha^{-1})	75	27	69	25	29	6	43	17

2.2. Data Collection

Meteorological, hydrological, and water quality data were collected from January 2017 to December 2018. These include groundwater table depth and precipitation. In addition, pH, electric conductivity, NO_3^-, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and Fe^{2+} were analyzed in groundwater samples. Additionally, chloride in precipitation and nitrate concentration in streams were measured.

2.2.1. Precipitation

In Dangishta, the rainfall depth was recorded every 10 min with a tipping bucket located in the middle of the catchment (Figure 1C). In addition, a bucket-type rainwater gauge collected water samples for chloride concentration. Missing precipitation data were filled in by linear regressing of rainfall recorded at the National Meteorological Agency (ENMA) weather station 5.3 km away [29].

For Robit Bata, in 2017, precipitation data were obtained from the National Meteorological Agency (NMA) Zenzelima weather station located at a 3.4 km distance away. Precipitation was measured on-site using a tipping bucket in 2018.

2.2.2. Data Collected at the Monitored Shallow Wells

One-meter-diameter hand-dug wells used for domestic water supply and irrigation were monitored. The wells were dug until bedrock along fault lines where water is available most of the year. In Dangishta, 32 wells were monitored. The well depth varied with topography and was around 21 m upslope and 4 m in the valley bottom. In Robit Bata, 35 wells were observed (Figure 1F). Well depths varied from 6 to 18 m. Wells with the shallowest depths were close to the river. Tilahun et al. (2020) [20] used some of these wells to determine the groundwater potential for irrigation beginning in 2015.

Groundwater levels were measured monthly using a tape measure in the dry phase and weekly in the rain phase. The pH and electrical conductivity (EC) were measured on-site using Yellow Springs Instrument (YSI) ProDSS (digital sampling system) multi-parameter. Monthly groundwater samples were collected: 748 samples from 32 wells in Dangishta and 792 from 35 wells in Robit Bata. The samples were filtered through Whatman filter paper with a 0.45 µm pore size filter and stored below 4 °C until analyzed within a week. The standard Palin test method was used to analyze all chemical parameters [34,35] using photometer 7100. The detailed analysis methods are described in the Palintest Operation Manual [36].

2.2.3. Analysis of Chloride in Precipitation and Nitrate in Streams

The chloride concentration in the rain was measured in Dangishta in 45 rain events in the rain phase from April to October 2017. The rainwater was collected in a bucket 2 m above the ground surface.

The nitrate and ammonium concentrations in the stream at the outlet in the rain phase were measured for 34 runoff events in Dangishta and 47 in Robit Bata. Between 4 and 15 water samples were collected per storm event. On days without a runoff event, the baseflow was sampled once. In the dry phase, the concentrations in baseflow were measured once a month. The stream in Robit Bata did not have water from January to May, and concentrations were not recorded for these months. Based on these data, average monthly flow-weighted concentrations were calculated. The detail on the streamflow measurements and sampling handling are published in [29].

2.2.4. Land-Use and Cover Data Acquisition

The land use for Dangishta was obtained from the Amhara Design and Supervision Works Enterprise [37]. Land use was classified as natural forests, grassland, eucalyptus, shrubs, homestead (residential), and rainfed cropland. For Robit Bata, land use was summarized by Takele [37] and consisted of natural forests, grassland, irrigated land, eucalyptus, shrubs, homestead, and rainfed cropland.

2.3. Data Analysis

2.3.1. Surface and Groundwater Interaction

The effect of fertilizer application on groundwater nitrate concentrations level was investigated by cataloging the land use in a sphere around each well with GIS (Figure S1). Spheres with radii of 25, 50, 100, and 150 m were examined based on the work of [38–40]. Spheres with a 100 m radius in Dangishta and 50 m in Robit Bata were selected because nitrate concentrations in wells were most closely related to land-use-associated fertilizer applications shown in Supplementary Materials A (Tables S1 and S2). Nitrogen fertilizer applications based on farmers' survey data are shown in Supplementary Materials A (Table S3).

2.3.2. Groundwater Redox Potential

The redox framework of McMahon et al. [41], which is based on the dissolved concentrations of Fe^{2+} and $NH_4{}^+$, was used to assess the redox condition of the groundwater. Concentrations for oxic and anoxic conditions are listed in Table S4.

2.3.3. Mapping of Groundwater Constituents

The ordinary kriging option in the Spatial Analyst Tool of ArcGIS 10.8 was used [42,43] to spatially interpolate the monthly collected concentration data in portions of watersheds with a sufficient number of wells (Figure 1D,F). The semi-variogram spherical model [44] had the smallest root mean square error and was used for interpolation. The kriged areas were 346 ha in the eastern part of the Dangishta area and 413 ha in the northern part of Robit Bata. Kriged maps were prepared for nitrate and those parameters that affected the nitrate distribution in the watershed, such as water table depth, chloride nitrate ratio, and Fe^{2+}.

2.3.4. Statistical Data Analysis

Statistical testing was performed to identify processes that influence temporal nitrate in shallow groundwater. Using the monthly measurements, we first employed the Pearson correlation test to evaluate the relationship between nitrate and groundwater constituents and the groundwater table. Then, the multiple linear regression model test was implemented to explain the combined effects of biogeochemical and physical factors on nitrate concentrations. Parameters included were precipitation (P), groundwater depth (GWD), and all groundwater constituents including pH, EC, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and Fe^{2+}. A stepwise regression procedure was employed to remove variables in the model by checking their significance ($a > 0.05$ for removing a parameter from the model). Seventy percent of the data were used to train the model and 30% for validation. The goodness of fit of the regression models was judged by maximizing the adjusted R-squared values. Histogram and Q–Q plots were used to verify the normality assumption in the residuals. The R programming statistical software package was used.

3. Results

3.1. Precipitation

Figure 3 shows rainfall amounts over the two years. It rained more in 2017 than in 2018 with a difference of 620 mm in Dangishta and 480 mm in Robit Bata (Supplementary Materials A Table S5). July and August were the wettest months. The highest recorded daily rainfall was 123 mm on 21 July 2017 in Robit Bata and 61 mm on 28 August 2017 in Dangishta (Figure 3A,C). The rainfall intensities are less than soil infiltration rates in unsaturated soils [20].

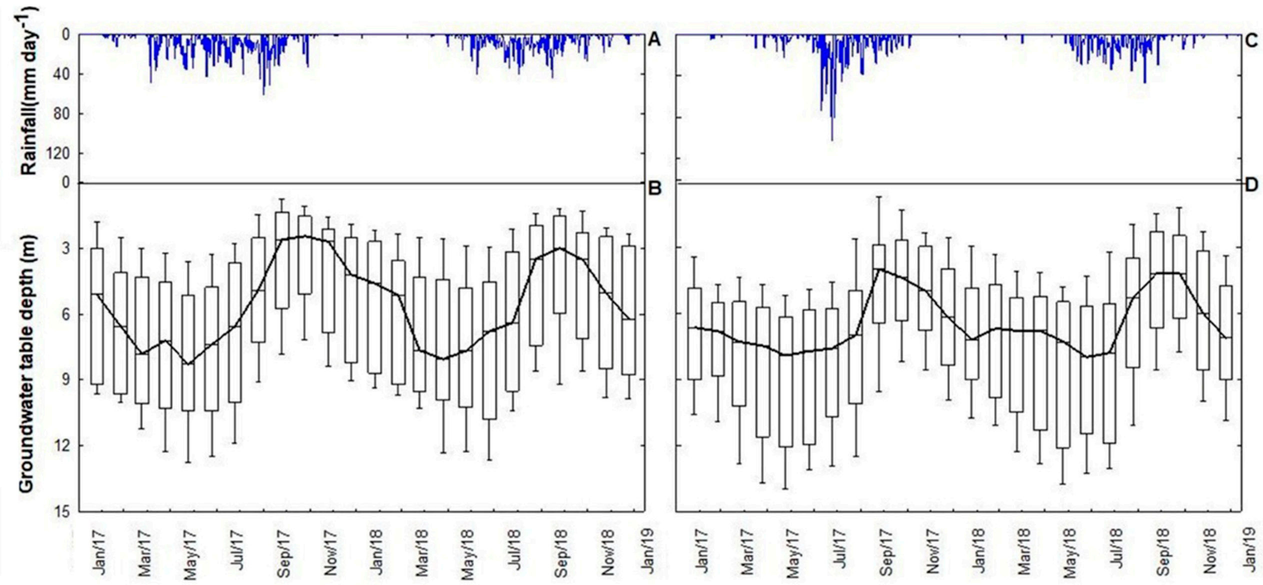

Figure 3. Boxplots of water table depth of 2017 and 2018. (**A**,**B**) is for Dangishta, and (**C**,**D**) is for Robit Bata watershed. Each box plot is based on data from 32 wells in Dangishta and 35 in Robit Bata, with 25th and 75th percentiles lower and upper ends. The black line passes through the median.

3.2. Chloride Concentration of the Precipitation

Average chloride concentrations in rainwater measured in Dangishta early in the 2017 rain phase were 10 mg L^{-1} from April to June (Figure 4). Concentrations decreased to an average of 5 mg L^{-1} in the remaining months. The same trend of Cl^- concentration in rainfall in Ethiopia's highlands was reported by Banks et al. [8], but concentrations were slightly lower compared to this study.

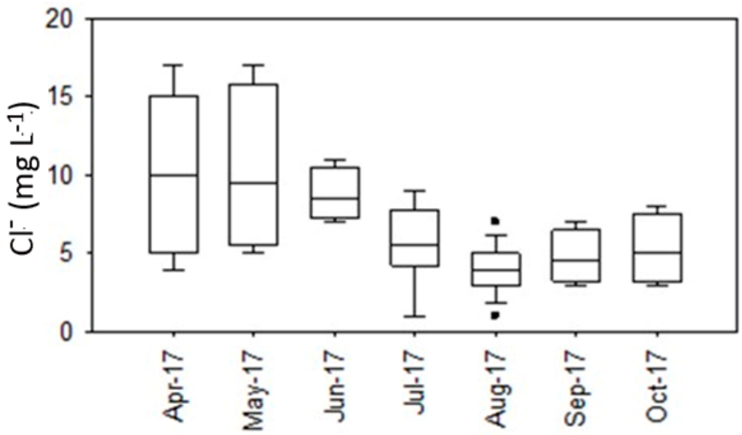

Figure 4. Boxplots of month chloride concentrations in precipitation in Dangishta in the 2017 rain phase. The dots placed above and below whiskers indicate outliers.

3.3. Groundwater

The water table measurements from 1 January 2017 to 31 December 2018 are summarized in Figure 3B,D and Figure 5 in Dangishta and Robit Bata.

3.3.1. Temporal Variation in Groundwater Levels

The temporal characteristics of the rise in the groundwater table at the beginning of the rain phase were the same in the two watersheds (Figure 3B,D). The rains and runoff began in May in Dangishta (Figure 3A) and in June in Robit Bata (Figure 3C). Otherwise, the watersheds behaved differently. The groundwater table reached the maximum level in September for Dangishta and in August for Robit Bata. After September, when the rains had stopped, water tables decreased. In Robit Bata, the rivers dried up in December, after which the groundwater was only found near the faults [20]. In Dangishta, volcanic dikes across the valley prevented subsurface flow from leaving [21,45]. The water table was maintained year-round in the lower part of the valley bottom, and the river flowed all year long in Dangishta.

3.3.2. Spatial Occurrence of the Groundwater Table

The monthly water table depths averaged over both years are shown in Figure 5. As expected, groundwater tables were the shallowest at the lowest elevations in Dangishta (west) and Robit Bata (north). At the end of the rain phase (August and September), the water tables were near the surface in both watersheds (i.e., the blue-colored areas in Figure 5 with depths less than 3 m). It remained at less than 4 m during the dry phase in the flood plain near the outlet in Dangishta (Figures 2A and 5A), where volcanic dikes blocked the subsurface flow, forcing the water to the surface and to appear as springs (Figure 2B). This also kept the water table elevated during the dry phase. Volcanic dikes are absent in Robit Bata. The groundwater depth near the faults varied from 6 to 8 m during the dry phase.

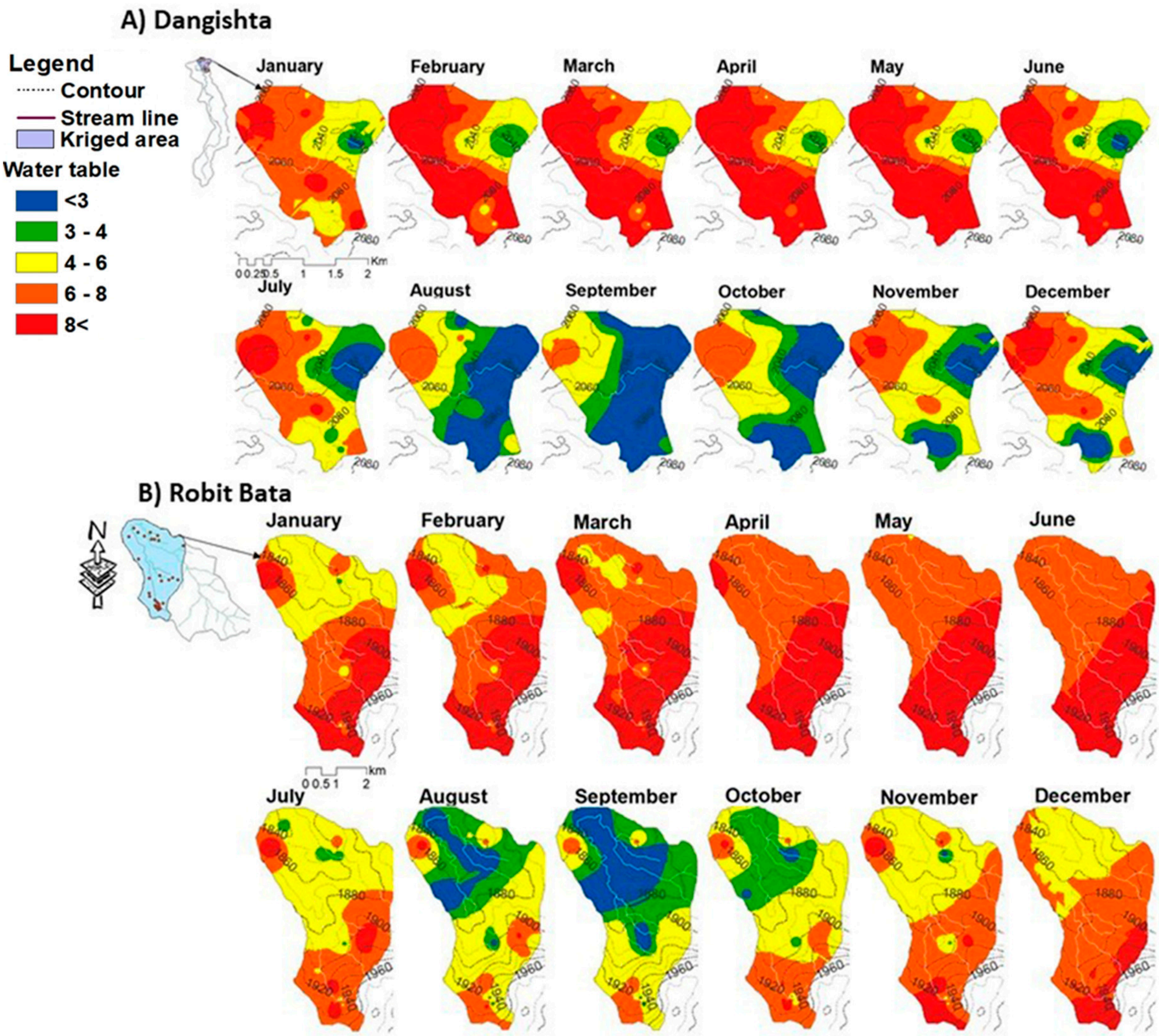

Figure 5. Kriged groundwater table level averaged over 2017 and 2018 for January to December (**A**) Dangishta and (**B**) Robit Bata.

Close inspection of Figure 5A shows that in northwest Dangishta at the watershed boundary, the water table remained below 6 m throughout the year. In contrast, the water tables increased during the rain phase to near the surface in the southeast. The land surface is less sloping and has a larger contributing area in the southeast than in the northwest (Figure 1D). Since the land slope and the water table gradient nearly coincide, the downslope velocity is smaller in the southeast, and the subsurface flow is greater. Consequently, the water builds up. In the northeast, where the steep slopes border the watershed divide, the subsurface flow is faster, and the water table does not increase as much [20]. In Robit Bata, the upper slopes are steeper in the south of the aquifer area than at the outlet (Figure 1F). In addition, the flow increases going downhill. It results in a water table closer to the surface during the rain phase near the outlet in the north.

3.4. Groundwater Constituents

3.4.1. pH

In Dangishta, the pH of the groundwater ranges from 5.1 to 7.1, with an average of 5.8. The surface soil pH was slightly more acidic, with a pH of 5.0 [29]. In Robit Bata, the groundwater pH ranged from 5.6 to 7.5, with an average of 6.7 (Table 2). The average surface soil pH was 5.6. The pH in the humid Dangishta with high rainfall was lower than in the sub-humid Robit Bata because more cations such as Ca^{2+}, Mg^{2+}, and K^{+} were leached out of the topsoil with the higher rainfall. In the southern part of Ethiopia in the Dawa River basin, Woldemariyam and Ayenew [46] similarly found that groundwater in volcanic formations in the upper reach of a basin with more than 1500 mm rainfall had a pH below 7. The lower reach that received 200 mm of rain had a pH greater than 7.

Table 2. Maximum, minimum, and average EC (μS cm^{-1}), pH, and constituent concentrations (mg L^{-1}) in the groundwater of Dangishta and Robit Bata.

Watershed	Statistic	pH	EC	N-NO_3^-	N-NH_4^+	Cl^-	K^+	Mg^{2+}	Ca^{2+}	Fe^{2+}
Dangishta	Min.	5.1	44	0.1	<0.01	<0.01	<0.01	2	1	<0.01
	Max.	7.1	296	20.2	4.4	82	31	41	44	0.7
	mean	5.8	152	4.6	0.1	6.9	1.8	9	12	0.2
	Sd.	0.4	56	3.9	0.3	9.1	2	8	12	0.1
	Med.	6.1	150	4.0	0.1	4	1.5	6	7	0.3
	%Cv.	6.7	37	84.4	289	132.1	90.4	71	56	83.3
Robit Bata	Min.	5.6	43	0.1	<0.01	<0.01	<0.01	4	1	<0.01
	Max.	7.5	646	19	2.4	38	10.5	42	48	0.8
	Mean	6.7	144	4.0	0.1	4.1	1.3	10	13	0.1
	Sd.	0.3	59	2.6	0.2	4.6	1	9	12	0.1
	Med.	6.5	138	4.1	0.1	3	1.2	5.5	6.8	0.11
	%Cv.	4.8	41	65.3	199	112	80.2	57.7	51.3	89.9

3.4.2. Calcium, Magnesium, and Potassium

The yearly averaged cations (Ca^{2+}, Mg^{2+}, and K^{+}) were insignificantly different between the two watersheds (Table 2). However, the monthly concentrations were different between the watersheds. Ca^{2+} was high from April to June and less in September (Figure 6B) in Dangishta. In Robit Bata, Ca^{2+} and Mg^{2+} were high from January to June, when the groundwater was only available near the faults and evaporation was much greater than the rainfall. The cation concentrations were low from July to September when groundwater was recharged [47].

Potassium concentrations in both watersheds hardly varied throughout the year, except some wells recorded high concentrations in Robit Bata following high rainfall (Figure 6D,I). The order of cation abundance was ranked (i.e., $Ca^{2+} > Mg^{2+} > K^{+}$), and was the same as reported by Fenta et al. [14] in groundwater around Dangila town near the Dangishta watershed.

3.4.3. Chloride

The average chloride (Cl^-) concentration in Dangishta was nearly 7 mg L^{-1}. It was only 4 mg L^{-1} in Robit Bata (Table 2). The higher Cl^- concentrations in the groundwater of Dangishta were caused by the high chloride concentration in the early rainfalls in April, May, and partially in June (Figures 4 and 7D). These early rains with high Cl^- did not fall in Robit Bata (Figure 7F), and consequently, the chloride contribution of the rainfall to the groundwater was less. The monthly Cl^- concentration in the groundwater in Dangishta followed the precipitation with a high concentration early in the rain phase and gradually declined (Figure 7D). The groundwater chloride concentration in Robit Bata was less in the dry phase than in the rain phase. In volcanic highlands, Cl^- geological formation for halide dissolution is negligible [8,14,48]. In contrast, adsorption in the soil is expected [49], and it is likely the reason that the chloride concentration declined in the dry phase during transient unsaturated flow.

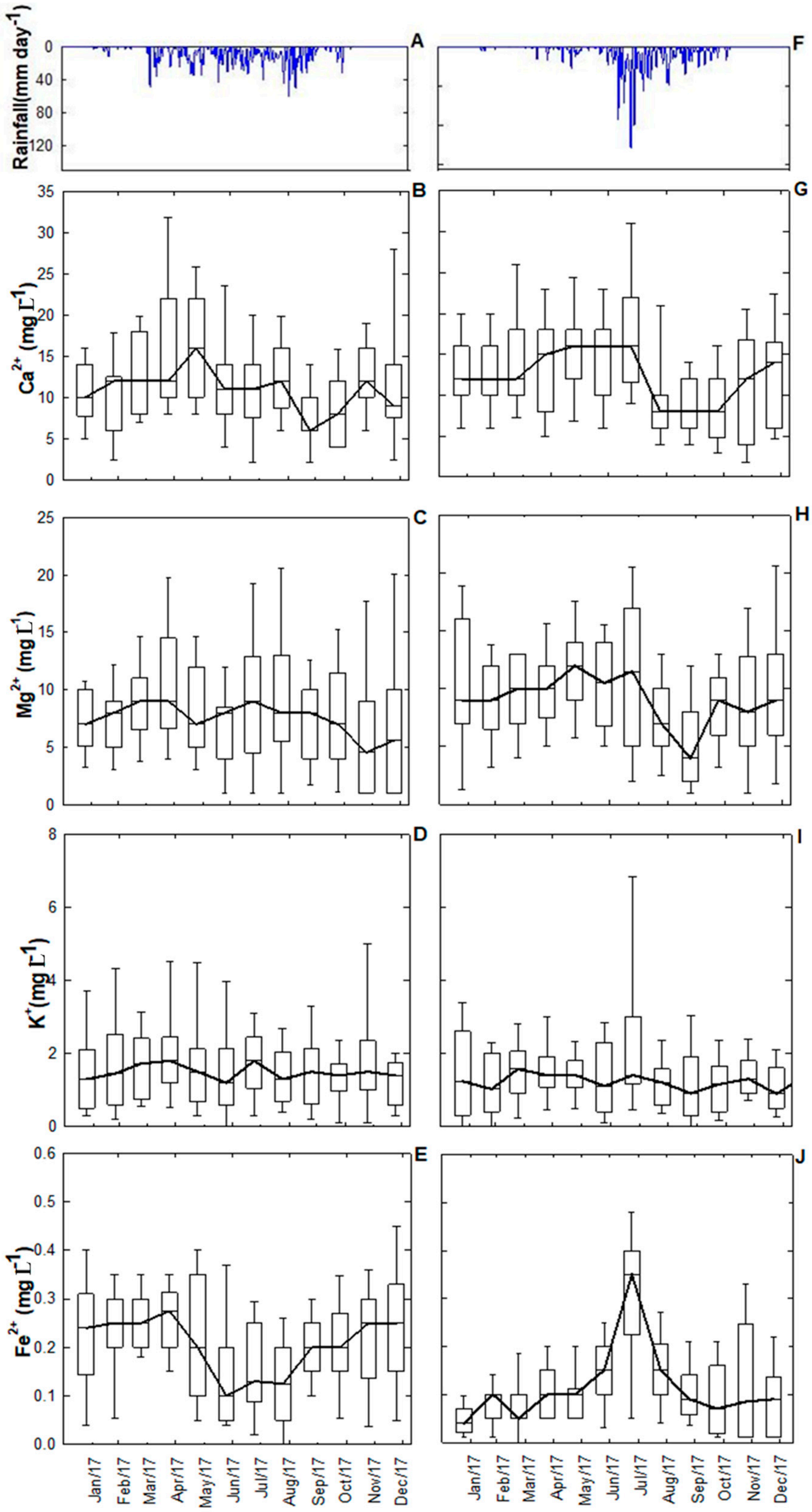

Figure 6. The concentration of major cations (Ca^{2+}, Mg^{2+}, and K^{+}) and iron (Fe^{2+}) in groundwater in 2017. (**A**–**E**) is for Dangishta, and (**F**–**J**) is for Robit Bata watershed. The box plots are based on data from 32 wells in Dangishta and 35 wells in Robit Bata.

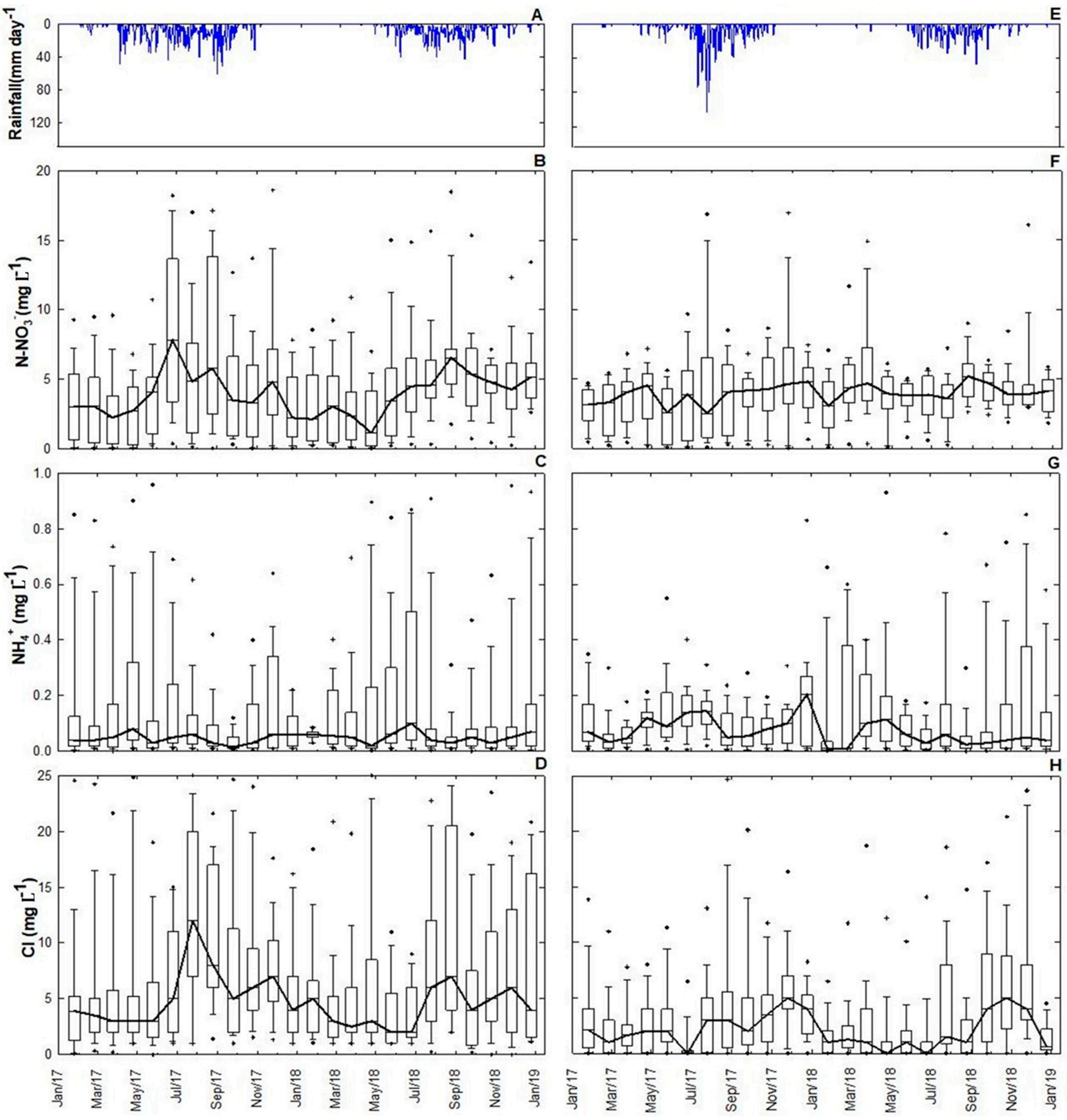

Figure 7. Box plots indicating perched groundwater nitrate ammonium and chloride concentrations in 2017 and 2018. (**A**–**D**) is for Dangishta, and (**E**–**H**) is for Robit Bata. Each box plot is based on data from 32 wells in Dangishta and 35 in Robit Bata. The dots placed above and below whiskers indicate outliers.

3.4.4. Nitrate

Nitrate concentrations (expressed as N-NO_3^-) averaged 4.6 mg L^{-1} in Dangishta and 4.0 mg L^{-1} in Robit Bata over the study period (Table 2). They were not significantly different between the two watersheds. Despite this, the monthly concentrations throughout the year differed between the watersheds.

Concentrations were unusually high in Dangishta from June to August in the cropped part of the watersheds on the well-drained soils (Figure 7B), with concentrations of over

7 mg L^{-1} and in portions of the aquifer over the drinking water standard of 10 mg L^{-1} (Figures 7A and 8A). In June, the crop growing area had a higher nitrate concentration than the old forest in the west and grassland (pasture) and eucalyptus (plantation forest) in the periodically saturated valley bottoms in the east near the outlet, which were too wet for cropland [29] (Figure 8A). The groundwater moves from the croplands to the grass and eucalyptus, causing the concentrations to rise in August to above 7 mg L^{-1} in the valley bottoms (Figure 8A). In August, the concentrations under cropland were nearly the same as the valley bottom after fertilizer application in July. In September, concentrations in the valley bottom started declining to less than 5 mg L^{-1} (Figure 8A). The cropland sections remained at 7 mg L^{-1} despite the water moving downhill. Akale et al. [50] also noted that nitrate concentrations in other parts of the Lake Tana basin were relatively higher in cropland areas.

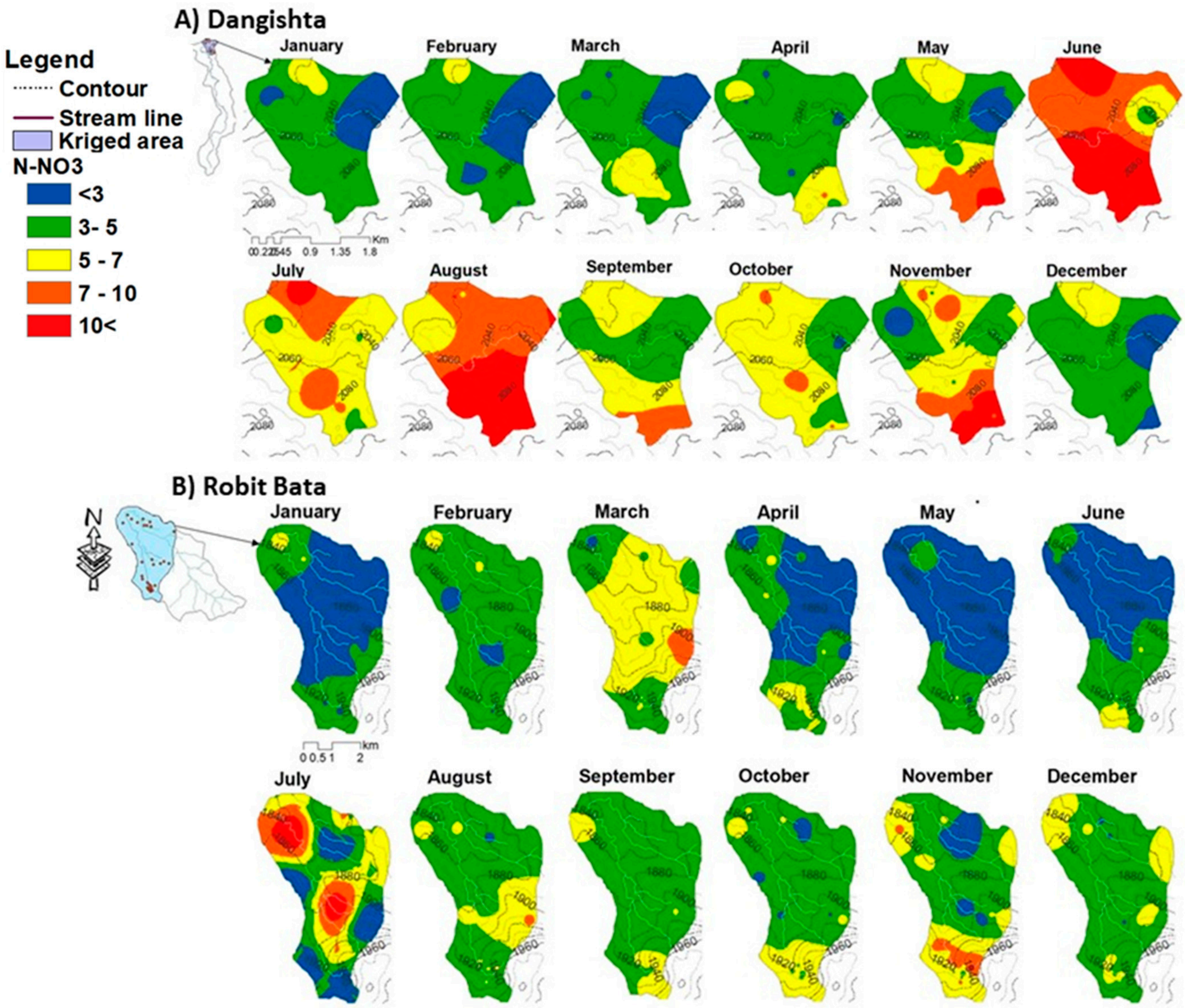

Figure 8. Monthly, two-year-averaged kriged nitrate concentration (2017 to 2018) in mg N-NO_3^- L^{-1} in the aquifers of (**A**) Dangishta and (**B**) Robit Bata watersheds.

In Robit Bata, median nitrate concentrations were nearly steady, around 4 mg N-NO_3^- L^{-1} throughout the two years, except with slight increases in July after fertilizer application on rainfed crops at the end of June (Figures 7F and 8B). In addition, nitrate was slightly elevated in November and March when the khat was irrigated on plots close to wells. Nitrate, derived from applied fertilizers, leached with excess irrigation water in the groundwater from fields close to the wells. Similar observations were reported by Lentz and Lehrsch [51].

3.4.5. Reduced Iron and Ammonia (Fe^{2+} and $NH_4{}^+$) Concentration

Reduced iron concentrations were greater in Dangishta than in Robit Bata (Table 2 and Figure 9). The pattern of monthly concentrations of reduced iron in the two watersheds was opposite (Figure 6E,J). During the rain phase, from June to September, Fe^{2+} concentrations were between 0.1 to 0.2 mg L^{-1} in Dangishta (Figure 9). In Robit Bata, the peak was 0.4 mg L^{-1} (Figure 6E,J). The reverse was true during the dry phase in Robit Bata. The mean Fe^{2+} concentration was less than 0.1 mg L^{-1}; in Dangishta, the concentrations range between 0.2 to 0.3 mg L^{-1} (Figure 9). The reasons are discussed in Section 4.1.

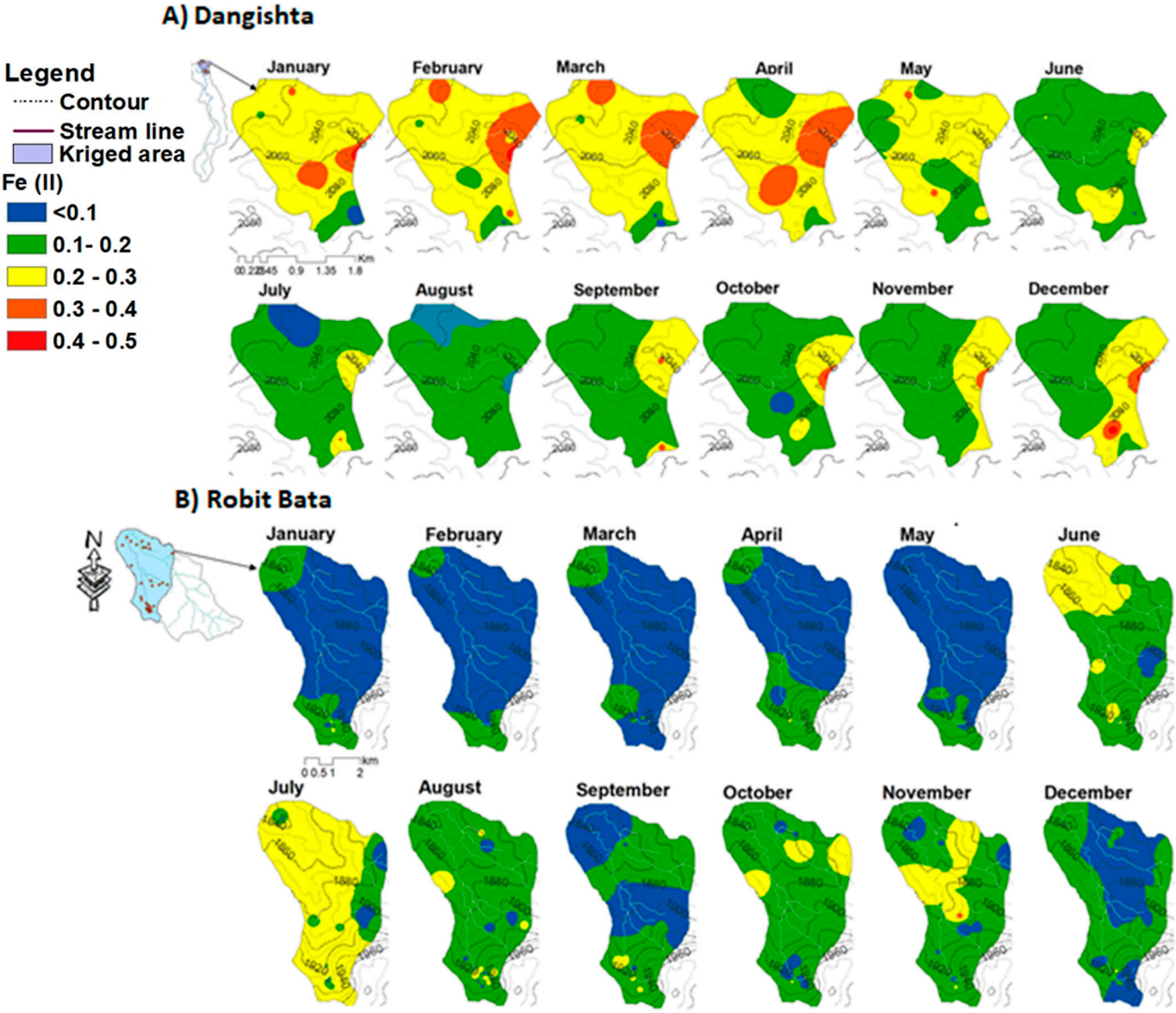

Figure 9. Monthly, kriged Fe^{2+} concentration (2017 to 2018) in mg L^{-1} in the aquifers of (**A**) Dangishta and (**B**) Robit Bata watersheds.

The averaged ammonium concentrations were around 0.1 mg L^{-1} in both watersheds (Table 2). In some wells, the ammonia concentrations were elevated. In the dry period, consistent with the iron level, the ammonium concentration increased when nitrate was reduced in Dangishta and decreased in the rainy period (Figure 7C,G) [52]. The coefficient of variation of NH_4^+ was the largest of all groundwater constituents, indicating leaching preferentially of NH_4^+ from the surface (Figure 7C,G). The matrix flow of NH_4^+ is hampered by the adsorption of NH_4^+ to negatively charged soil particles.

3.5. Surface Runoff Nitrate and Ammonia Concentrations

The monthly averaged nitrate and ammonia concentrations in the stream differ between the two watersheds (Figure 10). In Dangishta, the nitrate concentrations at the outlet follow the same pattern as the nitrate concentration in the groundwater. The concentrations are elevated during the rain phase when the crops are fertilized, and the groundwater is recharged. Nitrate concentrations decrease in the dry phase to the lowest levels (Figures 7C and 10A). Monthly nitrate concentrations in the stream were approximately half of the groundwater concentrations due to denitrification in the wetlands around the streams (Figure 2C, Figure 7C, and Figure 10A). The ammonia mobility pattern was the same with the phosphorus reported by [29]. We hypothesize runoff fertilizer transport and also that the wetlands are likely the cause of the high ammonia concentrations due to the cattle grazing the wetlands. The urea in the urine of grazing cattle is transported directly to the stream by the overland flow in the saturated area. Urea is rapidly converted to ammonia with the prevailing temperatures in the highlands.

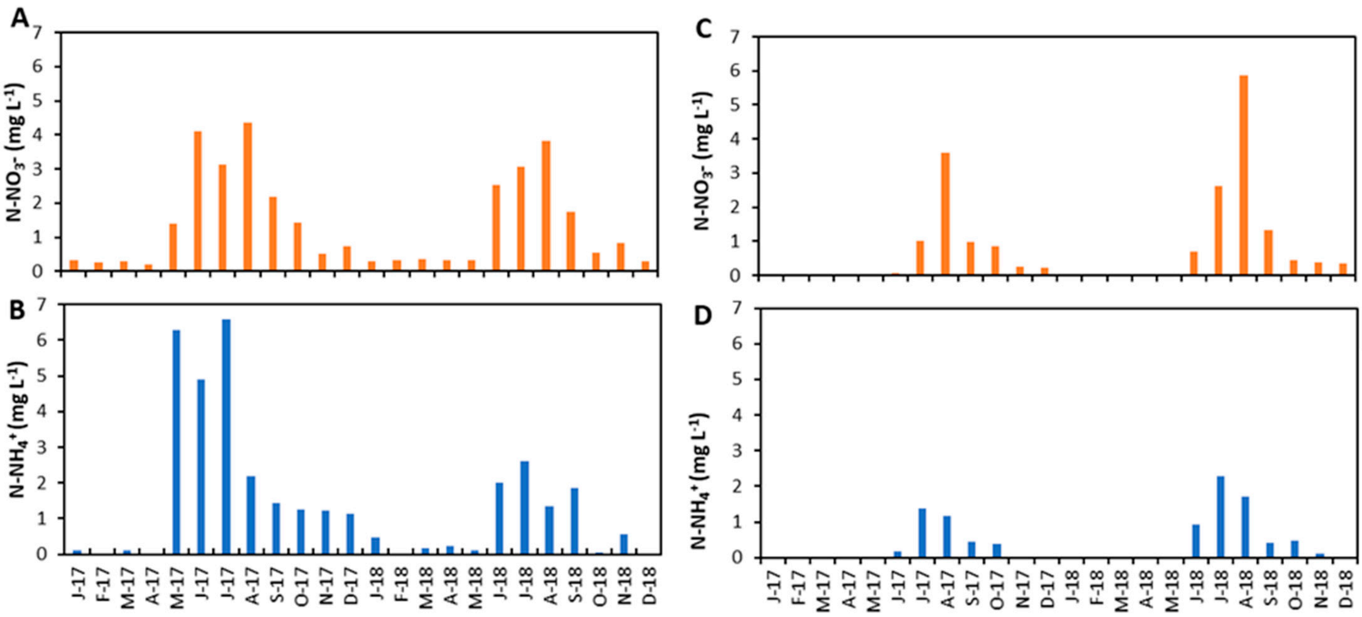

Figure 10. Monthly stream nitrate and ammonium concentrations (2017 to 2018). (**A**,**B**) are for Dangishta, and (**C**,**D**) are for Robit Bata watershed.

In Robit Bata, the average monthly nitrate concentrations in groundwater (Figure 8) and surface runoff (Figure 10C) were elevated after the urea fertilizer was applied. The greatest concentration occurred in July (Figure 8) and in August in the surface runoff (Figure 10). The average nitrate concentration in groundwater was 4 mg $N\text{-}NO_3^-$ L^{-1} (Table 2, Figure 7F). The nitrate concentration in the stream comprises the nitrate transported in the overland flow due to saturated excess runoff from the upper area and the baseflow from the middle and lower part. The concentration in the baseflow is diluted by the water coming from the upper part. Hence the lower concentration of nitrate in the stream compared with the groundwater.

The ammonia transport in a stream had the same pattern as the dissolved phosphorus reported by [29]. It transports with the saturation excess surface runoff from the upper part of the watershed and valley bottom.

3.6. Relating Nitrate with Groundwater Constituents and Hydrology

This section investigates the spatial and temporal interactions of nitrate concentrations in groundwater with water table depth, precipitation, and other groundwater constituents. It illustrates the different processes in the two watersheds that govern the fate of nitrate.

3.6.1. Relationships between Nitrate, Hydrology, and Groundwater Constituents

The results of the Pearson correlation test showed that precipitation, groundwater table depth, and chloride concentration were significantly and positively correlated with nitrate concentrations in both watersheds (Tables 3 and 4). The pH, Fe^{2+}, and N-NH_4^+ were negatively correlated with nitrate in Dangishta but not in Robit Bata (Table 3A,B). Magnesium and calcium were not correlated with nitrate levels in groundwater in either of the two watersheds.

Table 3. (**A**) Pearson correlation coefficients between hydrological and chemical parameters for Dangishta; (**B**) Pearson correlation coefficients between hydrological and chemical parameters for Dangishta.

(A)	**P**	**GWTD**	**pH**	**EC**	**Mg^{2+}**	**Ca^{2+}**	**K^+**	**Fe^{2+}**	**N-NH_4^+**	**Cl^-**	**N-NO_3^-**
P	1										
GWTD	−0.191 **	1									
pH	0.044	−0.105	1								
Ec	−0.361 **	0.029	0.323 **	1							
Mg^{2+}	0.038	−0.040	0.007	0.320 **	1						
Ca^{2+}	0.009	−0.020	0.008	0.357 **	0.981 **	1					
K^+	−0.002	0.156 **	0.313 **	0.235 **	−0.007	−0.015	1				
Fe^{2+}	−0.256 **	0.106	0.064	0.030	−0.064	−0.064	0.162 **	1			
N-NH_4^+	−0.04	0.095	0.088	0.098	−0.081	−0.088	0.420 **	0.136	1		
Cl^-	0.196 **	−0.110 *	−0.162 *	−0.096	0.242 **	0.235 **	0.092	−0.168 **	−0.012	1	
N-NO_3^-	0.127 **	0.197 **	−0.248 **	−0.128 **	0.089	0.099	−0.060	−0.551 **	−0.136 **	0.511 **	1
(B)	**P**	**GWTD**	**pH**	**EC**	**Mg^{2+}**	**Ca^{2+}**	**K^+**	**Fe^{2+}**	**N-NH_4^+**	**Cl^-**	**N-NO_3^-**
P	1										
GWTD	−0.216 **	1									
pH	−0.156 *	−0.190 **	1								
Ec	−0.295 **	0.259 **	0.010	1							
Mg^{2+}	−0.153 *	0.077	0.232 **	0.265 **	1						
Ca^{2+}	−0.113	0.347 **	0.117 *	0.412 **	0.286 **	1					
K^+	0.148 *	0.222 **	0.165 **	0.131 *	0.228 **	0.124 *	1				
Fe^{2+}	0.236 **	−0.077	0.174 **	−0.037	−0.015	−0.015	0.022	1			
N-NH_4^+	−0.005	−0.018	0.138 *	0.074	0.094	0.196 **	0.288 **	0.083	1		
Cl^-	0.129 *	−0.170 **	0.091	−0.122	0.025	−0.104	−0.032	−0.019	0.024	1	
N-NO_3^-	0.162 *	0.144 *	−0.008	−0.053	0.106	−0.044	0.291 **	−0.059	−0.035	0.672 **	1

** Correlation is significant at the 0.01 level, and * correlation is significant at the 0.05 level (two-tailed).

Table 4. Coefficient of the regression equations to estimate nitrate concentration.

Watersheds	**Name**	**Coefficient (β)**	***t*-Test**	***p***	**Adjusted R^2**	**Relative Importance**
Dangishta	Intercept	8.6	3.6	0.02	0.70	
	Cl^-	0.31	13	<0.001		0.52
	Fe^{2+}	12.6	−6.7	<0.001		0.39
	GWD	0.25	5.5	<0.001		0.08
Robit Bata	Intercept	0.55	1.3	0.09	0.63	
	Cl^-	0.62	15.1	<0.001		0.84
	Fe^{2+}	−1.85	−2.0	0.042		0.01
	GWD	0.14	3.5	<0.001		0.07
	P	0.002	3.2	0.002		0.06

3.6.2. Multiple Linear Regression Model for Nitrate Concentrations

The monthly nitrate concentration can be expressed by following multiple linear regression models. The multiple regression models also fulfilled all the assumptions, such as normality, equal variance, and linearity indicates.

$$\text{Dangishta}: \quad N\text{-}NO_3{}^- = 8.6 + 0.31Cl^- + 0.25GWT - 12.3Fe^{2+} \tag{1}$$

$$\text{Robit Bata}: \ N\text{-}NO_3{}^- = 0.55 + 0.62Cl^- + 0.002P + 0.14GWT - 1.85Fe^{2+} \tag{2}$$

where the concentrations are expressed in (mg L^{-1}) and groundwater table (GWT) in (m).

The variance explained by the model was 70% in Dangishta and 63% in Robit Bata (Figure 11). Ranking the variables by their relative importance (Table 4) shows that Fe^{2+} made a 1% contribution to the overall adjusted R^2 in Robit Bata and 40% in Dangishta. Thus, nitrate concentration in Dangishta is affected by the redox potential of the groundwater, while in Robit Bata, the transport-related parameters, chloride, and precipitation together explain 90% of the variation (Table 4). In Dangishta, 50% of the variance was transport-related.

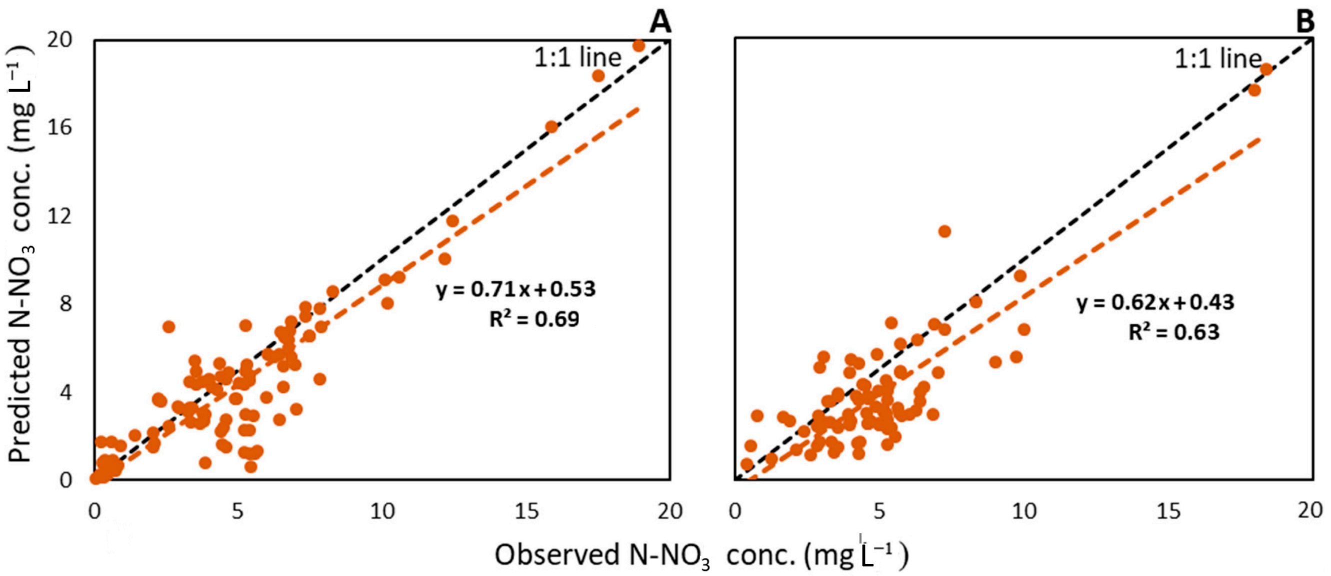

Figure 11. Predicted vs. observed nitrate concentration for the multiple linear regression model. (**A**) Dangishta and (**B**) Robit Bata watershed.

The model was validated using an independent data set collected from nine wells among monitored wells in the study (i.e., 30% of the total data set). A plot of the model predicted vs. observed fit (Figure 11) for validation showed that the analytical models satisfactorily predicted the monthly nitrate concentrations. The observed versus predicted values have an R^2 of 0.69 in Dangishta and 0.63 in Robit Bata, indicating that the model fit is acceptable (Figure 10). The fit line is very close to the 1:1 line.

4. Discussion

In this discussion section the reasons for the differences in groundwater constituent concentrations between the two watersheds are first discussed. Next, the fate and transport of nitrate in sloping hillside aquifers are discussed in relation to the watershed properties.

4.1. Constituent Concentrations in Sloping Hillside Aquifers

The groundwater table depth and nitrate concentrations in both watersheds were correlated (Table 3). At the same time, the temporal and spatial changes in groundwater depth and nitrate concentrations were different in the two watersheds (Figures 4, 5, 8 and 9). To explain these almost contrary findings, we will first discuss geology and hydrology.

The geology in Dangishta influenced water residence time. The decrease in groundwater level was slower in Dangishta than in Robit Bata. Hence, the residence time was greater in Dangishta (Figure 5A). The volcanic dikes nearly perpendicular to the streams in the valley bottom formed a barrier for the interflow. It prevented incision of the streams (Figure 2C) and resulted in a 400 m-wide strip along the river covered by grass during the rain phase because it was too wet to grow crops (Figure 2A). It is clearly shown in the kriged area (Figure 5A) near the outlet in the east part. The water tables remained within 3 m from the surface from June to January. The rivers also flow throughout the year in Dangishta. Thus, the water was held back.

In Robit Bata, volcanic dikes were absent, and the stream formed a gully at the outlet, enhancing the groundwater drainage in the watershed [29]. As a result, the water table at the outlet dropped rapidly from the surface to 4 to 8 m depth after September, when the rains stopped (Figure 5B). The water table disappeared around December in wells away from fault lines [20]. The river stopped flowing at this time as well. The groundwater is relatively fast-flowing in this aquifer, with an approximate slope of 8% and a high transmissivity.

Tilahun et al. [20] confirmed high groundwater flux in Robit Bata. They found that approximately two-thirds of the recharge became interflow by September, and by the end of the rain phase, only 10% of the water recharged to the aquifer was still left as storage. Setargie et al. [53] showed using isotopes that in Robit Bata, after the aquifer reached its maximum level, 90% of all discharge at the outlet was pre-event water, indicating a significant subsurface flow component.

The chloride concentrations in groundwater confirm these differences in hydrology as well. During the rain phase, when rain moves preferentially to the groundwater and has a short residence time, the median chloride concentration in the groundwater is in the same order as in Robit Bata (see Section 3.3.2 and Figure 7H). Concentrations remained rising after the rains ended in October until December. Starting from January, the groundwater dropped below 6 m (Figures 3D and 5B) and remained low until June. In this period, groundwater near the faults (tapped by the wells) originated from the unsaturated soils and has a median Cl^- concentration below 2 mg L^{-1}. The unsaturated flow in volcanic soil is subject to the adsorption of negative ions [49] and decreasing chloride concentration to below that of the rainfall. In Dangishta, the same adsorption of ions occurs in unsaturated soil. Still, the water in the wells is a mixture of groundwater from the summer stored behind the volcanic dikes and the unsaturated flow. It resulted in a greater concentration in Dangishta than in Robit Bata in the dry monsoon phase. In the volcanic terrain of Ethiopia, groundwater Cl from halide dissociation is not significant; rainfall is the source of chloride [8,46].

On average, the two watersheds had similar groundwater cation concentrations of Ca^{2+}, Mg^{2+}, and K^+, but concentration for Ca^{2+} and Mg^{2+} varied during monthly measurement. These indicate similarities of rock and soil minerals, but differences in hydrogeology between the watersheds. High concentrations in the dry period and low concentrations in the rainy period indicate evaporation and dilution processes controlling Ca^{2+} and Mg^{2+} in watersheds [14]. The K^+ in both watersheds remained nearly the same throughout the year except for the peak concentration observed in July in Robit Bata (Figure 6D,I).

The concentrations of Fe^{2+} were greater in Dangishta than in Robit Bata, and thus groundwater in Dangishta is more anoxic (Table 2; Figure 6E,J and Figure 10 [51]. In Dangishta, one possible reason for the low concentration of Fe^{2+} in the rain phase from June to October (Figure 7E) is that the nitrate was reduced instead of the iron [40,41] when the nitrate concentrations were high. In Robit Bata, Fe concentration rose in the summer monsoon period for a few months but declined fast. Perhaps the groundwater reached more organic-rich layers, the water fill-up soil matric that blocks oxygen transfer and increases iron reduction [52]. From January to May, when the groundwater was concentrated near the faults, nearly the groundwater was oxic, i.e., less than 0.1 mg L^{-1} of Fe^{2+} (Figure 9B).

4.2. Fate and Transport of Nitrate in Sloping Hillside Aquifers

Understanding the fate and transport of nitrate in watersheds requires knowing the sources of nitrate and factors that control nitrate mobility through the hydrologic pathways [7,39,40]. Applied N fertilizer is a primary source of nitrate concentrations. In Dangishta, the nitrate correlated positively to land use and associated N fertilizer (Table S2). Shallow groundwater wells in homestead and cultivated land-use areas had high nitrate concentrations (Table S3 in Supplementary Materials A). However, the amount of N fertilizer input was not correlated to nitrate concentration in Robit Bata, indicating a fast transport downwards in the interflow of nitrate from the application area.

Figure 12 displays the ratio of chloride and nitrate for each month. It aids in understanding the relative importance of transport and denitrification processes on the nitrogen concentrations in the aquifer. Almost the entire Robit Bata aquifer and the northwestern portion of the Dangishta aquifer have chloride and nitrate ratios of less than three all year long (dark blue color). In addition, in June, when fertilizers were applied and nitrate increased (Figure 8A), the whole watershed had a ratio below three. During the remainder of the rain phase, variable nitrate and chloride are added with the recharge, while denitrification occurs at the same time, while water moves downhill, making interpreting the pattern of the ratios difficult. After September, when the rain phase has ended, there is little recharge, and the ratio increase can be attributed to denitrification in the water that moves down to the river. Figure 12A shows that the ratio is the greatest in the eastern portion of Dangishta. Thus, denitrification occurs in the region. Many wells are located near the river where the groundwater is shallow (Figure 5A). As noted in Section 3.5, the concentration of $N\text{-}NO_3^-$ in the surface water is approximately half of that in the surface water, confirming the denitrification effect.

In Robit Bata, travel times are short; consequently, applied nitrate is transported rapidly out of the watershed. Thus, little groundwater is mixed with the recharge water. Most of the applied nitrogen fertilizer left the watershed within two months, as seen in Figure 10C of nitrate concentration in the stream. Nitrate concentration in the groundwater remained likely from irrigation water that leached the fertilizers into groundwater.

The reduced iron concentrations in groundwater confirm differences in denitrification as well. The negative correlation of Fe^{2+} with nitrate concentration in Tables 3 and 4 for Dangishta can be seen by comparing Figures 8 and 9, where Fe^{2+} and $N\text{-}NO_3^-$ juxtapose each other. When $N\text{-}NO_3^-$ concentration increased, Fe^{2+} concentration decreased. It is especially obvious in the dry phase.

In Robit Bata, reduced iron correlated insignificantly, and multiple linear regression indicates that it only contributed 1% in explaining the variation of nitrate. It implies less loss of nitrate due to denitrification. Rather, the nitrate is affected by its rapid transport out of the watershed. The short residence time of the groundwater in Robit Bata explains why chloride, a function of the rainfall-related transport, explains the nitrate concentration (Tables 3 and 4). It also explains why, in Figure 8B, the NO_3^- peak concentration increase in July after the June fertilizer application is hardly visible after a month. In Figure 12, almost the entire Robit Bata aquifer and the northwestern portion of the Dangishta aquifer have chloride and nitrate ratios of less than three during the whole year.

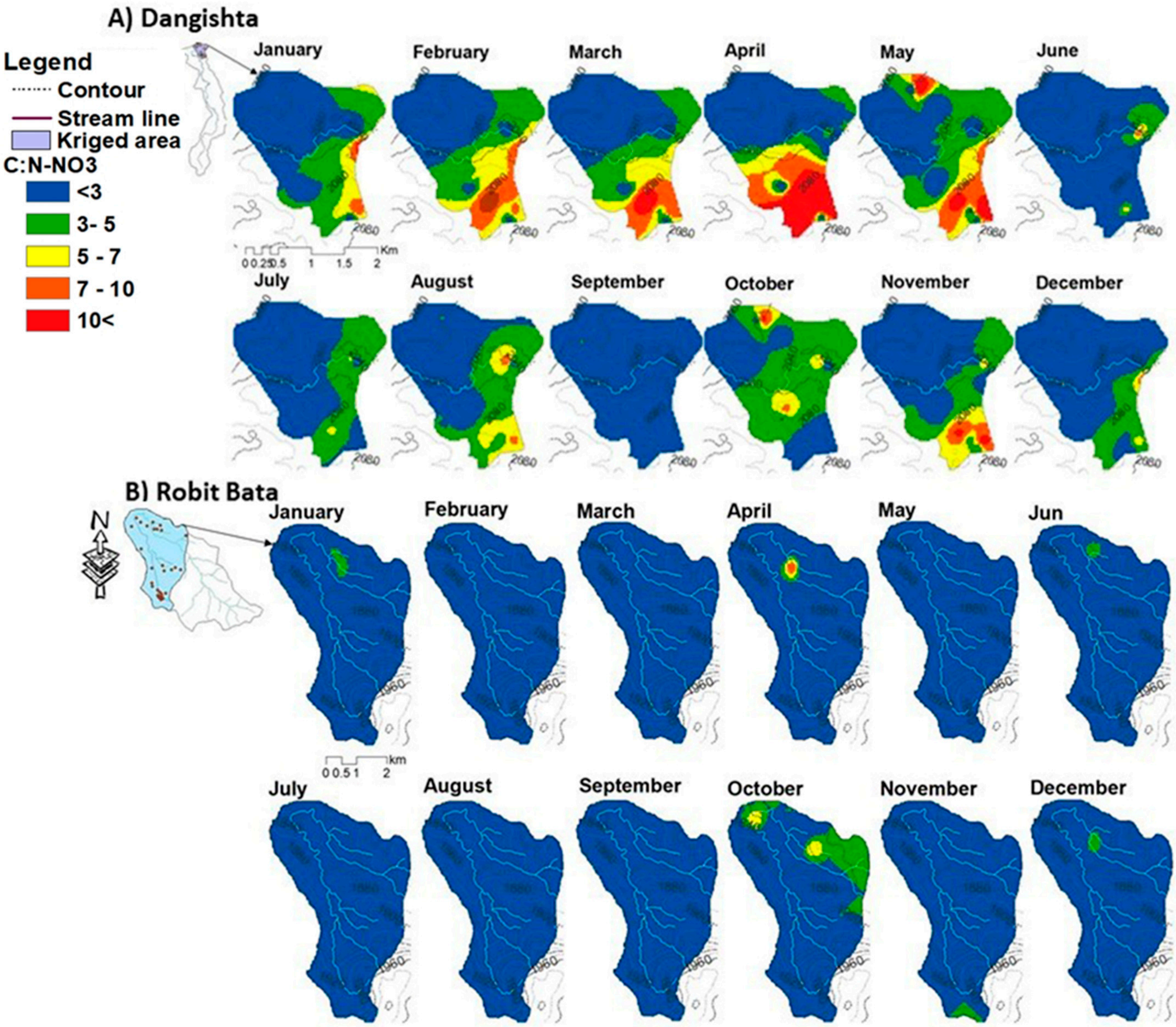

Figure 12. Monthly, two-year-averaged kriged ratio of chloride to nitrate concentration (2017 to 2018) in the aquifers of (**A**) Dangishta and (**B**) Robit Bata watersheds.

5. Conclusions

This study investigated nitrate concentration in groundwater in two contrasting volcanic watersheds (Dangishta and Robit Bata). Dangishta had lava intrusion dikes in the valley bottom that blocked subsurface flow, maintaining a permanent groundwater table. In Robit Bata, transmissivity was high, and volcanic dikes were absent. As a result, the groundwater residence time was short, the water table dropped rapidly, the river stopped flowing three to four months after the rain phase ended, and only near faults was groundwater available.

The average nitrate concentration in Dangishta was 4.6 mg N L^{-1} and not significantly different from Robit Bata, with average concentrations of 4.0 mg N L^{-1}. However, the monthly concentrations between the two watersheds varied greatly due to geohydrology. Interpretation of the results is extremely complex because, in the hillslopes aquifers, the water flows under gravity down the river. Consequently, wells do not sample the same water from one month to the next. Despite these complications, we concluded that in Robit Bata, due to the short residence time, nitrate concentration only increased the month after fertilizer application and was minimally affected by denitrification. In Dangishta, nitrate concentration remained high during the rain phase after fertilizer application because water moved slower than in Robit Bata. Therefore, in Dangishta, denitrification, besides transport out of the watershed, played a significant role in the decrease in nitrate concentrations.

Implications

Understanding the nitrate transport and controlling factors in groundwater is important to evaluate the fate of nitrogen derived from N fertilizer and to design best management practices. Since agricultural intensification has been advocated as one of the options to fulfill the food demand, N fertilizer application has increased by twofold in the last two decades to the current magnitude of 43 kg N ha^{-1} in Ethiopia [25]. Although this rate application is low compared with the application in temperate and sub-tropic regions [54], N-NO_3^- loss is high with the current application in the sub-humid tropical highland area because leaching is enhanced with monsoon rains. Above 10 mg N-NO_3^- L^{-1} concentrations were recorded for several months in wells used as drinking water. Akale et al. [50] also reported a similar order of nitrate concentrations in the groundwater of a sub-humid watershed. Nitrate concentrations in a rural catchment in Tigray [55] with a semi-arid climate and an annual rainfall of less than 1000 mm were much smaller than in this study. Therefore, best practices that improve fertilizer leaching loss such as applying at the right rate, time, and place should be implemented for sub-humid and humid highland regions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/hydrology10040082/s1, Supplemental Materials A: Tables S1 and S2 contain a correlation coefficient between nitrate, land use, and cover around the well. Table S3 shows averaged nitrate concentration and N-fertilizer input in in buffer area around wells. Table S4 details the threshold concentrations for identifying redox processes in groundwater. Table S5 contains the monthly and annual precipitation for the two watershed. Figure S1 shows land-use land cover. Figure S2 details the assumption test for the MLR analysis model—Supplemental Materials B: an excel file with detailed information on nitrate and other groundwater constituents.

Author Contributions: F.K.S. contributed to the experimental design, data analysis, interpretation, and writing—original draft preparation; S.A.T. contributed to project administration, funding acquisition, and experimental design, and revised the manuscript for scientific content; P.S. contributed to project administration, acquisition of the financing, and experimental design; T.S.S. contributed to data analysis, interpretation, and writing—review and editing of the manuscript for the scientific content. All authors have read and agreed to the published version of the manuscript.

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