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Hydrochemical Characterisation of the Basement Aquifer with a Focus on the Origin of Nitrate in the Highly Urbanised Niamey Region, SW of Niger

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Abstract: This study investigated the basement aquifer beneath the urbanised city of Niamey and the agricultural fields of Kollo, SW of Niger. During the observation period spanning from 2021 to 2023, groundwater and surface water samples were collected for analysis of major ions and the stable isotopes oxygen-18 and deuterium ($\delta^{18}O$ and $\delta^{2}H$) of water. To trace the origin of high nitrate concentrations (NO_3^-) found in several observation and drinking water wells in both areas, $\delta^{15}N$ and $\delta^{18}O$ isotope values of NO_3^- were analysed in groundwater and eluted soil samples. The observed hydrochemical patterns mainly reflect the heterogeneity of the weathered fringe of the basement aquifer. Decreasing concentrations of NO_3^- and $\delta^{18}O$ and $\delta^{2}H$ values were observed in relation to the distance of the Niger River and increasing thickness of the clay layer on the surface. The wells close to the river in Niamey show a dilution effect during the flood season, and the NO_3^- concentrations displayed a continuous increasing trend. The $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 values confirmed that septic tank water is spreading in the region of Niamey and that manure originating from livestock in Kollo is the main source of NO_3^-. The patterns of $\delta^{15}N$ in the soil samples coincide with those of cattle's manure spread in both areas. The shallow wells show significantly higher values of electric conductivity and NO_3^- concentrations compared to the deeper wells, which clearly indicates the influence of shallow septic tanks on water quality.

Keywords: nitrate; stable isotopes; hydrochemistry; Niamey; Niger River

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1. Introduction

Groundwater serves as a crucial source of potable water for both urban and rural populations. In many African regions, due to the lack of water and sanitation services, along with the absence of piped systems, groundwater resources are increasingly vulnerable to anthropogenic contamination [1]. Water quality data and their consequent linkage to the origin are scarce especially for African countries. Contamination with nitrate (NO_3^-) in highly urbanised areas caused by anthropogenic influence was reported by several studies for West African countries. Ohou et al. reported NO_3^- concentrations from the Ivory Coast, which exceed the thresholds suggested by the World Health Organization (WHO), due to the impact of wastewater in the region [2]. In Yaounde, Cameroon, groundwater quality was proven to be influenced by infiltrating wastewater [3]. Similarly, elevated NO_3^- concentrations were measured in the aquifer used for water supply in N'Djamena, Chad [4]. Several wells in the area of Niamey in Niger, which belong to the continental terminal aquifer and the basement aquifers, have been shown to be influenced by wastewater contamination [5–9].

Niger, belonging to a region in West Africa with a population of around 24 million inhabitants and a high annual population growth rate of 4.5% [9], is considered to be

one of the poorest countries in the world, with 80% of its area located in the Sahara. Satellite images from 1984 to 2020 show an increase in urbanisation for Niamey, the capital of Niger, from 35 km^2, mainly concentrated north of the Niger River, to 142 km^2, with increased spreading on both sides of the river. The main populated area is located in the plateau region.

Environmental change, which is accompanying such high-urbanisation development, may lead to a change in the availability of water resources in terms of quality and quantity. Several industries (leather and food industry), hospitals, hotels, and further facilities discharge solid wastes and wastewater into the Niger River. Consequently, groundwater samples from several boreholes show high concentrations of heavy metals and nitrogen compounds. In addition, the landscape in Niamey is prone to floods caused by heavy rains, river floods, or even elevated groundwater levels [10]. Several studies have evaluated groundwater quality, recharge, and hydraulic connections between the different aquifers. Sources of pollutants were shown to be related to wastewater, mainly in the shallow wells of the basement aquifer [5–14].

This study was conducted as part of a technical cooperation project with the Niger Basin Authority (NBA), which has run a monitoring program for surface- and groundwater since 2012 and for rainwater since 2017 in the area of Niamey. Since the urbanisation in Niamey together with the agriculture and refugee camps in Kollo may have a great impact on groundwater quality, these two areas were selected for an investigation of groundwater quality, with that water partially used for drinking purposes. Furthermore, these investigations were aimed at obtaining a better understanding of the main hydrogeological components and the parameters that influence the groundwater quality. Between 2012 and 2019, the monitoring program included shallow dug wells, deep wells, and ponds belonging to the three different aquifers in the area of Niamey [7]. Since 2020, the monitoring has focused on deep wells belonging to the weathered fringe of the basement aquifer in the area of Niamey and has been expanded to the area of Kollo, 20 km southeast.

The isotope composition of nitrogen ($\delta^{15}N$) has been used as a distinguisher for sources of NO_3^- contamination of water systems over the last 50 years [15]. In particular, the combination of $\delta^{15}N$ and $\delta^{18}O$-NO_3 allows us to trace NO_3^- sources and identify denitrification processes [15]. Distinct but partly overlapping ranges of isotope values have been used to separate NO_3^- sources such as NO_3^- from atmospheric sources ($\delta^{15}N$-NO_3 −8 to +8‰, $\delta^{18}O$-NO_3 +60 to +90‰), nitrification of ammonium-based fertilisers ($\delta^{15}N$-NO_3 −10 to +4‰, $\delta^{18}O$-NO_3 −10 to +15‰), soil ammonium ($\delta^{15}N$-NO_3 +2 to +7‰, $\delta^{18}O$-NO_3 −10 to +15‰), and animal and human waste ($\delta^{15}N$-NO_3 +4 to +25‰, $\delta^{18}O$-NO_3 < +15‰) [16]. However, often, a clear separation is limited by mixtures between more than one of these sources [17].

The objectives of this study were to (i) characterise the hydrochemistry of groundwater and surface water in an urbanised area of Niamey; (ii) evaluate the spatio-temporal evolution of the hydrochemistry and stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) of groundwater of the basement aquifer and its interaction with surface water; and (iii) determine the source of high nitrate concentrations using the stable isotopes of NO_3^- ($\delta^{15}N$ and $\delta^{18}O$). In contrast to previous groundwater studies in Niamey [9,10,14], this study focused on the hydrochemical characteristics of the basement aquifer. The analysis of soil and groundwater samples from the same locations in combination with long-term sampling in monthly intervals allowed us to trace the origins of contaminants such as NO_3^- and to identify concentration changes during the rainy and the dry seasons.

2. Study Site

The study area of Niamey and Kollo is located in the Sahel region between 2.05° and 2.35° E and 13.35° to 13.65° N in the transition zone between the Sahara Desert in the north and the savanna in the south. Agricultural activities, mainly rice cultivation, imprint the surrounding region and are mostly concentrated at the riverbanks (Figure 1). Irrigation water comes from the surface water of the River Niger or from the rainfall

in the rainy season. The drinking water supply system in Niamey depends mainly on the treatment of the surface water from the Niger River and covers around 65% of the households in the city [9]. With an increasing distance from the river to the poorer quarters of the suburbs, groundwater takes on a significant role in the water supply, as is the case in Kollo (Figure 1d). A wastewater sewer system exists only for a few facilities such as some hotels and hospitals. No data are available on the produced wastewater, which is usually transported from some parts of the region to collection basins northwest of the city without further treatment. Septic tanks for domestic wastewater are visible all over the urbanised part of the city; most of them are not sealed at the bottom.

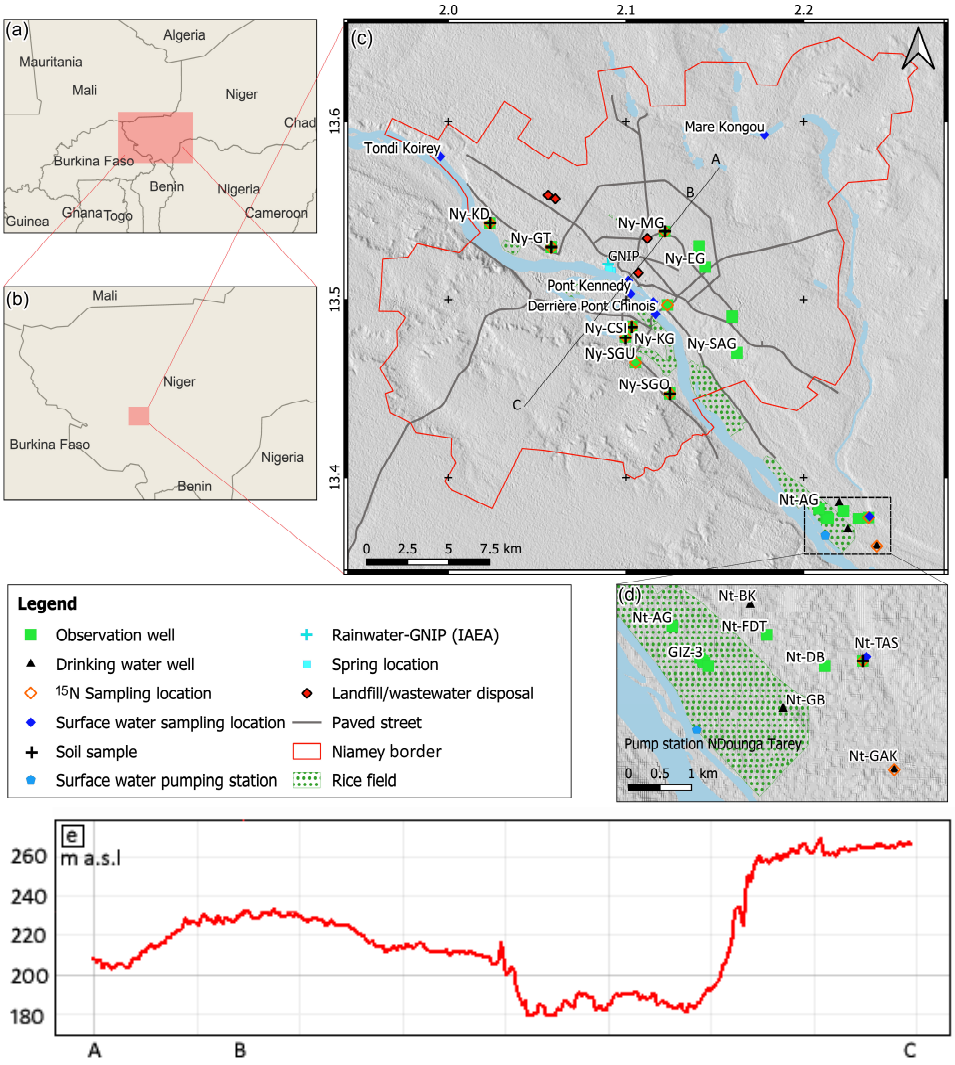


Figure 1. (**a**) Location of Niamey, Niger within the Sahel region, (**b**) location of Niamey in the far SW part of Niger, (**c**) sampling locations of surface- and groundwater sites in the study area, (**d**) zoomed sampling locations in Kollo, (**e**) topographic cross-section along the line A-B-C in part (**c**).

The topographic elevations on both sides of the city vary between the Niger River bed at around 180 m and 260 m above sea level (asl) on the SW side and 230 m asl on the NE side (Figure 1e).

The precipitation in Niger, as a part of the Sahel region, is controlled by the summer southwest monsoon and thunderstorms. The mean annual precipitation recorded at the Niamey airport station is 541 mm based on a 30-year rainfall record [8]. The rainy season starts in May and ends in October with 60% of the rainfall concentrated between July and

August. [18] estimated the annual potential evapotranspiration to be about 2000 mm, which is lower than the rainfall only in the two months of July and August.

The monthly average temperature and relative humidity were determined using climate data provided by [19] for the period between January 2013 and December 2018 (Figure 2). The average air temperature ranges between 25 and 35 °C. The temperature can reach 40 °C between March and May and may decrease to 15 °C in December. The relative humidity reaches its average maximum in August with 73%, and the lowest values occur during the hottest months between March and May.

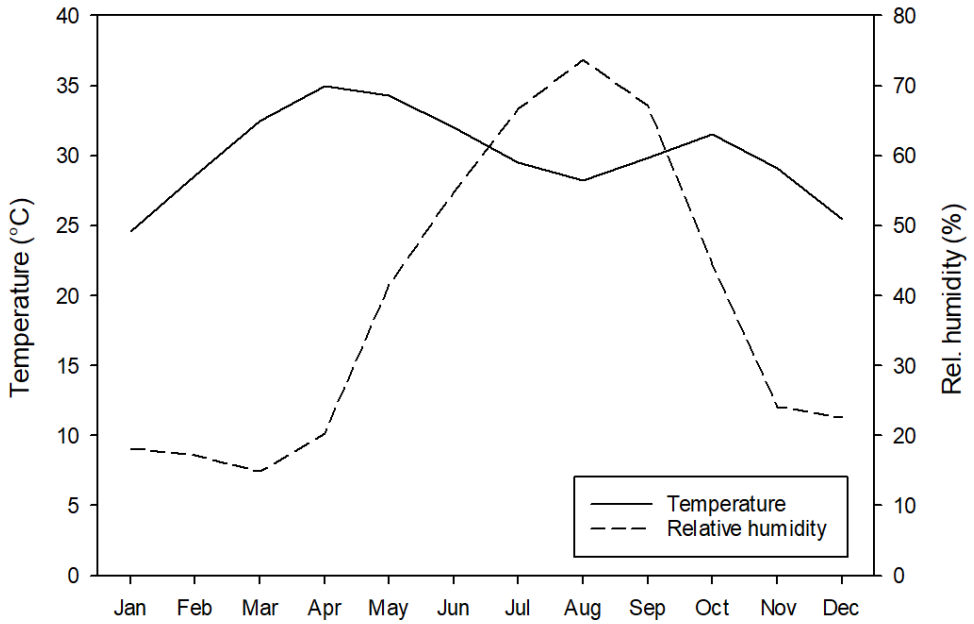


Figure 2. Mean temperature (left axis) and relative humidity (right axis) recorded in Niamey (based on 3 h time series January 2013 to February 2018).

The study area is located on both sides of the Niger River, which represent a transition zone between the Precambrian basement and the Eocene to Pliocene Continental Terminal (CT) basin deposits (Figure 3) [5,6,20,21]. Both geological units are partially covered by quaternary and recent alluvial and aeolian deposits. The basement rocks locally crop out near the bed of the Niger River, where the CT is absent and where quaternary alluvial deposits form a discontinuous cover layer. The basement consists of plutonic rocks of granites, metamorphic rocks like gneisses, quartzite and green schists, and meta-volcanic sediments in different stages of weathering [22].

The basement is overlain uncomfortably by Upper Precambrian sandstones (Niamey sandstones) [21] followed by clayey to silty sandstones [23]. In the Niamey area, the sandstone unit of the Continental Terminal is represented by CT3, which covers a large area of Niamey and its surroundings (Figure 3) [24]. This consists mainly of sandstone, which alternates with clay intercalations. The alluvial deposits consist of alternate layers of sand, clay, and gravel, with reported thicknesses of up to 7 m along the Niger River banks [11].

Three main aquifers are documented by borehole records in Niamey: (i) the weathered and fractured basement aquifer, (ii) the Continental Terminal sedimentary aquifer CT, and (iii) the alluvial aquifer [25]. A schematic morphological cross-section (Figure 3) running through the line A-B-C on the geological map in Figure 3 shows the distribution of the aquifers in the study area.

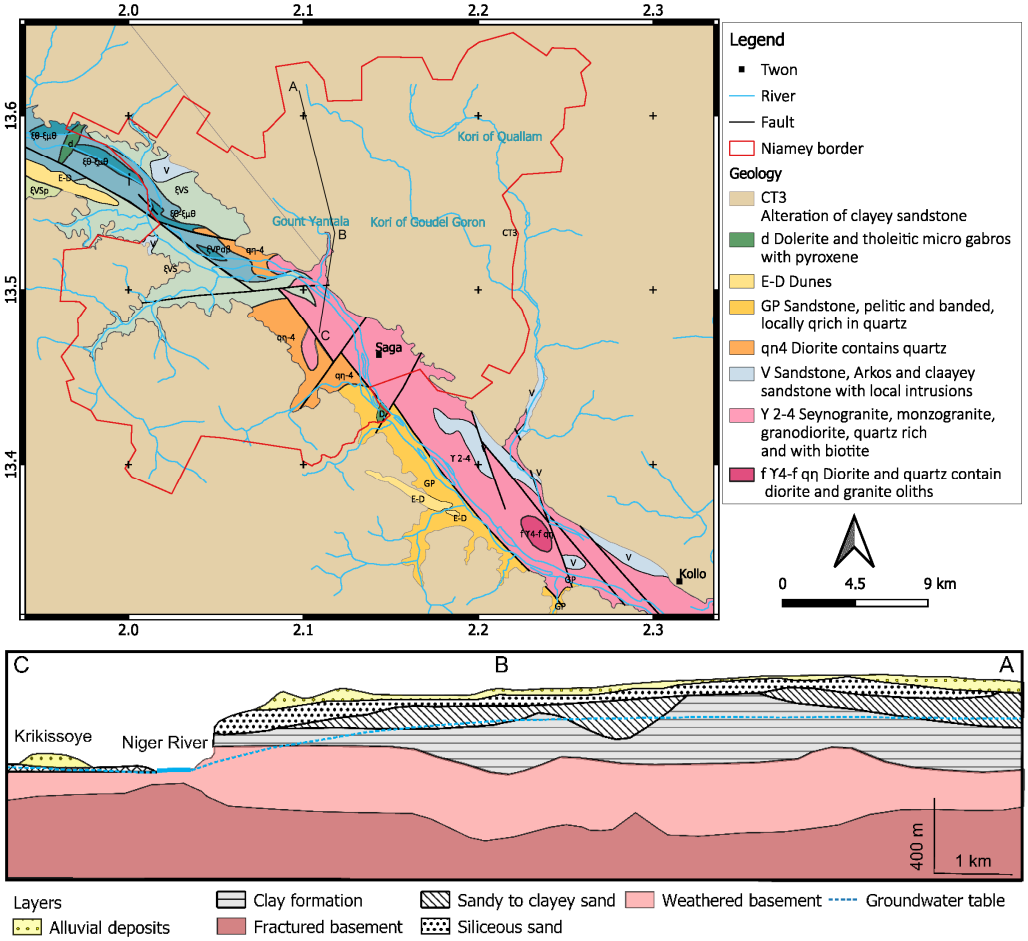


Figure 3. Geological map for the area of Niamey with the main geological units (modified after [22]), where the lower figure represents a schematic hydrogeological cross-section through the line A-B-C (modified after [9]).

The alluvial aquifer is a porous aquifer that is locally confined close to the Niger River valley, and to a limited extent near the Kori depressions (intermittent streams). This aquifer is used in certain areas for irrigation. Wells belonging to this aquifer are shallow with large diameters of up to two meters and a depth range between 5 and 15 m. The Continental Terminal sedimentary aquifer, CT, is a porous multi-layered aquifer formation with a sub-regional extension. Niamey is located at the extreme southwestern edge of the large sedimentary basin, and there, the CT is only represented by the CT3 series [6,11,26]. The basement aquifer is generally present where weathering and fracturing of the crystalline basement result in secondary porosity and permeability of the rock. In Niamey, the basement has weathering fringes up to 30 m thick (Figure 3), and around 55 m in Kollo, SE of Niamey [27].

Several studies [9,28–30] investigated groundwater recharge in the Continental Terminal aquifer and concluded that this process is mainly governed by depression-focused recharge through ponds [28]. The average value of groundwater recharge in this aquifer was estimated to be about 32–41 mm/a [9].

Static water levels were measured in the wells of Niamey aquifers on both sides of the Niger River [12]. They indicate that the water divide is associated with the topographic watershed on the plateau area NE of Niamey and that the groundwater flow direction is towards the river, which was similarly described by other authors [6–9,31–33]. According to [9], the flow regime is not homogeneous and local flow systems (e.g., the effluent conditions in the area of Gount Yantala) exist, which are mainly controlled by topography (Figure 4). Some springs that emerge from the basement aquifer have been documented

during field work on the NE side of the Niger River where the flow gradient becomes steep. The discharge of two springs was measured in December 2022 with 1.3 and 0.3 L/s. The groundwater flow on the southwestern part of the river (the plain side) implies an interrupted regime within the fractures [5,31–33].

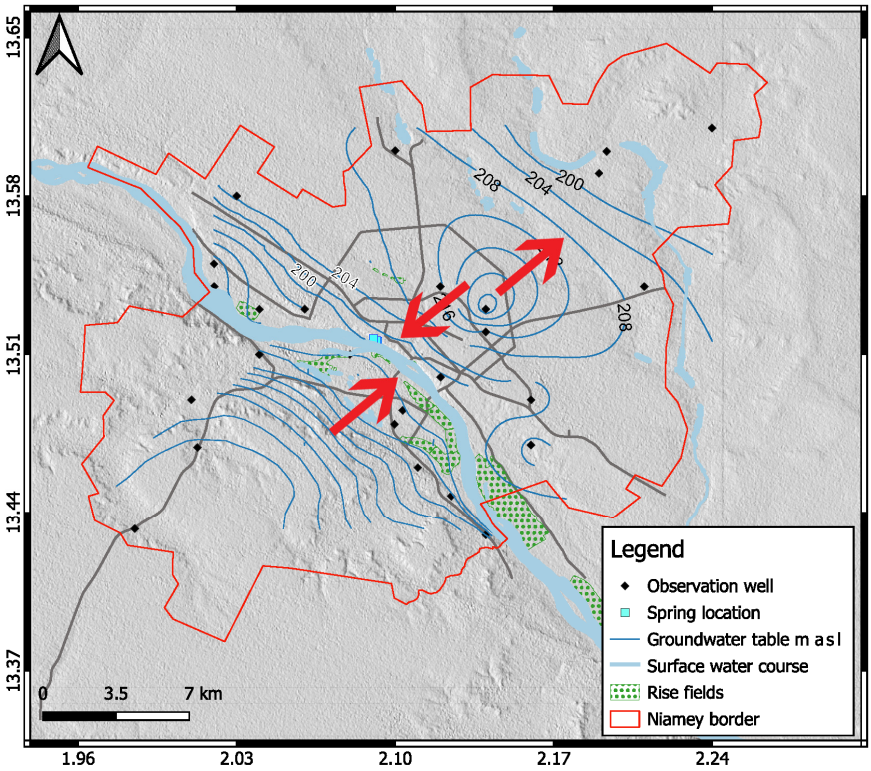


Figure 4. Groundwater flow direction based on the measurements of a static water table in the observation wells in 2017 by [12].

Long-term observations of the groundwater table of the basement aquifer on both sides of the Niger River in Niamey show an increasing groundwater level in the period between 2012 and 2023 [34]. For instance, groundwater levels in the Gaweye district raised two meters over this observation period and more than 2.5 m at the location of Kirkissoye. A one-year record of daily groundwater table measurements in the same aquifer in Kollo shows the groundwater level as upraised during and shortly after the rainy season [27].

Previous fieldwork on hydrochemical and stable isotope data (2020 to 2021) indicated that wells used for groundwater sampling do not always have appropriate details on, e.g., well construction, proper aquifer separation, screening length, and the material used for the filter and tubing [7]. According to the drilling and hydraulic test protocols presented by the Bureau de Recherches Géologiques et Minières (BRGM) [35], all wells that were sampled in the area of Niamey were drilled and filtered in the weathered fringe of the basement. Such drilling protocols for the wells used for groundwater sampling in the area of Kollo do not exist.

3. Materials and Methods

Groundwater samples from 3 springs and from 10 wells with a diameter of 12 cm and different depths (Table 1) were collected during the time between November 2020 and May 2023 on a monthly basis. These wells tap the weathered fringe of the basement and were drilled by BRGM [35]. They are currently partially used as observation wells by the Ministry of Hydraulics in Niger. The investigated springs emerge from the same basement aquifer in Niamey. Furthermore, 11 wells in the area of Kollo, which belong to the weathered fringe of the basement, were surveyed and sampled monthly between

March 2022 and May 2023 (Figure 1). For most of the wells, no information on the elevation reference of the wells heads is available. According to BRGM protocols [35], the wells are not fully penetrating, and screen lengths are generally not available. Groundwater samples were collected after purging at least two well-volumes. The pump used for groundwater abstraction (MP1, Grundfos, Erkrath, Germany) was connected to a flow meter to observe the pumped volume and to supply water to a flowthrough cell for analysis of field parameters (specific electrical conductivity (EC), pH, and water temperature (T)). Probes were calibrated in the field prior to measurement. Table 1 summarises the number of samples collected over the observation period together with the technical data of the observation wells and the pumping rate applied during sampling. To simplify the names of the sampling locations, each observation well is referred to by a symbol as indicated in Table 1. Ny refers to the location Niamey and Nt to the location in Kollo. GIZ refers to wells drilled by the Gesellschaft für Internationale Zusammenarbeit. SW refers to surface water. Two permanent ponds in Bangoula and Champs De Tire were sampled regularly to detect the source of water, which is used mainly for livestock. At the same time, surface water samples were collected from two surface water locations in Niamey (Pont Kenney and Tondi Koiry) and two pumping stations in N'Dounga Tarey and Kollo. The pumping stations provide surface water from the Niger River to the adjacent agricultural rice fields. Temporary streams (koris) flow through N'Dounga Tarey, and one of these is located adjacent to Nt-TAS (Figure 1). The water that runs through this stream was sampled, starting from the beginning of the rainy season until the middle of the dry season.

Table 1. Type, location, and details of all wells, springs, and surface water sampled during the period 2021–2023.

Location	Symbol	Longitude	Latitude	No. of Samples [-]	Well Depth [m]	Average Pumping Time [min]	Range of Applied Q [L/min]	Composite Soil Sample
Groundwater (GW)								
Kossey Djerma	Ny-KD	2.0234	13.5432	20	34	88	0.22	1
Eglise Garbado	Ny-EG	2.1446	13.5183	19	85	190	0.18–0.2	none
Gamkale Sebangue	Ny-GS	2.1234	13.497	20	57	267	0.17–0.2	1
Kirkisoye Garage	Ny-KG	2.0997	13.4791	20	45	159	0.21–0.27	none
Saga Gourma	Ny-SGO	2.2112	13.5388	20	26	192	0.19–0.23	1
Mairie Garage	Ny-MG	2.1218	13.5383	20	70	114	0.20	1
Goudel Tassiba	Ny-GT	2.0579	13.5296	17	68	40	0.19	1
CSI Gaweye	Ny-CSI	2.1033	13.4850	19	40	100	0.23	1
Saga Gassia	Ny-SAG	2.1625	13.4702	4	75	80	0.15–0.19	none
Dan Gao	Ny-DG	2.1412	13.5299	6	81	100	0.20	none
Ndounga Tarey borehole	Nt-FDT	2.2225	13.3813	6	54	160	0.2	none
Abara Gongou	Nt-AG	2.2087	13.3826	4	32	90	0.17	none
Digua Banda	Nt-DB	2.2311	13.3768	6	106	330	0.2	none
Tassoura borehole	Nt-TAS	2.2366	13.3775	6	34	125	0.2	1
Bella Koira	Nt-BK	2.2201	13.3857	6	n.d.	20	n.d.	none
Gala Berri	Nt-GB	2.2249	13.3706	5	n.d.	20	n.d.	none
Alpha Koira	Nt-GAK	2.2413	13.3616	5	75	30	n.d.	1
GIZ-1	GIZ-1	2.2139	13.3768	5	52	20	n.d.	none
GIZ-2	GIZ-2	2.2134	13.3773	6	52	20	n.d.	none
GIZ-3	GIZ-3	2.2132	13.3776	6	52	20	n.d.	none
GIZ-4	GIZ-4	2.2127	13.3779	3	52	20	n.d.	none
Spring-1	S1	2.0922	13.5158	n.d.	n.d.	n.d.	n.d.	none
Spring-2	S2	2.0917	13.5160	n.d.	n.d.	n.d.	n.d.	none
Spring-3	S3	2.0904	13.5170	n.d.	n.d.	n.d.	n.d.	none
Surface water (SW)								
Pump.St. Ndounga Tarey	SW-PNT	2.2123	13.3674	6	n.d.	n.d.	n.d.	none
Koris Tassoura	SW-TAS	2.2372	13.3782	4	n.d.	n.d.	n.d.	none
Pump.St. Kollo	SW-Kol	2.3284	13.2966	5	n.d.	n.d.	n.d.	none
Koris Bangoula	SW-BAN	2.0291	13.5694	6	n.d.	n.d.	n.d.	none
Koris Champs de tire	SW-Cdt	2.0260	13.5791	6	n.d.	n.d.	n.d.	none
Tondi Koiry	SW-TK	1.9955	13.5805	6	n.d.	n.d.	n.d.	none
Pont Kennedy	SW-PK	2.1027	13.5034	11	n.d.	n.d.	n.d.	none

Several wells in the area of Kollo including the group of GIZ wells and Alpha Koira are equipped with an electrical submersible pump, but these were locked, such that the groundwater and well depths could not be measured. Groundwater was pumped and the samples were taken after field parameter readings stabilised. For two locations (Gala Berri and Bella Koira), wells are used for drinking purposes; these are equipped with a pedal pump and locked to be protected against vandalism. Here, groundwater samples were taken after 30 min of pumping.

The field parameters pH, T, and EC (Table 2) were measured in the field (WTW® portable device). The samples for analysis of cations were filtered through a 0.45 µm filter and acidified with HNO_3 (69%) to pH < 2 directly in the field, then later cooled at 4 °C for further transport. PE bottles of 500 and 100 mL were used for anion and cation samples, respectively.

Soil samples were collected at depths of 3 m at seven selected locations within a distance of less than 1 m from an observation well (Table 3). At each sampling location, 6 samples were taken with a depth interval of 50 cm each using a manual auger. Finally, the soil samples belonging to each profile were mixed to obtain a representative sample from the profile at the different depths. The soil samples were kept away from contact with air and later eluted in the laboratory. The eluate was prepared by leaching for 24 h using distilled water [35]. The eluate was then filtered through a 0.45 µm filter and analysed for NO_3^- concentrations and nitrate isotopes.

The main cations (K^+, Na^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Mn^{2+}) were analysed by inductively coupled plasma-optical emission spectrometry (ICP-OES, SPECTRO ARCOS, Kleve, Germany) with a limit of quantification (LOQ) less than 0.04 mg/L. The analytical uncertainties are ±5% for all anions and cations. Anions (Cl^-, SO_4^{2-}, NO_3^-, F^-, Br^-) were analysed by ion chromatography (Thermo Scientific Dionex ICS-5000+, Darmstadt, Germany) using a guard and analytical column (Dionex IonPac AG19; Dionex IonPac AS19), and neutralisation of the alkaline KOH-eluent a with membrane suppressor technique (ADRS600). The LOQ for all anions is less than 0.03 mg/L. Alkalinity (acid-neutralising capacity) was determined using a 50 mL aliquot of the unfiltered sample, which was titrated (Mettler-Toledo T90) with 0.05 N HCl down to pH = 4.3. The endpoint is determined potentiometrically using a 2-cell pH-glass electrode. Charge balance error calculations were performed on all water samples and were usually better than ±3%.

Stable isotope analyses of water samples were conducted at the stable isotope laboratory of BGR in Hannover (Germany) using a Picarro L2120-i water vapor analyser (Santa Clara, CA, USA) connected to a vaporiser and autosampler system. Isotope values of water samples are given in the standard delta notation per mil (‰) versus VSMOW. We used two laboratory standards for two-point standardisation, one standard for drift correction and one standard for quality checking, which were all calibrated against international standards (VSMOW2, VSLAP2). All laboratory standards are stored in metal kegs under He pressure, and brown glass bottles are filled with them for daily use. The data sets were corrected for machine drift during the run and normalised to the VSMOW/SLAP. Analytical precision levels given by a quality check (QC) sample measured in each run were better than 0.2‰ and 0.8‰ for $\delta^{18}O$ and δ^2H, respectively. Deuterium excess values (d-excess) are calculated as $d = \delta^2H - 8 \times \delta^{18}O$ and given without comma digits.

Ten groundwater samples and seven soil samples were collected from Niamey and Kollo in March 2023 for the analysis of the stable isotopic composition of NO_3^-. For this purpose, groundwater was filtered into 500 mL bottles and stabilised with 10 drops of chloroform in the field. $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ were analysed using the bacterial denitrifier method [36] at the laboratory of Hydroisotop GmbH (Schweitenkirchen, Germany). In this method, NO_3^- and NO_2 contained in the water samples are quantitatively converted to N_2O gas using bacterial strains of *Pseudomonas chloroaphis* ssp. *aureofaciens*, followed by simultaneous determination of the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ isotope ratios of N_2O by isotope ratio mass spectrometry (Thermo Scientific, Delta V Plus, Bremen, Germany). Each sample is prepared and analysed for the isotopic composition in triplicate. For calibration, the

N_2O gas obtained by denitrification from at least five aliquots of the international standards USGS 34, USGS 35, and IAEA-NO3 is measured against a N_2O-lab standard (Tyczka Industrie-Gase GmbH, Geretsried, Germany) in each sample run. Nitrogen and oxygen isotope ratios ($\delta^{15}N\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$) are reported per mil (‰) relative to atmospheric air (AIR) and the Vienna Standard Mean Ocean Water (VSMOW), respectively. Analytical uncertainties are usually better than 0.5‰ for $\delta^{15}N$ and better than 0.6‰ for $\delta^{18}O$.

4. Results

The temporal means of major ion concentrations as well as stable isotopes in groundwater and surface water samples over a period of more than two years are listed in Table 2. The full data set comprising all individual samples, which were used to calculate the average values, is provided in the Supplementary Materials. The pH of groundwater varies in the area between 6.4 in Nt-TAS and basic values above 8 in Ny-KG. EC values scatter in space over a wide range between 220 µS/cm at Ny-SAG and 4300 µS/cm at Ny-CSI. The wells in Ny-CSI, Ny-KG, and Ny-KD show increasing values of EC over the observation period. Furthermore, the change in EC through the rainy season differs among the observation wells, as indicated by the data series from November 2020 to May 2023. The groundwater from several boreholes shows decreasing EC values after the beginning of the rainy season (Ny-KD, Ny-CSI, Ny-KG, Ny-EG, Ny-GT). Ny-MG and Ny-SGO seem to sustain the values over the monitoring period.

Table 2. Average concentrations of major ions and stable isotopes δ^2H and $\delta^{18}O$ in groundwater samples in Niamey and Kollo.

Sample ID	Type	pH	EC [µS/cm]	K [mg/L]	Na [mg/L]	Cl [mg/L]	Mg [mg/L]	Ca [mg/L]	F [mg/L]	SO_4 [mg/L]	HCO_3 [mg/L]	NO_3 [mg/L]	$\delta^{18}O$ [‰]	δ^2H [‰]	d Excess [‰]
Groundwater (GW)															
Ny-KD	Well	7.6	1625	1.24	197.6	121.5	53.1	94.2	1.2	121.7	617.6	108.0	−3.19	−20.6	5
Ny-EG	Well	7.9	574	3.8	27.3	6.6	33.3	40.2	0.2	53.1	277.4	14.5	−5.13	−32.9	8
Ny-GS	Well	8.5	486	1.0	12.8	18.9	22.4	43.2	0.2	3.9	131.9	114.2	−3.69	−24.4	5
Ny-KG	Well	8.3	1031	2.2	33.8	104.5	38.8	106.6	0.3	41.7	186.8	202.5	−3.87	−21.5	9
Ny-SGO	Well	8.1	375	0.9	19.9	4.2	19.6	26.0	0.4	20.9	126.3	67.6	−3.89	−24.2	7
Ny-MG	Well	7.5	355	1.8	36.0	0.7	13.6	21.9	0.2	7.3	216.8	4.9	−5.16	−32.1	9
Ny-GT	Well	7.3	348	4.3	13.4	10.8	13.1	28.8	0.2	9.6	56.1	105.6	−3.61	−22.2	7
Ny-CSI	Well	7.5	3992	4.2	131.6	438.2	186.1	371.2	0.2	47.9	285.6	1373.4	−2.56	−17.3	3
Ny-SAG	Well	7.8	208	4.6	12.9	0.9	9.7	13.5	0.5	9.9	113.3	2.1	−4.63	−28.3	9
Ny-DG	Well	7.2	226	2.2	21.3	0.4	7.7	14.5	0.2	3.0	132.0	5.7	−4.58	−29.0	8
Nt-FDT	Well	7.2	876	3.7	42.1	40.6	40.9	80.4	0.3	50.2	343.2	99.8	−2.71	−19.0	3
Nt-AG	Well	8.3	756	17.8	88.7	92.9	33.9	63.1	0.6	28.7	409.5	7.6	−0.59	−9.6	−5
Nt-DB	Well	7.4	323	3.9	14.1	15.6	12.3	28.4	0.6	13.2	109.0	38.2	−0.77	−9.54	−3
Nt-TAS	Well	6.9	577	3.8	24.2	39.9	22.0	52.4	1.6	17.9	154.6	99.9	−1.01	−12.5	−4
Nt-BK	Well	7.7	808	3.1	44.7	17.7	40.5	66.5	0.3	11.4	468.8	17.1	−2.09	−15.8	1
Nt-GB	Well	7.3	798	7.2	92.5	14.9	27.4	43.7	0.1	87.8	379.8	8.6	−0.44	−7.2	−4
Nt-GAK	Well	7.3	738	6.1	70.8	10.5	30.8	36.1	0.5	60.6	304.4	63.1	−3.74	−23.6	6
GIZ-1	Well	7.2	777	7.6	51.4	15.3	36.4	62.3	0.5	13.5	480.8	0.7	−0.05	−5.7	−5
GIZ-2	Well	7.1	738	7.2	54.1	14.4	33.5	55.9	0.6	11.8	455.7	0.2	0.39	−3.6	−7
GIZ-3	Well	7.2	640	6.4	47.3	9.4	29.8	46.8	0.7	10.2	401.8	0.4	0.37	−4.1	−7
GIZ-4	Well	7.5	731	8.0	77.6	11.8	26.6	40.3	0.7	15.1	439.7	0.2	−0.40	−8.9	−6
S1	Spring	7.3	372	3.6	32.6	32.5	8.6	17.6	0.1	10.0	27.2	97.5	−1.30	−12.2	−2
S2	Spring	7.2	328	5.1	25.7	29.6	6.9	18.5	0.1	13.0	34.7	69.0	−1.40	−12.7	−2
S3	Spring	7.6	288	6.0	25.8	26.6	4.9	15.5	0.1	5.2	38.2	61.9	−1.30	−12.9	−3
Surface water (SW)															
SW-PNT	River	7.7	78	2.8	4.6	1.2	2.3	4.6	0.1	0.6	36.9	0.4	−0.47	−10.1	−6
SW-TAS	Stream	7.4	96	2.8	5.7	1.4	2.9	6.1	0.0	0.5	47.4	1.2	2.12	−1.4	−18
SW-Kol	River	7.8	78	3.9	8.1	3.1	2.5	5.0	0.0	1.3	44.3	2.6	3.50	5.6	−22
SW-BAN	Pond	7.5	317	1.1	13.2	3.2	10.7	28.7	0.0	20.9	140.0	1.3	−3.30	−21.5	5
SW-Cdt	Pond	7.3	197	0.9	11.8	0.5	5.6	16.4	0.0	0.7	107.4	0.2	−3.65	−23.0	6
SW-TK	River	7.6	72	1.7	2.9	0.4	1.7	3.8	0.0	0.2	29.1	0.2	−3.13	−23.6	1
SW-PK	River	7.6	65	1.8	3.1	0.5	1.7	3.9	0.1	0.3	29.8	0.4	−5.51	−21.3	23

Most groundwater samples in Niamey and Kollo belong to the Ca-Mg-HCO_3 type (Figure 5). The dominating anion for most of the samples is HCO_3; however, groundwater from the locations of Ny-KG, Ny-CSI, Ny-GT, Nt-TAS, and GIZ-4 falls into a chloride domi-

nation type. Surface water from the Niger River plots within the Ca-Mg-HCO_3 type but with a much lower dissolved mineral content in comparison to groundwater samples. Koris Bangoula (SW-BAN) and Koris Champs de Tire (SW-Cdt) are two permanent water ponds located in the NW part of Niamey. The samples of SW-BAN plot among the groundwater samples and show a higher mineral content compared to other surface waters. Samples stemming from SW-Cdt plot among the surface water samples. Groundwater samples from Kossy Djerma in Niamey (Ny-KD) together with samples from Abara Gongoun (Nt-AG) and Gala Beri (Nt-GB) plot in the area of no dominating cation type; however, these samples have higher concentrations of Na and K compared to other samples.

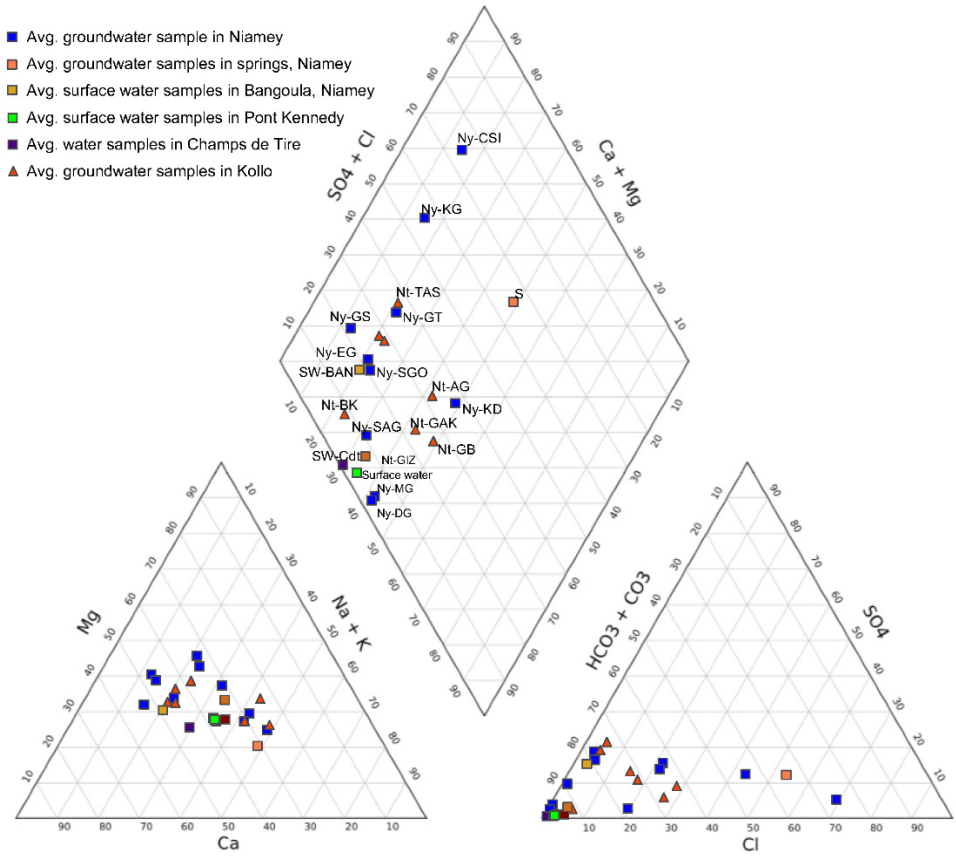


Figure 5. Distribution of surface- and groundwater samples within Piper diagram.

The time series of EC and NO_3^- over the observation period is shown in Figure 6. Some of the investigated wells in Niamey (Ny-KD, Ny-GS, Ny-KG, Ny-SGO, Ny-GT, Ny-SCI) show much higher concentrations than the guideline values recommended by the WHO (50 mg/L) and reach even 30 times higher concentrations at the location Ny-SCI. Groundwater nitrate concentrations from the wells Ny-MG, Ny-EG, and Ny-SAG are lower than 50 mg/L and are in the range between 1 and 10 mg/L. For Ny-KG and Ny-KD, a trend of gradual increase in NO_3^- and Cl^- over the sampling period can be observed (see Supplementary Materials). The hydrochemical composition in wells Ny-MG, Ny-SAG, and Ny-GS remains constant over the sampling period, while well Ny-KD shows a gradual increase in NO_3^- and Cl^- but with a higher Na concentration. In general, this increase has different rates for the different observation wells. The change at Ny-KG takes place faster than at the others (this will be discussed in Section 6). Ny-DG and Ny-SGO do not show this trend and plot very close to the samples from SW-BAN.

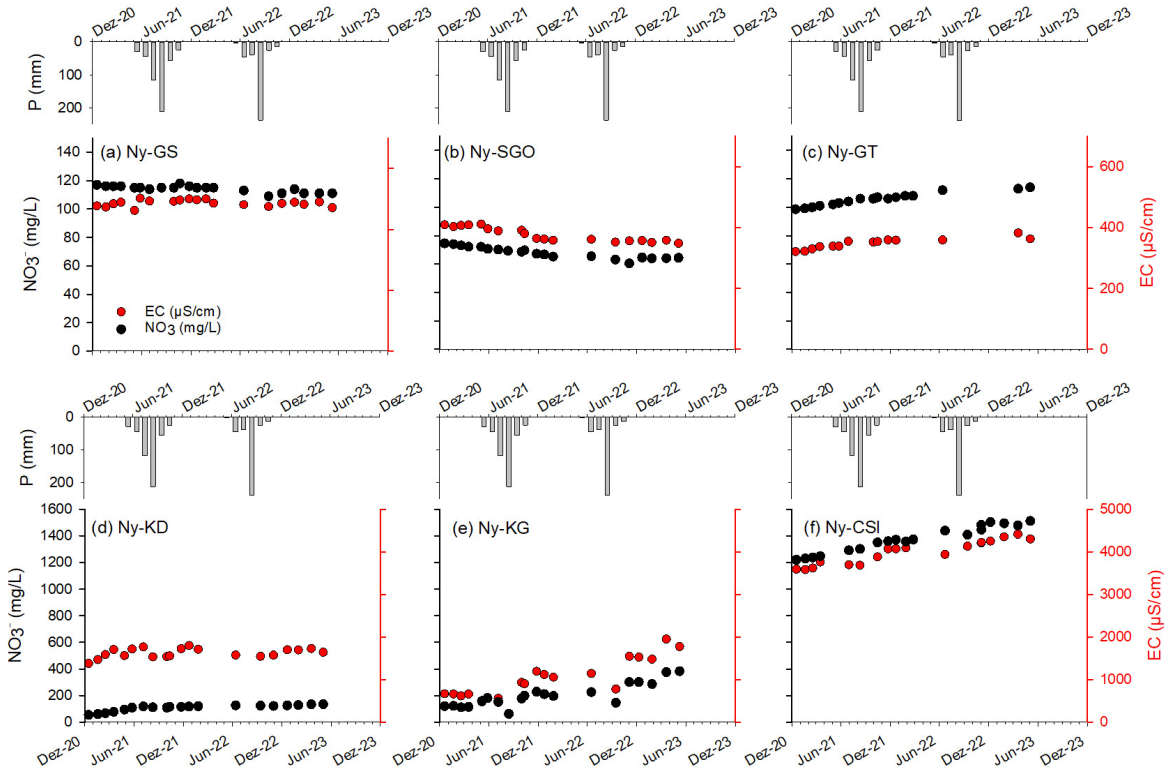


Figure 6. (**a**–**c**) EC values and NO_3^- concentrations of wells with stable NO_3^- concentrations over the observation period; (**d**–**f**) EC values and NO_3^- concentrations of wells with an overall increase in NO_3^- concentrations over the observation period. (Please note the different scales for the upper and lower panels.)

Groundwater and surface water from the area of Kollo plot similarly to those from Niamey, but with a more scattered pattern (Figure 5). Groundwater samples from the wells of Nt-TAS, Nt-FDT, and Nt-DB show a similar increasing trend to that observed in Niamey over the sampling period. The NO_3^- concentrations in the region plot in a range between less than 5–15 mg/L in Ny-MG and Ny-EG and reaching 1500 mg/L in Ny-SCI. Concentrations between 60 and 300 mg/L were observed in the wells of Ny-GS, Ny-GT, Ny-SGO and Ny-KG, Nt-TAS, and Nt-GAK.

To detect the variability over the rainy and dry seasons, monthly measured concentrations were plotted together with EC values and rain amounts [19] over the two years of the observation period (Figure 6). In general, the wells with NO_3^- concentrations in the range of 60–100 mg/L show constant concentrations over the sampling period with relatively low EC values, which implies that there is no dilution over the rainy season. Samples with NO_3^- concentrations above 100 mg/L show a slight to significant dilution influence during the rainy season between May and September and a continuous increase in EC and nitrate over the observation period.

Stable isotope results over the whole observation period are plotted in Figure 7. The Local Meteorological Water Line (LMWL, y = 7.15x + 8.08) is plotted based on monthly mean values of $\delta^{18}O$ vs. $\delta^{2}H$ in precipitation collected in Niamey City between 2009 and 2018 [37,38]. The intercept of the LMWL (+8.08) indicates evaporation at a relative humidity of approximately 80% [39]. While the surface water samples plot on a line with a slope of approximately 4.5, groundwater samples plot on a line with a slope of 6.0. $\delta^{18}O$, and $\delta^{2}H$ values of surface water start to increase from the end of the rainy season (−4‰ and −33‰), to reach 3‰ and 2‰ at the end of the dry season. Groundwater samples vary over a wide range between −5.1‰ and −33‰ at Ny-EG, with the most negative δ-values of −2.6‰ and −17‰ at Ny-CSI.

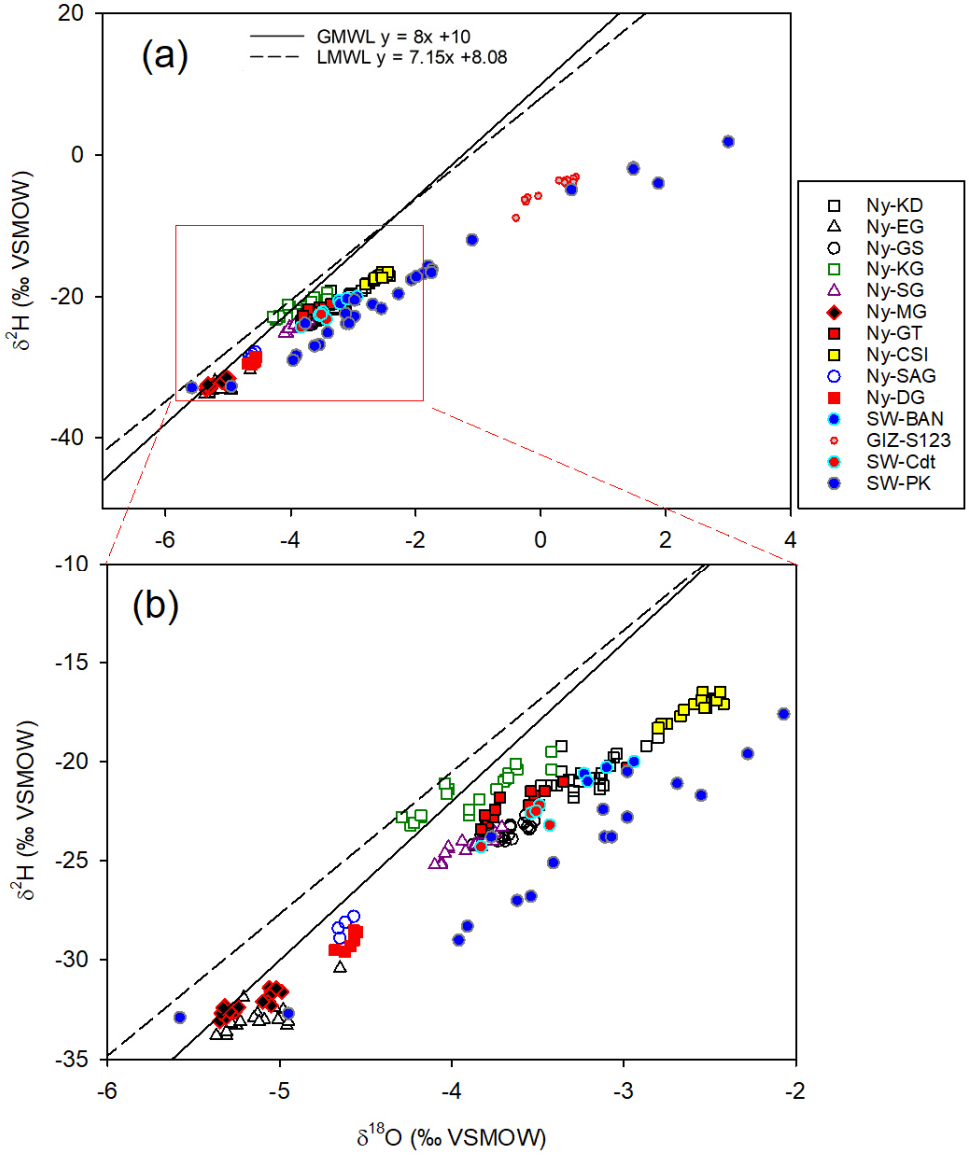


Figure 7. (**a**) Relationship of $\delta^{18}O$ and $\delta^{2}H$ in surface water (symbols starting with SW) and groundwater in the area of Niamey. (**b**) Zoomed into the marked area in panel (**a**).

While most of the groundwater samples plot close to the regression line, the samples belonging to Ny-KG plot close to the LMWL and the GMWL. δ-values are increasing over the observation period at all sampling locations (Figure 7b, Supplementary Materials).

Groundwater and surface water samples from the Kollo region are plotted together with the samples from Niamey in Figure 8. Groundwater from the Kollo region also plots on a line with a slope of 4.8, lower than for groundwater samples from Niamey. Most of the groundwater samples tend to be more positive, with values between −0.5 and −10‰, compared to values between 0.6 and −3‰ for groundwater from Niamey. Samples belonging to Nt-GAK and Nt-FDT plot among those from Niamey.

The analytical results of $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ for groundwater and soil samples taken once between 19 March 2023 and 22 April 2023 are presented in Table 3. The groundwater and soil samples taken from Ny-MG with a very low concentration of NO_3^- are given for comparison. All groundwater samples show $\delta^{15}N$ values in the range between 6.8‰ and 18.7‰. Although no clear trend is visible, the highest $\delta^{15}N$ values between 15.0 and 18.7‰ coincide with high NO_3^- concentrations at the locations Ny-KD, Nt-TAS, Ny-KG, and Ny-SCI. Most soil samples from the Niamey area plot in the $\delta^{15}N$ range between 10‰ and 12‰. The soil sample from Nt-TAS displays the lowest $\delta^{15}N$ value, with a value

of 5‰. The soil profiles collected from Niamey consist mainly of fine red sand. The first meter in the profile of Ny-KG consists of mudstone with sand. The mudstone disappears with depth and the soil then consists mainly of wet sand. Traces of industrial oil were observed during the field work at the surface, which is used in car workshops. Black mud was observed in the first meter of the soil profile at Ny-KD, transitioning into a mixture with gravels down to a depth of 3 m. Plots of δ^{15}N-NO_3 against NO_3^- and δ^{15}N-NO_3 against δ^{18}O-NO_3 are shown in Figure 9.

Table 3. Nitrate isotope concentrations of soils and respective water samples collected in Niamey and Kollo.

Borehole Location	Sampling Date	Samples ID	NO_3 [mg/L]	δ^{15}N-NO_3 Water [‰]	δ^{18}O-NO_3 Water [‰]	NO_3 [mg/L]	δ^{15}N-NO_3 Soil [‰]	δ^{18}O-NO_3 Soil [‰]
Kossey Djerma	20/03/2023	Ny-KD	120	18.4	20.7	5.5	11.2	15.4
Gamkale Sebangue *	22/03/2023	Ny-GS	110	11.2	9.2			
Kirkisoye Garage	21/03/2023	Ny-KG	350	18.7	16.9	3.4	36.7	21.3
Saga Gourma	21/03/2023	Ny-SGO	63	7.1	9.6	0.5	11.5	10.5
Mairie Garage	20/03/2023	Ny-MG	4.2	6.8	11.9	2.5	10.2	11.1
Goudel Tassiba	20/03/2023	Ny-GT	110	8.1	10.8	1.1	11.3	33.4
CSI Gaweye	19/03/2023	Ny-CSI	1300	15.4	16.7	10	11.4	18.5
Alpha Koira *	14/04/2023	Nt-GAK	58	10.8	12.9			
Tassoura borehole	21/03/2023	Nt-TAS	86	15.7	18.7	1.3	5.5	5.8
Saguia *	20/04/2023	Ny-SGU	120	11.0	13.3			

Note: * Samples for nitrate isotopes were only taken in groundwater.

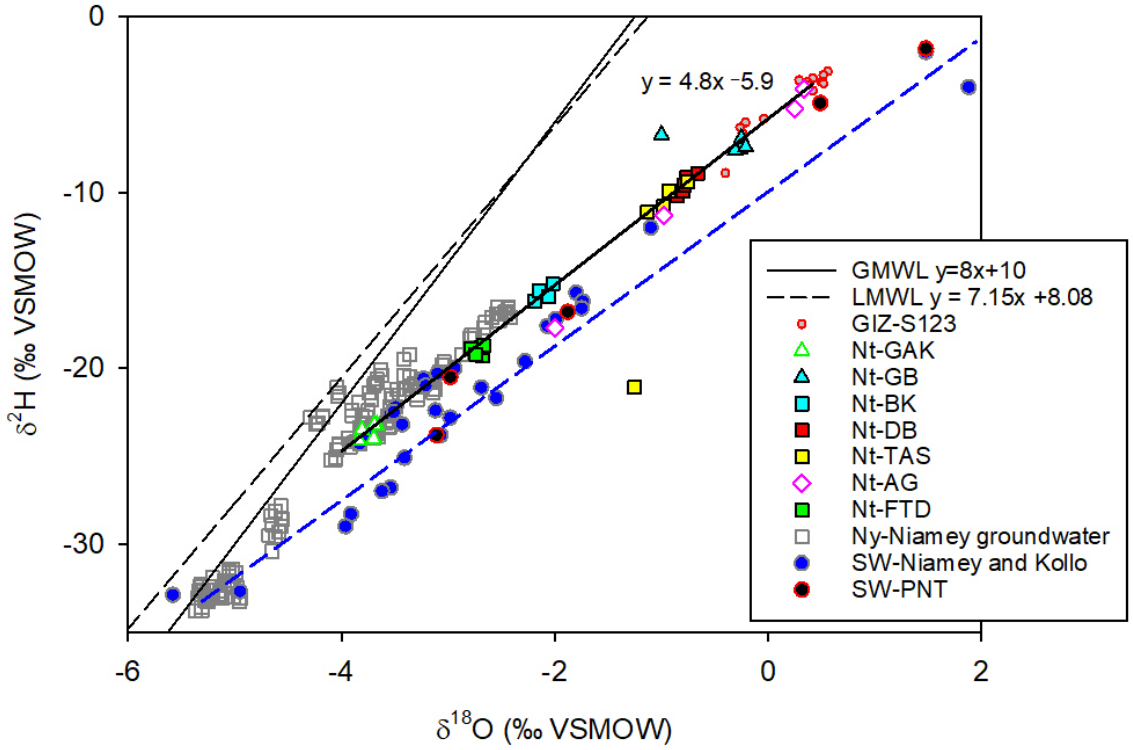


Figure 8. Relationship of δ^{18}O and δ^{2}H in surface and groundwater in the area of Niamey and Kollo (N'dounga Tarey). Solid black line and blue dashed line indicate regression lines for the groundwater of Niamey and Kollo, respectively.

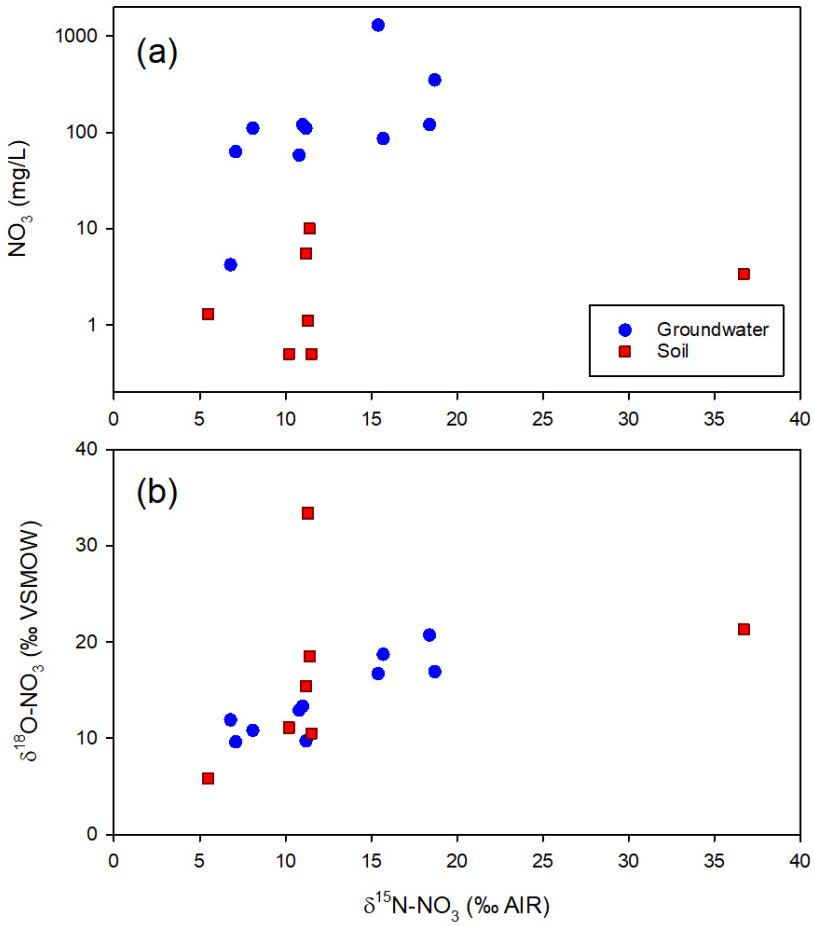


Figure 9. Relationship of (**a**) δ^{15}N-NO_3 values vs. NO_3^- concentrations and (**b**) δ^{15}N-NO_3 vs. δ^{18}O-NO_3 values for groundwater and soil samples from Niamey and Kollo, Niger.

5. Discussion

The processes that affect the hydrochemistry and the stable isotope composition of groundwater in the basement aquifer can be attributed (besides rock–water interaction) to recent groundwater recharge and possible anthropogenic inputs including water and pollutants from the urban area of Niamey (such as the locally common septic tanks) or from agricultural activities. The wells investigated in this study belong to two different groundwater flow systems located on both sides of the Niger River. The periodic decrease in EC values of groundwater in the well Ny-KD (Figure 6d) is probably related to a dilution effect by recharge taking place during the rainy season. However, it is not clear whether this recharge occurs through vertical infiltration or through river water infiltrating into the aquifer. To trace this component, the average measured δ-values of water were plotted against the distance from the riverbank (Figure 10). However, it is not clear whether this recharge occurs through vertical infiltration or through river water infiltrating the aquifer. Surface water is usually more influenced by evaporation, resulting in an enrichment of δ^{18}O and δ^{2}H so that the data points shift away from the meteoric water line with a slope substantially lower than 8. This is confirmed by the observed progressive enrichment of δ^{18}O and δ^{2}H of surface water samples towards the end of the dry season (Figure 7), which fall on a slope of about 4.5. The distinct isotopic composition of surface water influenced by evaporation has been used to identify interactions between groundwater and surface water and to investigate groundwater–surface water mixing [39,40]. To trace components of river water infiltration, the average measured δ-values of water samples were plotted against the distance from the riverbank (Figure 10).

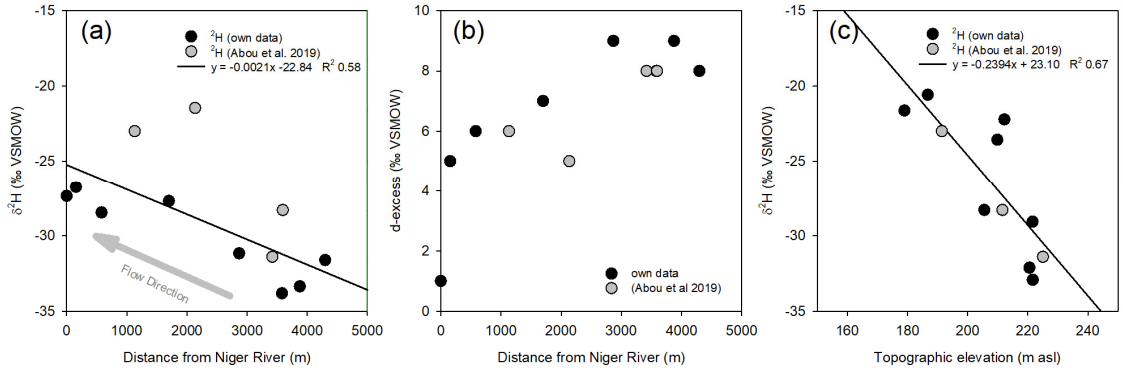


Figure 10. (**a**) δ^2H values and (**b**) d-excess values vs. distance from Niger River. (**c**) δ^2H values vs. topographic elevation. Four additional locations were added from [12].

Considering the sampled wells on the NE part of the Niger River, the δ-values of Ny-KD, which plot very close to those of the river water in Pont Kennedy, suggest an interaction between river water and groundwater in the bedrock aquifer. The location of this well in the flood plain reveals that a component of the surface water, e.g., during floods, might also cause the dilution effect of EC values during the rainy season (Figure 6). The trend of the stable isotope values (Figure 7b) also implies mixing with surface water, which is more positive due to evaporation. The increasing shift of the δ-values at this location in the direction of the surface water might be related to the fact that the Niger River experiences two flood peaks during the year: a first quick and sharp one followed by a second peak with an interval of two to three months. A similar but faster dilution effect (Figure 6) can be observed in well Ny-KG, where the EC values decrease in the rainy season. This well is located close to a permanent pond, which seems to contribute to recharge during the flood period as well. The stable isotope composition at Ny-KG, which plots on the LMWL, starts to deviate from it with progressing time and implies therefore a mixing influence with water exposed to evaporation.

The low δ-values located close to the topographic shed and far from the river (Ny-SG, Talladje, Ny-EG, Ny-MG, Kourame, Ny-DG) are probably not influenced by surface water but represent the isotopic composition of regional groundwater recharge near the plateau. Moving closer to the river, the influence of the surface water increases, especially at the locations of Ny-KD and Ny-GS. This reveals that the areas where the wells are located are either impacted by surface water (irrigation, rain infiltration), or by river water due to their close proximity to the flood plain. Taking the topographic elevations of the different wells into account, it can be observed that the difference in δ-values between the lowest point (surface water) and the higher elevations (e.g., Ny-MG and Ny-EG) is about −10.5‰ for δ^2H (−2.39‰ for δ^{18}O), as is shown in Figure 10c. Furthermore, a correlation exists between the increasing topographic elevation and decreasing δ-values, which reveals an altitude effect on the δ-values (Figure 10c), leading to lower δ-values at locations closer to the higher topographic levels. Deuterium excess values (d-excess) plotted in Figure 10b emphasise that the influence of surface water dominates the stable isotope values, because groundwater d-excess values are lower (more influenced by evaporation) closer to the surface water.

Several factors may influence the groundwater flow and composition in the fractured aquifers and their weathered fringes [41]. A continuous increase in EC values together with Cl^- and NO_3^- concentrations is observed in groundwater extracted from wells (Ny-KD, Ny-KG, Ny-GT, Nt-TAS) (Figure 11). A slight increase in Ca concentrations can be observed in Ny-KG.

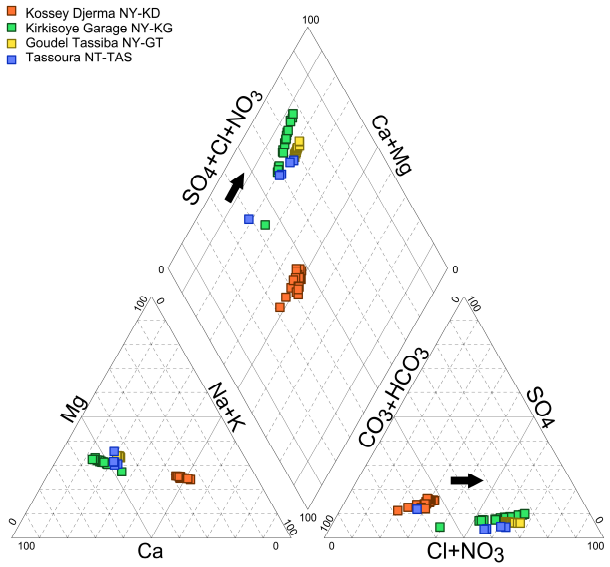


Figure 11. Observed increases in NO_3^- and Cl^- in four observation wells over the observation period. The arrows denote the increases in the ion concentrations with progressing time.

Given the wells are not fully penetrating to the base of the bedrock aquifer, the flow during pumping is not strictly lateral towards the well; instead, there is a vertical component from below. The increase in EC together with Cl^- and NO_3^- suggests that groundwater entering the wells from deeper parts of the aquifer might be more mineralised than the groundwater closer to the surface. This implies that the EC values increase with an increasing depth in the aquifer. Moreover, the depths of the wells vary strongly, in particular, between the SW part of the region where wells Ny-KG and Ny-SCI are located and the rest of the wells in the NE part. Hassane et al. (2016) [9] gave an estimation for the thickness of the weathered fringe to be approximately 100 m in the area of Kirkossye and 400 m on the plateau side (Figure 3). To trace the possible changes in groundwater quality with increasing depths, the average EC values measured over the observation period were plotted as a function of the well depth (Figure 12). The wells with greater depths between 70 and 80 m in Ny-MG, Ny-DG, and Ny-GT showed much lower EC values compared to those at shallow depths. Considering the whole range of the EC values, two outliers can be observed in Figure 12: Ny-CSI and Ny-SGO. This probably indicates that the change in the EC at these two locations is related not only to the influence of the lithology but also to anthropogenic effects.

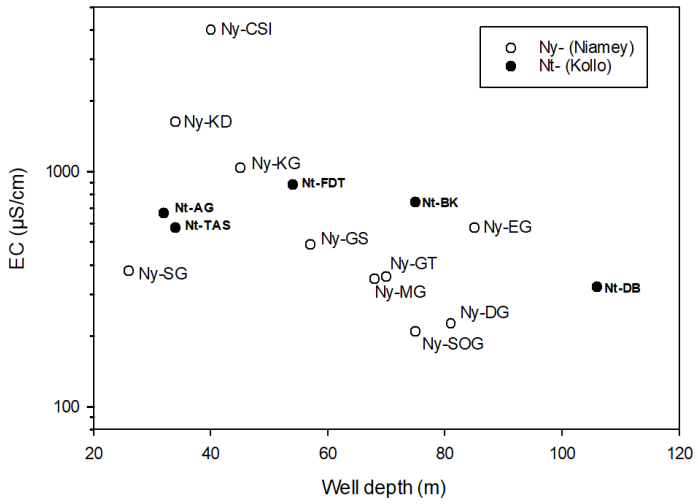


Figure 12. Relationship between average EC values and well depths at Niamey and Kollo.

Figure 12 shows as well that three wells have EC values higher than 1000 µS/cm, at Ny-SCI, Ny-KD, and Ny-KG; in other words, these are the wells that display a diluted EC in the rainy season, as was demonstrated in Figure 6. Therefore, the enhanced EC values observed in shallow wells are likely related to anthropogenic influences and not necessarily to increasing salinity over the increasing depth of the aquifer. Enhanced Na concentrations in the well of Ny-KD (Figure 11) were observed to be almost constant over the observation period and did not correlate with the increasing Cl^- and NO_3^- concentrations. Since the increase in NO_3^- and Cl^- had no correlation with depth, the possible source of these two ions may be related to septic tanks [42].

Since irrigation in Niamey occurs only at a limited scale, the influence of mixing with surface water can be attributed to flood events during the rainy season. In contrast, mixing with more evaporated and isotopically heavier surface water is evident in the area of Kollo, where surface water samples partly plot among the groundwater samples (Figure 8).

A clear indication of anthropogenic influence on groundwater is provided by extremely elevated concentrations of NO_3^- in most of the sampled wells in the region (Figure 6). At the same time, $\delta^{15}N$ values are higher than those of nitrate of natural origin (+4 to +8‰) measured in the region [43] and therefore are potentially caused by NO_3^- from anthropogenic sources such as agricultural fertilisers, manure from livestock, or leakage of sewage from latrines. This is supported by the $\delta^{15}N$ values of nitrate from soil eluates, which plot between 10 and 11‰ (Figure 9) with two outliers, one at Nt-TAS with 5.5‰, and another at Ny-KG with 37‰. The δ-values in the range of 10 to 11‰ are comparable with values that were measured in animal manure [44]. The low value at Nt-TAS is comparable to values reported by [43] for plant source accumulates at the surface. The high value is typical for $\delta^{15}N$ values of NO_3^- in wastewaters reported in other studies from Africa and elsewhere [44,45]

Combining $\delta^{15}N$-NO_3 with $\delta^{18}O$-NO_3 values of groundwater (Figure 9b) reveals two different groups of data points that are separated by a systematic shift towards more positive δ-values with a slope of approximately 2:1. This shift (or rudimentary trend) might be caused by denitrification or by distinct sources of NO_3^- of the respective groundwater samples. Denitrification is usually indicated by enrichment of the δ-values with a slope similar to the observed shift [16]. However, denitrification should be accompanied by a strong decrease in NO_3^- concentrations [46], which is not clearly recognisable for the related groundwater samples showing high, non-systematic concentrations (Figure 9a). While the high $\delta^{15}N$-NO_3 can be explained by larger contributions of NO_3^- from wastewater or sewage, the positive $\delta^{18}O$-NO_3 values additionally require different ^{18}O sources during nitrification in the subsurface. Such conditions might be provided by ^{18}O-enriched surface water that is used to form NO_3^- from reduced N species in wastewater. This is supported by the wells showing high $\delta^{18}O$-NO_3 values, which are located close to the Niger River (e.g., Ny-KD). The decreasing thickness of the clay-rich sediments at the top of the bedrock aquifer [22,28,35] in the flow direction from the catchment border towards the Niger River possibly enhances the N input from latrines at the locations of Ny-CSI, Ny-KD, and Ny-KG. As shown in Figure 6, the NO_3^- concentrations at the location Ny-GS maintain constant values over the observation period. An exceptionally high value of 33‰ for $\delta^{18}O$-NO_3 was measured at Ny-GT, which is difficult to interpret. Böttcher et al. [47] suggested atmospheric nitrate in rainfall as a source of high $\delta^{18}O$-NO_3 values in groundwater that recharged in a sandy forest location. The presence of NO_3^- with an atmospheric isotope signature requires highly permeable soils without preventing the incorporation of reduced nitrate into soil organic matter after denitrification. This might be consistent with the soil at the location Ny-GT, which consists of dry sand becoming finer with an increasing depth. An alternative explanation might be isotopically (^{15}N and ^{18}O) enriched nitrate salts in evaporates [48] in the soil. The soil in the region is known to contain evaporation deposits [25]. Based on the data, an influence of denitrification on NO_3^- concentrations at some of the locations cannot be ruled out, particularly for well Ny-KG, but no clear

denitrification trend is recognisable due to the variable and heterogeneous NO_3^- inputs at the study site.

6. Conclusions

The wells tapping the weathered fringe of the basement aquifer in Niamey and Kollo show heterogeneous hydrochemical patterns on both sides of the Niger River. Nitrate concentrations differ over the observation period. Some wells have very low NO_3^- concentrations, of less than 10 mg/L. Others have high and constant NO_3^- concentrations between 60 and 100 mg/L, and some have very high concentrations that continuously increase from 300 to 1500 mg/L. The highest concentrations of NO_3^- occur in shallow wells that are closer to the Niger River or to surface water bodies that cause a notable dilution during the rainy season. A dilution effect observed in shallow wells on EC and NO_3^- concentrations seems not to be influenced by the hydraulic gradient between the surface and groundwater, but rather by flood events during and immediately after the rainy season.

The $\delta^{18}O$ vs. elevation distribution of the samples on the right side of Niamey suggests that despite the short distance, elevation influences the $\delta^{18}O$ content. This distribution also indicates a general homogeneous flow pattern with more negative $\delta^{18}O$ values with increasing altitudes.

Groundwater belonging to the weathered fringe in the agricultural area of Kollo is more influenced by infiltration of surface water, which is subjected to evaporation and seeps into the aquifer through irrigation practiced in the region. The $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- confirm that septic tanks are a significant source of NO_3^- in groundwater in both areas. The $\delta^{15}N$ levels measured from soil samples exhibit a wide range, which allows for distinguishing between natural plant sources and animal manure.

Because the investigated wells are partly used as drinking water, there is an urgent need to develop a better protection strategy for the groundwater resources and to involve wastewater treatment strategies, to avoid continuing contamination of the unprotected shallow wells with nitrate and other contaminants.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w16213016/s1, Table S1: Concentrations of major ions, minor ions, and stable isotopes δ^2H and $\delta^{18}O$ in groundwater samples in Niamey and Kollo.

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