

Article

# Seasonal Groundwater Quality Status and Nitrogen Contamination in the Shallow Aquifer System of the Kathmandu Valley, Nepal

Bijay Man Shakya <sup>1</sup>, Takashi Nakamura <sup>2,\*</sup>, Tatsuru Kamei <sup>3</sup>, Suresh Das Shrestha <sup>4</sup> and Kei Nishida <sup>2</sup>

<sup>1</sup> Integrated Graduate School of Medicine, Engineering and Agricultural Sciences, University of Yamanashi, Kofu, Yamanashi 400-8511, Japan; g17de002@yamanashi.ac.jp

<sup>2</sup> Interdisciplinary Center for River Basin Environment (ICRE), University of Yamanashi, 4 Chome-4-37 Takeda, Kofu, Yamanashi 400-8511, Japan; nishida@yamanashi.ac.jp

<sup>3</sup> School of Allied Health Sciences, Kitasato University, Sagamihara, Kanagawa 252-0373, Japan; tkamei@kitasato-u.ac.jp

<sup>4</sup> Central Department of Geology, Tribhuvan University, Kirtipur, Kathmandu 44613, Nepal; shrestha.sureshdas@gmail.com

\* Correspondence: tnakamura@yamanashi.ac.jp

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**Abstract:** The increasing concentration of nitrogen compounds in the groundwater is of a growing concern in terms of human health and groundwater quality. Although an excess of nitrogen compounds in the groundwater of the Kathmandu Valley has been reported, the seasonal variations of the fate of the nitrogen compounds and their relationships to the subsurface sediments are unknown. In this study, spatially distributed shallow dug well samples were collected during both the dry and wet seasons of 2016, and the nitrogen compound, chloride ( $\text{Cl}^-$ ), and iron ( $\text{Fe}^{2+}$ ) concentrations were analyzed. Two shallow dug wells and one deep tube well were monitored monthly for 2 years. Although  $\text{NH}_4\text{-N}$  concentrations were similar in the clay-dominated areas during both seasons (1 and 0.9 mg-N/L), they were lower in the gravel-dominated areas during wet season ( $1.8 > 0.6$  mg-N/L). The  $\text{NO}_3\text{-N}$  concentration differed depending upon the soil type which increased during the wet season (clay  $4.9 < 13.6$  mg-N/L and gravel  $2.5 < 6.8$  mg-N/L). The  $\text{Fe}^{2+}$  concentration, however, was low during the wet season (clay  $2.7 > 0.4$  mg/L and gravel  $2.8 > 0.3$  mg/L). Long-term analysis showed higher fluctuation of nitrogen compounds in the gravel-bearing areas than in the clay-bearing areas.

**Keywords:** shallow groundwater; water quality; seasonal variation; nitrogen contamination; nitrification; soil type

## 1. Introduction

Both developed and developing countries are experiencing serious issues due to anthropogenic groundwater contamination and recharge through leakage into the water supply network, municipal sewage, and onsite waste disposal [1–4]. These concerns are more severe in areas in which groundwater is the primary source of fresh water [5,6], as well as in the densely populated areas of developing countries due to improper infrastructure [7–9]. The groundwater beneath such areas may contain various organic and inorganic compounds that readily affect the groundwater environment [10,11].

Among the numerous chemical and biological contaminants of groundwater, there is growing concern regarding the fate and transformation of nitrogen contaminants in groundwater [2,5,6]. Since nitrogen derived from agricultural practices and human waste easily infiltrates into the groundwater system, the groundwater near the surface is more vulnerable to nitrogen contamination.

Individual health risks are higher due to the consumption of drinking water contaminated with mineralized nitrogen (nitrate) [6]. Long-term exposure to excess nitrate in drinking water induces methemoglobinemia in infants and may cause thyroid diseases, collateral cancer, neural tube defects, and even hypertension [12,13]. Although natural purification of groundwater contamination occurs from natural filtration, absorption, chemical equilibrium, microbial degradation, and dispersion [14] once nitrogen compounds enter the groundwater system; their residence periods in the subsurface depend on the leaching of nitrogen through various soil types [15,16] and transformation processes [14].

Asian cities are more substantially dependent than cities on other continents on groundwater sources even though they are contaminated with anthropogenic pollutants [17]. Umezawa et al. [5] compared the nitrogen pollution levels of the extensively used groundwater of three megacities in Asia—Bangkok, Manila, and Jakarta—where nitrogen compounds are contributed by anthropogenic sources depending upon the land use pattern. In the same study, although geological differences were mentioned, the combined effects of the soil type and season on the nitrogen levels were not included. In South Asia, the cities in Kathmandu Valley constitute one of the fastest growing urban sectors [18]. This area also has a long history of using shallow groundwater as a primary source of drinking water. The people in this valley currently extract groundwater from 38,634 shallow (dug and tube wells) sources [19]. The shortage of municipal water supply and the low cost of constructing shallow groundwater sources are the main reasons for the increase in such sources [20]. However, people in this area unknowingly choose poorer quality of drinking water from groundwater sources depending upon the taste i.e., related with iron contamination than the actual nitrate and other microbial contamination [21]. Meanwhile, long-term deterioration of groundwater quality is continuously being reported in this area, based on both chemical indicators [22–25] and microbiological indicators [21,26,27], where shallow dug wells are found to be more highly contaminated than other groundwater sources [23]. Furthermore, numerous studies have highlighted the severity of the nitrogen contamination in Kathmandu Valley [21,28–30]. Although the status of nitrogen contamination was reported previously, continuous monitoring of nitrogen contamination in groundwater is important to reveal the current conditions with respect to the growing population. Regardless of the contamination distribution, the availability of nitrogen compounds depends upon the redox processes in groundwater [7]. Rainfall also controls the redox processes in unsaturated zones by introducing dissolved oxygen during its infiltration. The rainfall infiltration, however, depends upon the soil type and the hydraulic properties of the aquifer. Important gaps remain in understanding the nitrogen contamination in the shallow groundwater of Kathmandu Valley. To the knowledge of the authors, the seasonal variations of nitrogen compound contamination considering the shallow subsurface soil type in this groundwater basin have not yet been reported.

In this study, long-term spatial and temporal data of the shallow groundwater were employed to identify the nitrogen contamination status in Kathmandu Valley. Based on this information, this paper presents the spatial distribution of the nitrogen contamination and temporal effects regarding the persistence of nitrogen with respect to the spatial distribution of the subsurface soil types in Kathmandu Valley. This study also utilizes the results of nitrogen compound concentration and isotope ratio in determining the prevalent nitrogen dynamics (nitrification) in this study area and provides the scientific basis in predicting the health risk of the people.

## 2. Methods

### 2.1. Study Area

Kathmandu Valley, which was the area investigated in this study, is an amphitheater-shaped basin surrounded by mountains reaching heights of over 2000 m on all sides. It lies in the midland of the Himalayas and covers an area of 650 km<sup>2</sup>. The valley basin is filled with fluvio-lacustrine deposits of Quaternary to Pleistocene sediments. They are composed mainly of unconsolidated clay, silt, sand, and gravel [31,32] and are separated into shallow (0–60 m depth) and deep (>60 m depth) groundwater systems [33]. The groundwater is recharged by the direct infiltration of rainfall [34]. The average

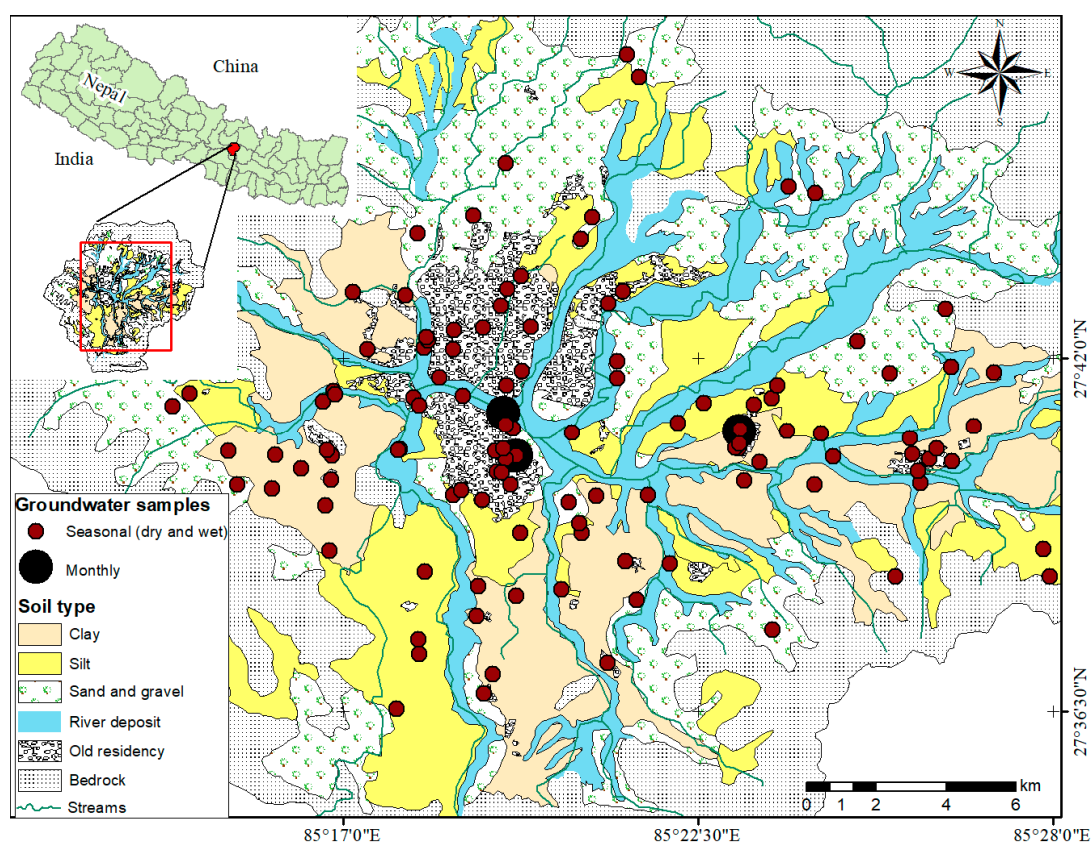
rainfall ranges from 1500 mm (in the city) to 1800 mm (in the surrounding hills) [35]. Of the total rainfall, 75% occurs during the monsoon (wet) season (June–September), 20% during the pre-monsoon season (March–May), and the rest during the post-monsoon (dry) season (October–February) [36].

The study area includes the capital city of Nepal, which is one of the major developing urban centers. The population of the valley is 2.5 million [19]. Currently, the potable water demand of the valley reaches 415 million liters per day (MLD), where the sole institutional drinking water supplier, Kathmandu Upatyaka Khanepani Limited (KUKL), supplies 123.6 MLD of the water during the wet season and 90.8 MLD during the dry season [37]. The drinking water deficit is then covered by tapping groundwater and spring water, utilizing traditional stone spouts, and purchasing water (jars, tankers) from private water vendors [35,38]. The extracted groundwater is consumed mostly for drinking and domestic purposes [27].

## 2.2. Water Sampling and Data Collection

A groundwater field survey was conducted to assess the spatial and temporal variations of nitrogen during two seasons, the dry (February–March) and wet (August–September) seasons of 2016. The groundwater samples were collected from easily accessible shallow dug wells with depths less than 20 m. In total, 182 samples, including 97 from the dry season and 85 from the wet season, were collected from the same locations (Figure 1). Samples from two shallow groundwater locations in Chyasaal and Thimi were collected from March 2017 to October 2018 and June 2017 to October 2018, respectively. The chemical data obtained in consecutive months were then averaged in 1-month intervals. In addition, deep groundwater samples were also collected monthly from Jwagal from June 2016 to October 2018 for long-term analysis. The water samples were collected using 100 mL polyethylene bottles, which were stored under  $-4^{\circ}\text{C}$  before analysis. No preservatives were used to preserve the samples. The water table depth of each sampled well was measured using a set of sensor and data logger.

Three years of daily rainfall data for the valley were obtained from the Global Historical Climatology Network-Daily [39]. To compare the monthly chemical concentrations in the groundwater, the daily rainfall data obtained were averaged monthly.



**Figure 1.** Spatial distribution of groundwater samples collected in both the dry and wet seasons. The background represents the shallow subsurface soil (after Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) [31], 1998).

### 2.3. Measurement Equipment

The collected samples were transported to the Interdisciplinary Centre for River Basin Environment, University of Yamanashi.  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  concentrations were measured using an ion chromatograph (ICS-1100, Dionex, Waltham, MA, USA) with an analytical error of  $\pm 5\%$ .  $\text{Fe}^{2+}$  concentration was measured using an inductively coupled plasma optical emission spectrometer (HORIBA, Ultima-2, KandaAwaji-cho, Chiyoda-ku, Japan) with an analytical error of  $\pm 5\%$ . The nitrogen and oxygen stable isotope ratios in nitrate were determined using the denitrifier method [40,41], using continuous-flow mass spectrometer (xHydra20-20, Sercon, Crewe, Cheshire, UK). The ratios of  $^{15}\text{N}:^{14}\text{N}$  and  $^{18}\text{O}:^{16}\text{O}$  were expressed relative to atmospheric nitrogen for nitrogen and relative to Vienna Standard Mean Ocean Water (V-SMOW) for oxygen; these ratios were calculated as from Equation (1):

$$\delta^{15}\text{N}, \delta^{18}\text{O} = \{R(\text{sample})/R(\text{standard}) - 1\} \times 1000 (\text{‰}), \quad (1)$$

where  $R = ^{15}\text{N}/^{14}\text{N}$  or  $^{18}\text{O}/^{16}\text{O}$ . The isotope values were calibrated using international standard materials (IAEA-N3, USGS34, and USGS 35), which were analyzed along with each batch of samples. The standard deviations of isotope determination for the water samples were  $\pm 0.2\text{‰}$  for  $\delta^{15}\text{N}$  measurements and  $\pm 0.3\text{‰}$  for  $\delta^{18}\text{O}$  measurements.

### 2.4. Statistical Analysis

The groundwater samples collected were classified as originating from clay and gravel and were analyzed accordingly. The classification was performed by referring to the barrier potential map of sediments in Kathmandu Valley. BGR [31] classified the soil as clay, silt, sand, or gravel (Figure 1); however, only two categories (clay and gravel) were used in this study due to the limited number

of samples and their statistical significance. High and moderate barrier potential areas (i.e., those consisting of clay and silt with a cation exchange capacity (CEC) >12 mmol<sub>c</sub>/100 g soil/sediment) were categorized as clay, while those with low barrier potentials (i.e., the areas containing sand, gravel, and silt with CEC <12 mmol<sub>c</sub>/100 g soil/sediment) were categorized as gravel. The nearby lithologies were referred to classify the sampled locations in case the subsurface information from the map was unclear, especially in the old residency area. An individual sample t-test was then performed to compare the soil type (clay and gravel) and temporal distribution (dry and wet). Furthermore, samples exceeding the inter-quartile range of 1.5 in each parameter were excluded from the calculations of the observed significance level (p-value). The p-value was taken as 0.05 in this study. The statistical analysis was performed using the Statistical Package for Social Studies version 20 (SPSS Inc., Chicago, IL, USA).

### 3. Results

#### 3.1. Spatial and Temporal Overview of Chemical Parameters

The statistical values for the water table level and chemical parameters collected from the shallow groundwater are presented in Table 1 which is then compared with Nepal Drinking Water Quality Standard (NDWQS). Since the drinking water quality standards are set depending upon nation or local environmental, culture and socio-economic factors, the standards are compared with cross country standards. NDWQS limit of Fe<sup>2+</sup> 0.3 mg/L and Cl<sup>-</sup> 250 mg/L are similar to the standards mentioned by World Health Organization (WHO) standard, US Environmental Protection Act (USEPA), and Indian Standard Specifications for Drinking Water. The desirable limits of NO<sub>3</sub>-N 11.2 mg-N/L in NDWQS is higher than the standard set by WHO, USEPA and Indian standard of 10 mg-N/L for NO<sub>3</sub>-N. No standards for NH<sub>4</sub>-N is set in USEPA and Indian Standards, however, the standard set by WHO for NH<sub>4</sub>-N 1.1 mg-N/L is slightly less than NDWQS of 1.2 mg-N/L. The spatial distributions of the nitrogen compounds (NO<sub>3</sub>-N, and NH<sub>4</sub>-N) and Fe<sup>2+</sup> along with the drinking water standard limit from NDWQS are shown in Figure 2. No clear indications of clustering among the respective parameters are observable within the neighboring wells (Figure 2), showing the point source contamination.

**Table 1.** Descriptive statistics of water table level and chemical concentrations collected from shallow dug wells.

Categories	Season	Dry		Wet		
		Soil Type	Clay	Gravel	Clay	Gravel
Parameters	Water table (m)	Min.	-0.7	-1.1	-0.2	-0.2
		Max.	-12.3	-13.4	-11.8	-8.6
		Average	-4.8	-4.2	-2.7	-2.4
	Cl <sup>-</sup> (mg/L)	Min.	2.3	3	3.3	2.2
		Max.	173.7	204.1	163.6	198.8
		Average	59.5	57.6	66.5	56.1
	NH <sub>4</sub> -N (mg-N/L)	Min.	nd.	nd.	nd.	nd.
		Max.	5.6	11.4	4.9	3.6
		Average	1	1.8	0.9	0.6
		% Exceeding Std. (NDWQS = 1.2)	29.8	40	27.3	16.1
	NO <sub>3</sub> -N (mg-N/L)	Min.	nd.	nd.	nd.	nd.
		Max.	27.6	13.4	60.3	21.6
		Average	4.9	2.5	13.6	6.8
		% Exceeding Std. (NDWQS = 11.2)	14.3	5.9	36.4	19.4
	Fe <sup>2+</sup> (mg/L)	Min.	0.02	0.03	0.02	0.03
Max.		13.3	18.3	2	1.9	
Average		2.7	2.8	0.4	0.3	
% Exceeding Std. (NDWQS = 0.3)		76.3	62.9	34	25	

(nd. = not detected, Std. = Standard NDWQS = Nepal Drinking Water Quality Standard).

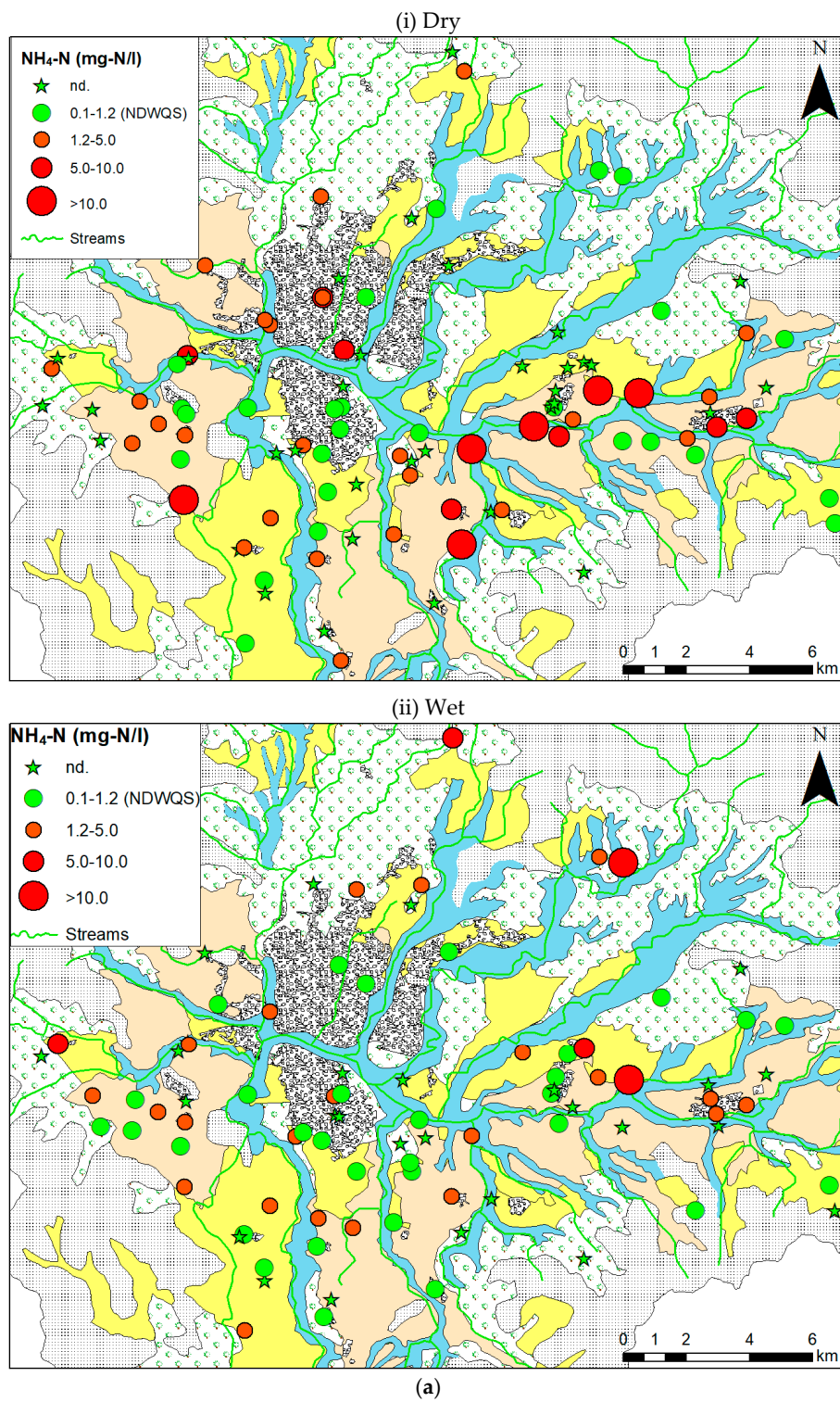
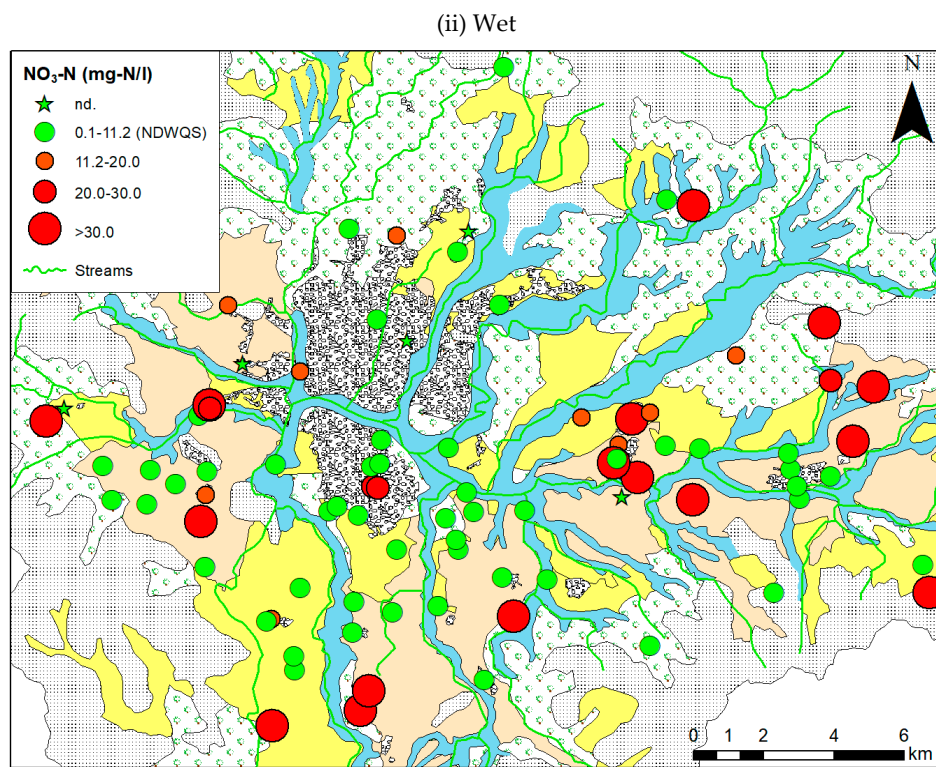
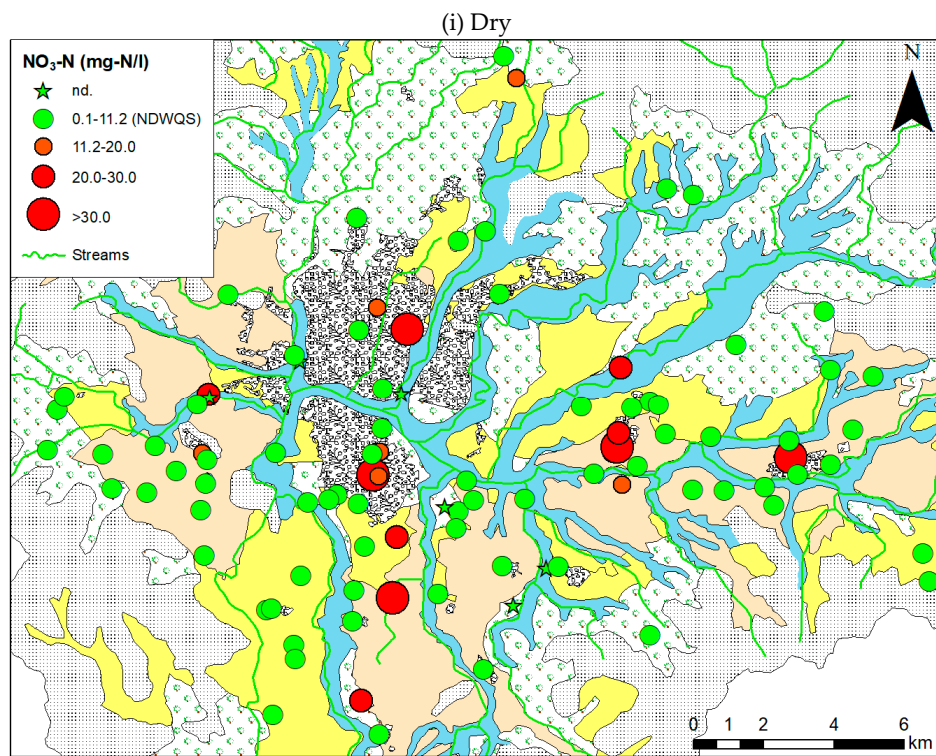
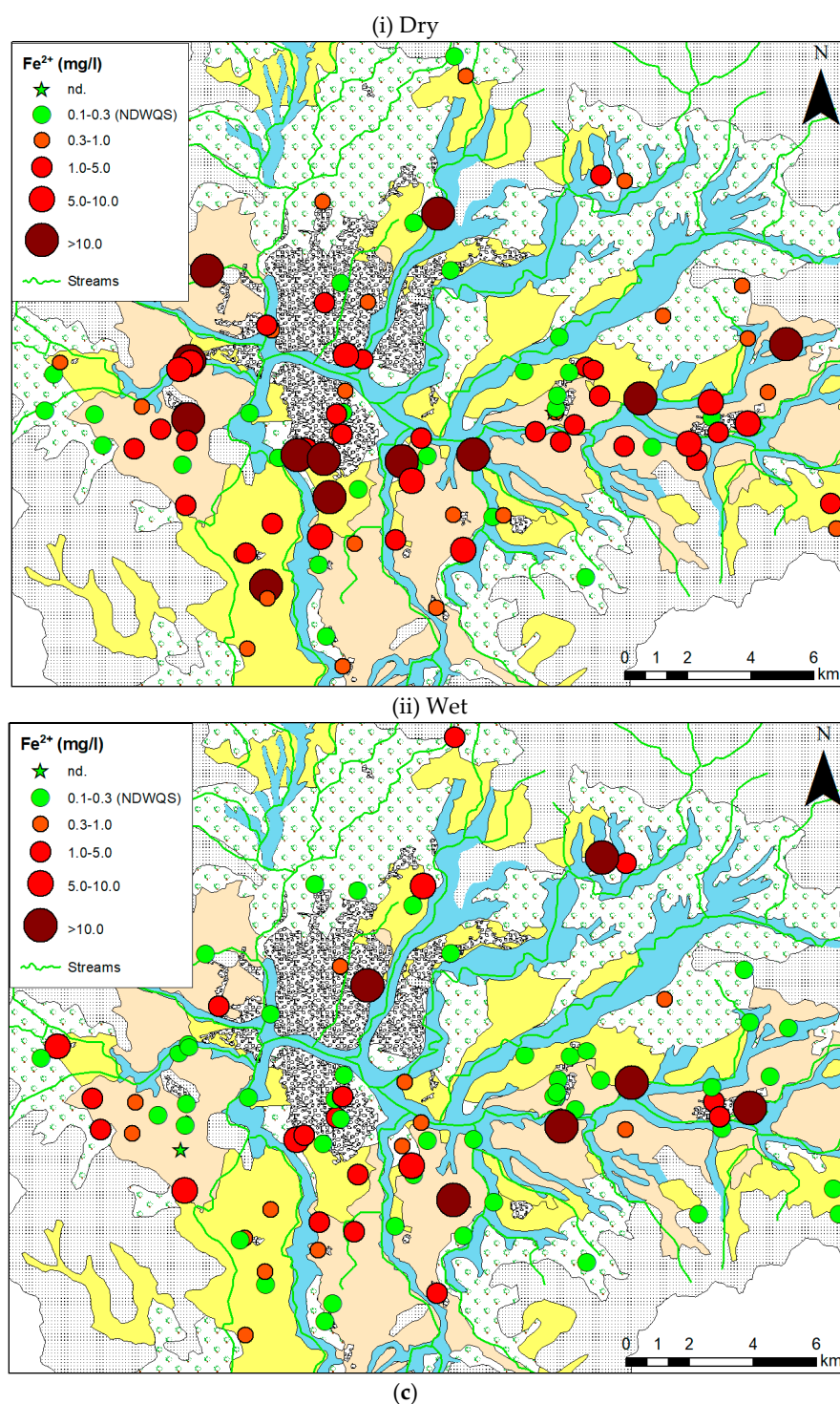


Figure 2. Cont.



(b)

Figure 2. Cont.



**Figure 2.** Spatial distributions of chemical concentrations from the sampled shallow dug wells in Kathmandu Valley: (a)  $\text{NH}_4\text{-N}$  (mg-N/L), (b)  $\text{NO}_3\text{-N}$  (mg-N/L), and (c)  $\text{Fe}^{2+}$  (mg/L).

The water table level range do not differ significantly between the clay and gravel in either the dry or wet season. The descriptive statistics (Table 1) and statistical comparison of water table levels (Figure 3a) show that the water table level in the Kathmandu Valley increases significantly during the wet season. Similarly, no categorical or temporal variations of the  $\text{Cl}^-$  concentrations between soil types are evident (Figure 3b). Statistical comparisons of the  $\text{NH}_4\text{-N}$  concentrations in the two major soil categories in the dry and wet seasons of the Kathmandu Valley are presented in Table 1 and



Figure 3c. The gravel aquifers have a higher average  $\text{NH}_4\text{-N}$  concentration (1.8 mg-N/L) than clay (1 mg-N/L) in the dry season. In the same season, 40% of shallow dug wells sampled in gravel and 29.8% in clay exceed the National Drinking Water Quality Standard (NDWQS). In the wet season, the average  $\text{NH}_4\text{-N}$  concentration in gravel (0.6 mg-N/L) is less than that of clay (0.9 mg-N/L) (Table 1). Similarly, only 16% of the shallow dug wells in gravel-bearing areas exceed the NDWQS, while 27.3% of those in clay areas exceed this standard (Table 1). Statistically, no significant difference in  $\text{NH}_4\text{-N}$  concentrations is observable between the clay and gravel areas in the dry ( $p = 0.1$ ) or wet ( $p = 0.3$ ) season (Figure 3c). With a p-value of 0.6, the  $\text{NH}_4\text{-N}$  concentrations in clay are similar temporally; however, temporal variations are evident in the gravel-bearing areas ( $p = 0.02$ ). On the contrary, the average  $\text{NO}_3\text{-N}$  concentration is increased in the wet season compared to that in the dry season in both soil categories (Figure 3d). The clay- and gravel-bearing areas differ significantly from each other in both seasons. Similarly, 14.3% of the shallow dug wells in clay and 5.9% of those in gravel exceed the NDWQS in the dry season, while 36.4% of those in clay and 19.4% of those in gravel do so in the wet season. These results show that the degree of  $\text{NH}_4\text{-N}$  pollution is less than the magnitude of  $\text{NO}_3\text{-N}$  pollution in the wet season. The temporal fluctuations of the  $\text{NO}_3\text{-N}$  concentration are larger than those of the  $\text{NH}_4\text{-N}$  concentration in both soil types. In contrast to the other parameters, the  $\text{Fe}^{2+}$  concentration shows a greater reduction in the wet season (Table 1). In the dry season, 76.3% of the shallow dug wells in clay-bearing areas and 62.9% of those in gravel exceed the NDWQS. These percentages decrease to 34% in clay- and 25% in gravel-bearing areas in the wet season. A student t-test of the  $\text{Fe}^{2+}$  concentration revealed that its variations in clay and gravel are alike (Figure 3e).

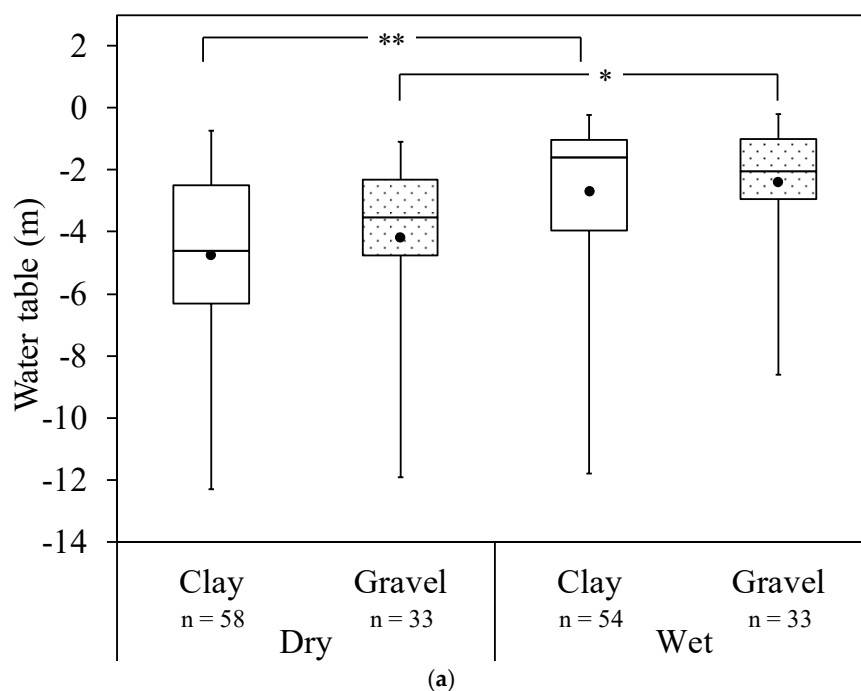


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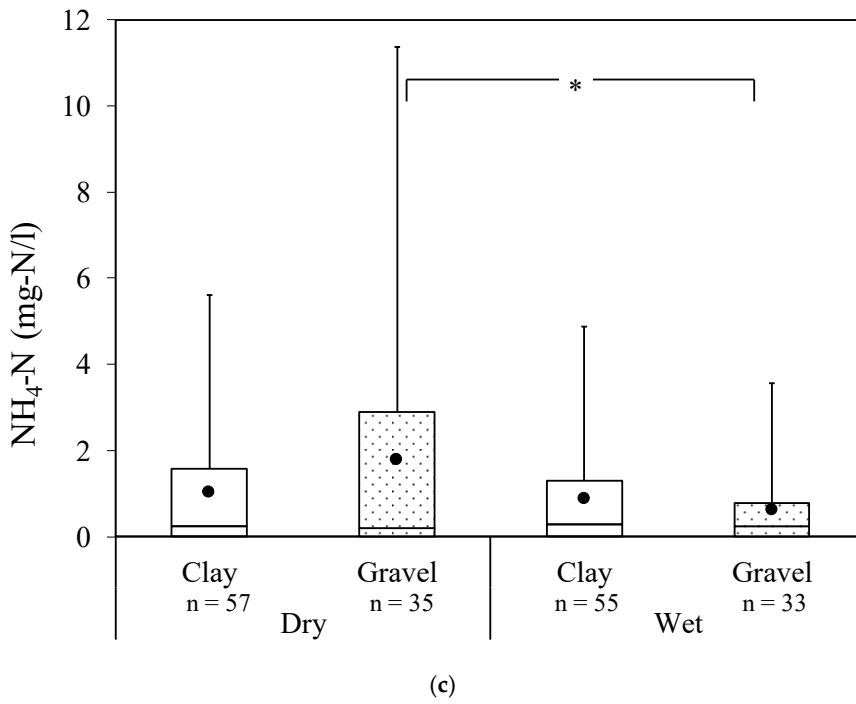
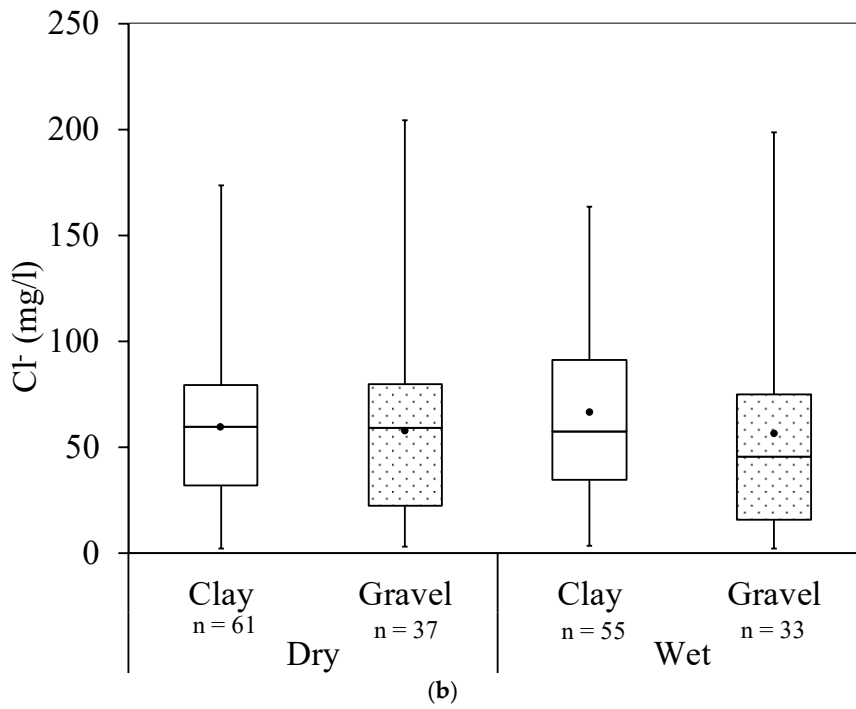
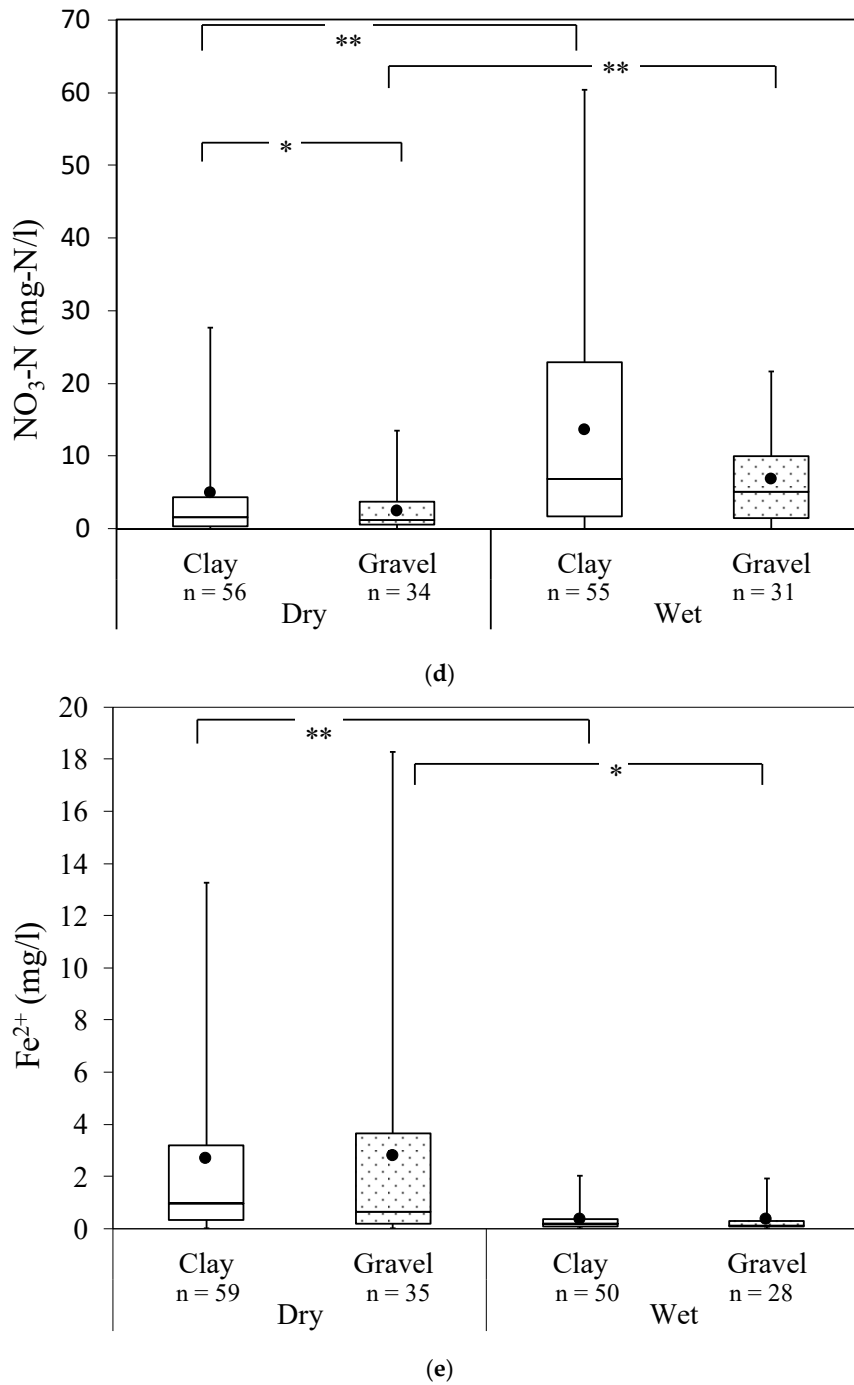


Figure 3. Cont.



**Figure 3.** Graphical representation of (a) water table level and (b) Cl<sup>-</sup> (mg/L), (c) NH<sub>4</sub>-N (mg-N/L), (d) NO<sub>3</sub>-N (mg-N/L), and (e) Fe<sup>2+</sup> (mg/L) concentration. Each whisker represents inter-quartile ranges up to 1.5; the dots represent average concentrations; the lines above and below the boxes represent the 90th and 10th percentile values, respectively. (\*) and (\*\*) above boxes represent observed significance levels (p-values) less than 0.05 and 0.01, respectively.

### 3.2. Site-Specific Nitrogen in Gravel and Clay-Dominated Areas

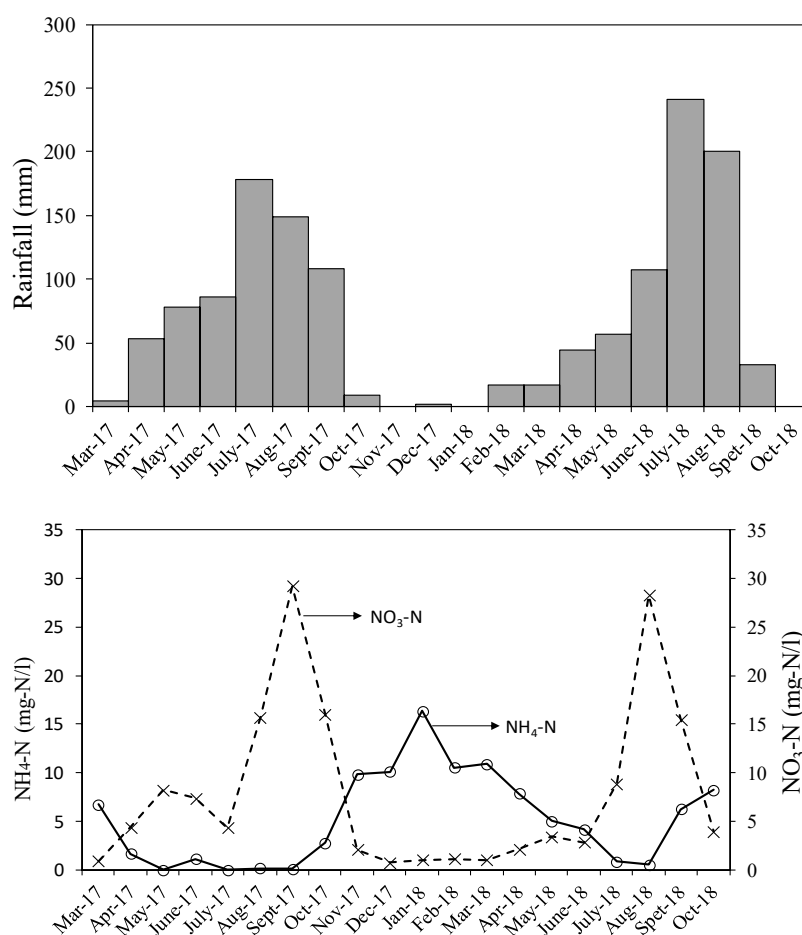
The fluctuations of the nitrogen compound concentrations in the two types of soil show various dynamics. To examine these fluctuations in detail, the monthly variations of the nitrogen compounds in the clay- and gravel-bearing areas were analyzed. The monthly nitrogen compound (NH<sub>4</sub>-N and NO<sub>3</sub>-N) data from two locations (Chyasal and Thimi) were used to identify the mechanism of nitrogen variation in shallow groundwater. Table 2 summarizes the statistical variations of the samples

collected monthly from these two locations. Figure 4a shows the trend lines of the NH<sub>4</sub>-N and NO<sub>3</sub>-N observations obtained from the shallow groundwater at Chyasal. Over the 20 months of observations, the NH<sub>4</sub>-N concentration is high (16 mg-N/L) during the dry season, whereas that of NO<sub>3</sub>-N is less than 5 mg-N/L during the same period. These results indicate the accumulation of NH<sub>4</sub>-N during the dry season. The inverse relationship between the nitrogen compounds during the dry and wet seasons suggests the site-specific nitrification of NH<sub>4</sub>-N into NO<sub>3</sub>-N and indicates effect of multiple factors rainfall, nitrogen loading etc. The spike in the NO<sub>3</sub>-N concentration even with the small rainfall increment in May and June shows the effect of rainfall in this gravel-bearing area.

**Table 2.** Statistical variations of the monthly samples collected from shallow groundwater (Chyasal and Thimi) and deep groundwater (Jwagal).

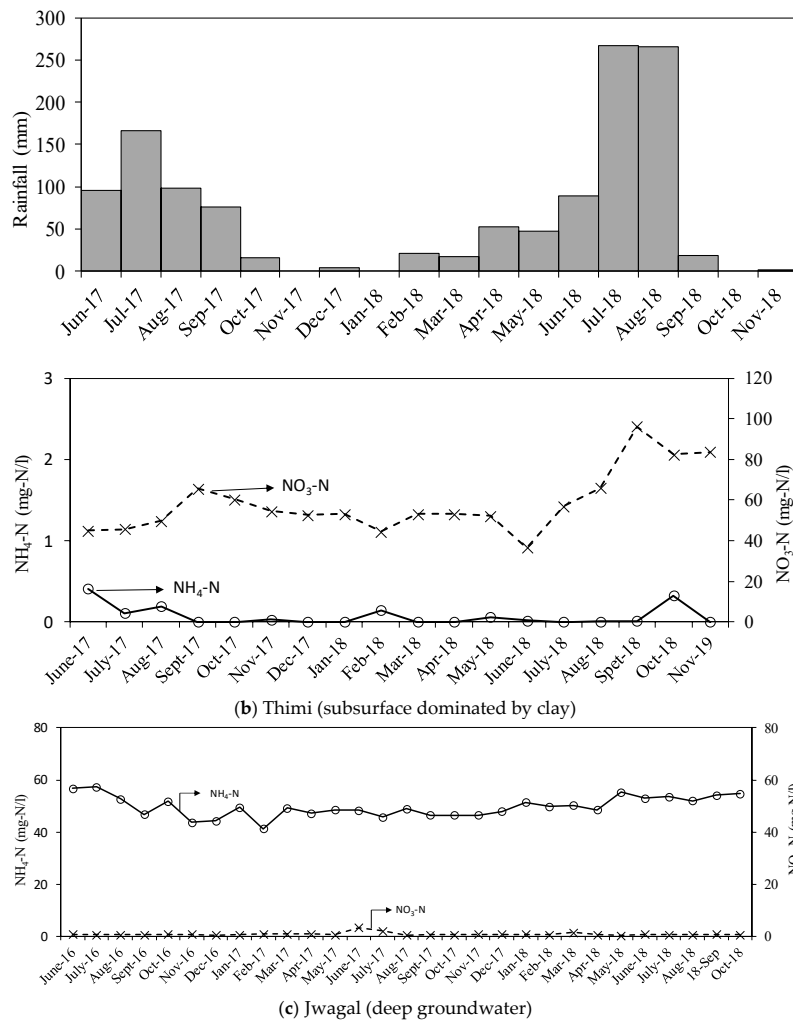
Location	NH <sub>4</sub> -N (mg-N/L)		NO <sub>3</sub> -N (mg-N/L)		Total Months Observed
	Min	Max	Min	Max	
Chyasal	nd.	16.3	0.7	16	20
Thimi	nd.	0.4	36.5	96.2	18
Jwagal	41.2	57.3	0.4	3.4	29

nd. = not detected.



(a) Chyasal (subsurface dominated by gravel)

**Figure 4.** Cont.



**Figure 4.** Monthly concentration variations in shallow groundwater from (a) Chyusal and (b) Thimi and (c) in deep groundwater from Jwagal compared with the rainfall data of the areas.

The shallow groundwater from the old town of Thimi, which is dominated by clay, revealed a different nitrogen compound concentration scenario during the 18 months of regular observations. Figure 4b depicts the monthly variations of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$ . The  $\text{NH}_4\text{-N}$  concentration shows a constant trend line in the range of 0.5 mg-N/L throughout the observation period. No strong seasonal effect in the variation of the  $\text{NH}_4\text{-N}$  concentration is observable. On the other hand,  $\text{NO}_3\text{-N}$  shows a higher concentration in Thimi than in Chyusal, ranging from 37 to 99 mg-N/L. The  $\text{NO}_3\text{-N}$  concentration exhibits seasonal effect with an increasing trend during the wet season, as shown in Figure 4b. The results also reveal a lag time in the  $\text{NO}_3\text{-N}$  increase during the wet season of nearly 1 month in clay. The dominance of the  $\text{NO}_3\text{-N}$  concentration and negligible  $\text{NH}_4\text{-N}$  concentration in this area suggest rapid nitrification at the surface and the addition of  $\text{NO}_3\text{-N}$  from surface leaching, which is greater during the wet season.

Monthly data obtained from deep groundwater were also used for comparison to determine whether or not the seasonal variations of the nitrogen compounds persisted. Figure 4c presents the observed nitrogen compound data for 29 months. Unlike shallow groundwater, deep groundwater shows contrasting nitrogen abundance.  $\text{NH}_4\text{-N}$  has an almost constant trend line throughout the observation period within the range of 41.2–57.3 mg-N/L. Meanwhile,  $\text{NO}_3\text{-N}$  is nearly absent or negligible, unlike in the shallow groundwater from Chyusal and Thimi. Thus, the shallow groundwater responded well to rainfall, with the  $\text{NH}_4\text{-N}$  concentration decreasing and the  $\text{NO}_3\text{-N}$  concentration

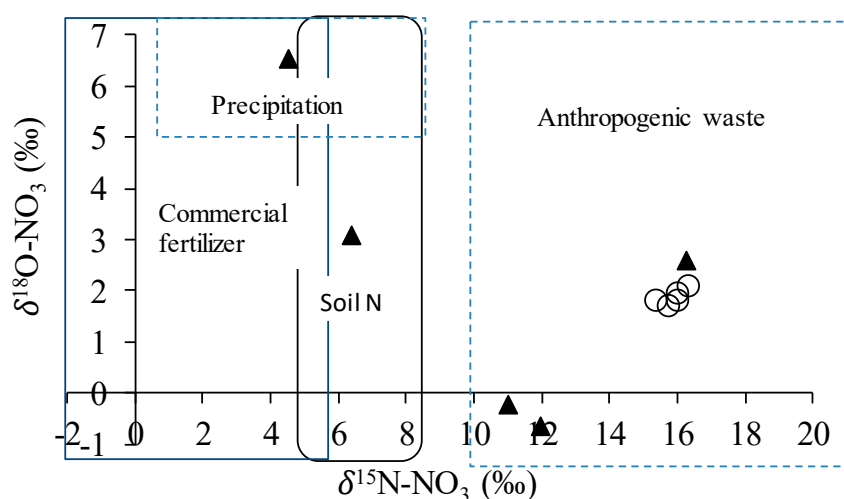
increasing during the wet season, mostly because of the loading from surface and nitrification of  $\text{NH}_4\text{-N}$ .

### 3.3. Monthly Nitrogen Isotope Variation

Table 3 shows the nitrogen isotope distributions from the nitrate in Chyasal and Thimi. Unfortunately, the samples from the dry season in Chyasal were not sufficient for the analysis; thus, the samples from the wet season, i.e., the pre-monsoon and monsoon periods, were used (Figure 5). In Chyasal,  $\delta^{15}\text{N-NO}_3$  varies from 4.5‰ to 16.3‰ and  $\delta^{18}\text{O-NO}_3$  varies from  $-0.7$ ‰ to 6.52‰. The isotopic variations are smaller in Thimi, where  $\delta^{15}\text{N-NO}_3$  varies from 15.4‰ to 16.4‰ and  $\delta^{18}\text{O-NO}_3$  varies from 1.7‰ to 2.0‰. The effect of seasonality is more clearly observed in the isotope distribution of the gravel-bearing area (i.e., Chyasal) than in that of the clay-bearing area (i.e., Thimi).

**Table 3.** Distributions of stable isotopes of oxygen and nitrogen from nitrate in Chyasal and Thimi.

Location	$\delta^{15}\text{N-NO}_3$ (‰)		$\delta^{18}\text{O-NO}_3$ (‰)	
	Min	Max	Min	Max
Chyasal	4.5	16.3	$-0.7$	6.52
Thimi	15.4	16.4	1.7	2



**Figure 5.** Stable oxygen and nitrogen isotope compositions for identifying the source and process of nitrate contamination from samples collected monthly from Chyasal (triangles) and Thimi (circles).

## 4. Discussion

### 4.1. Effects of Rainfall

The groundwater level varies between the dry and wet seasons, where the water level is high and near the ground surface during the wet season. Consequently, dilution after rainfall is also an important mechanism of the attenuation of contamination in aquifer systems [42]. According to Lasagna et al. [43], the dilution potential is independent of the chemical conditions which are mostly dominated by the volumetric flow. The specific parameters (hydraulic conductivity, hydraulic gradient, and thickness) of the aquifer are responsible for the volumetric flow. Thus, the dilution of groundwater contaminants can generally be expected with increased rainfall and a higher water table. However, some studies reported fluctuation of the chemical distribution during the rainfall [6,44]. The study by Gao et al. [6] showed the increment of  $\text{NO}_3\text{-N}$  during rainfall caused by infiltration of irrigation return flow and septic leakage. In this context, a study stated the risk of diarrhea among children below 5 years during the 10 mm increase of rainfall in the Kathmandu valley [45] stating the risk in human health during rainfall. This shows that, although the rainfall has a tendency to dilute the chemical

contamination, comparison of the difference of various chemical and nitrogen parameters during dry and wet season shows the negative effects on the dilution during the wet season.

Prior to the study by Shrestha et al. [46], in Kathmandu valley, the concentrations of  $\text{Cl}^-$ ,  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  in rainwater were found to be 1.5 mg/L, 1.6 mg-N/L and 0.06 mg-N/L which are quite low compared to sampled groundwater. As shown in Figure 6, the higher concentration of the chemical parameters than rainfall might be from the agriculture return [6,47,48], surface water interaction [44] and the subsurface processes explained in the following section.

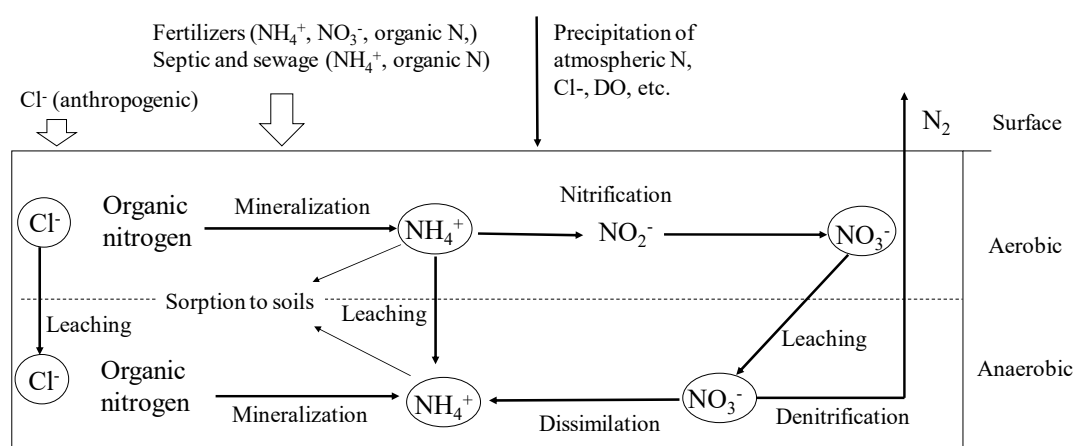
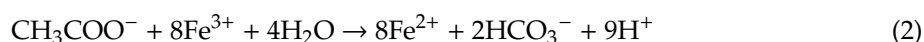


Figure 6. Schematic diagram of  $\text{Cl}^-$  leaching and Nitrogen dynamics under sub-surface.

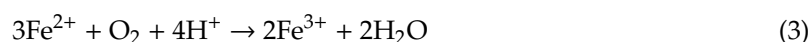
#### 4.2. Redox Environment

Redox condition in an aquifer is related with the groundwater residence time [49]. Basically, rainwater infiltration introduces oxic water into the groundwater with changes in Oxidation reduction potential (ORP) [44], thereby enhancing the initial oxygen level of shallow groundwater. An increased water table height in a wet season most likely increases the amount of dissolved oxygen in the groundwater carried by precipitation. On the other hand, a higher concentration of dissolved  $\text{Fe}^{2+}$  reflects the reducing condition of the groundwater [7] which is likely to be affected by the dominance of heterotrophic (in presence of carbon) and chemolithoautotrophic reactions (Equations (2) and (3)) [44]. The presence of  $\text{Fe}^{2+}$  in both the clay- and gravel-bearing areas in this study shows the prevalence of a reducing environment followed by the residence time during the dry season. The deduction in the chemical concentration of dissolved  $\text{Fe}^{2+}$  during the wet season indicates the effects of dilution and changes in the oxidation state of groundwater after rainwater infiltration. These reactions also show the increase in the hydrogen ions (pH) essential for other chemical reactions explained in the following sections.

Heterotrophic reaction



Chemolithoautotrophic reaction



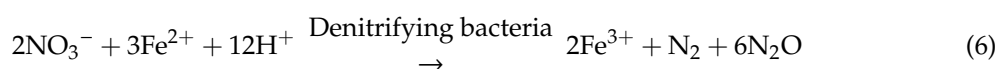
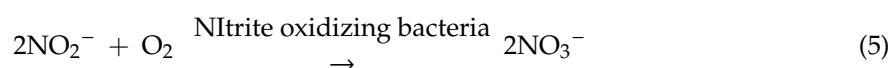
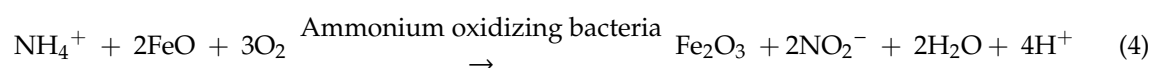
#### 4.3. Chemical Contamination in Groundwater

$\text{Cl}^-$  in groundwater is the least sorbed anion that is unaffected by microbial activity. The original  $\text{Cl}^-$  concentration in the groundwater is from precipitation, rock mineral dissolution and evaporation [50], agricultural and municipal wastewater [51], or both. In case of the Kathmandu valley, no halite deposition is ever reported as a  $\text{Cl}^-$  source anthropogenic contamination [52]. The average  $\text{Cl}^-$  concentration in groundwater is found to be nearly 40 times higher than in rainwater with

concentration (1.5 mg/L) [46], 120 times than spring water (0.55 mg/L) and 37 times higher than deep groundwater (4.7 mg/L) [34]. Similar results were also reported in the aquifers overlain by areas with on-site sanitation and unmanaged wastewater system [7]. Despite the dilution mechanism during the rainy season explained by Todd and Mays [42], the fact that the average  $\text{Cl}^-$  concentration during the wet season is similar to that during the dry season, indicates the infiltration of  $\text{Cl}^-$  from unsaturated soil. Although the velocity of groundwater varies between clay and gravel and from well to well, the consistency of the  $\text{Cl}^-$  concentration in the shallow groundwater of the study area suggests a continuous pollution load throughout the year from anthropogenic activities than from precipitation and rock mineral dissolution.

#### 4.4. Factors Controlling $\text{NH}_4\text{-N}$ in Shallow Groundwater

The results of this study indicate that the nitrogen compounds in groundwater are dependent upon rainfall and the in situ environment. An inverse relationship between  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  was observed in the shallow groundwater in the long-term analysis and in both soil types. The effects of nitrogen are influenced by the soil characteristics [16]. Generally, gravel has higher permeability and hydraulic conductivity and lower sorption than clay, for the lower retention time of contamination. After entering the groundwater,  $\text{NH}_4\text{-N}$  becomes attached to negatively charged clay particles [53,54] (Figure 6), transforms into  $\text{NO}_3\text{-N}$  due to chemical and microbial nitrification, and ultimately transforms to nitrogen gas via microbial denitrification (Equations (4) and (5)). Although these processes co-exist, the individual rate depends upon the sub-surface environment and materials. The concentration of  $\text{NH}_4\text{-N}$  in gravel bearing aquifers differed seasonally ( $p < 0.02$ ) (Figure 3b). The monthly variation data also revealed a  $\text{NH}_4\text{-N}$  plume during the dry season. A similar result of high  $\text{NH}_4\text{-N}$  was also reported by Sbarbati et al. [55], where they suggested the rapid and continuous loading of organic matter (natural or artificial) without sufficient retention time later transformed into  $\text{NH}_4\text{-N}$  by microbial oxidation. According to the study, the lack of rehabilitation of leaky sewer pipes, continual use of pit latrines, and improper construction of septic tanks [56] might be the major causes contamination in the Kathmandu valley. On the other hand, the lower  $\text{NH}_4\text{-N}$  concentration during the wet season, however, could be due to the oxidation of  $\text{NH}_4\text{-N}$  from the oxygen-enriched infiltration activated by oxidized  $\text{Fe}^{2+}$  and nitrifying bacteria (Equations (4) and (5)). In addition,  $\text{NH}_4\text{-N}$  can be reduced due to the dispersion process occurring because of the rise in the water table. The obtained result in the gravel bearing area can be mirrored with the change in redox condition due to surface water intrusion in the subsurface layer. Consequently, in an unsaturated zone, the percolated effluent contributes the increase in nitrogen by nitrification up to 50%–70% followed by 16%–19% of ammonification [14]. Basically, more nitrification occurs in areas with sufficient oxygen access, whereas ammonification occurs in areas with oxygen deficiency [14,57]. This evidence shows that  $\text{NH}_4\text{-N}$  during the dry season is due to the mineralization of organic matter, especially due to the contamination loading and anaerobic environment shown by the  $\text{Fe}^{2+}$  enrichment. In contrast, lower  $\text{NH}_4\text{-N}$  during the wet season is mostly due to oxidation which is also supported by decrease in  $\text{Fe}^{2+}$  concentration clarified from Equation (3) and nitrification of  $\text{NH}_4\text{-N}$ . These can be made clearer from the following equations.



Although the water table is also higher in the clay-bearing area than in the gravel-bearing area (Table 1), the similarity between the  $\text{NH}_4\text{-N}$  levels in the clay-bearing area ( $p > 0.05$ ) during the dry



and wet seasons is controlled by its hydraulic conductivity. The higher sorption in clay material delays the transport of  $\text{NH}_4\text{-N}$  in the clay-bearing area. The diffusion of oxygen in clay is slower than that in gravel causing higher chances of reduced environment [58]. Also, the presence of humic acid in the soil increases the nitrification delay in groundwater [59]. The aquifer material in the study area has been reported to be rich in naturally deposited organic matter [60], which is associated with humic clay [30]. This characteristic seems to be the primary factor controlling the dominance of nitrogen compounds in the clay-bearing area. Also, nitrification decreases the pH with the involvement of  $\text{Fe}^{2+}$  and oxygen, nitrification in dry season might get slowed down [61]. This finding implies that the  $\text{NH}_4\text{-N}$  that is formed naturally or intruded anthropogenically is sorbed by clay material, which seems to be retained in both the dry and wet seasons and for longer periods of times than in a gravel.

#### 4.5. Factors Controlling $\text{NO}_3\text{-N}$ in Shallow Groundwater

The concentration of  $\text{NO}_3\text{-N}$  collected spatially was found to be higher during the wet season than during the dry season. In addition, the monthly  $\text{NO}_3\text{-N}$  concentrations reached the highest values in August and September, i.e., during the wet season. As the pre-monsoon season (April–May) began, the  $\text{NO}_3\text{-N}$  concentration increases, becoming higher during the monsoon period (Figure 4). In contrast to our results, nitrogen compounds in the northwest of Croatia were found to be reduced during the rainy season [62]. However, the significant increase in  $\text{NO}_3\text{-N}$  during the wet season also contradicts the idea that dilution reduces the contamination. This finding indicates that other mechanisms control the changes in the fate and availability of nitrogen in groundwater of the study area. The higher  $\text{NO}_3\text{-N}$  concentration is attributable to the effects of human impact on the subsurface environment. The leaching of nitrate seems to be lesser during the dry season than the wet season; however, Trudell et al. [63] showed that denitrifying anaerobes in the presence of organic carbon in the soil (minimum range of 0.08%–0.16%) transforms the large amount of  $\text{NO}_3\text{-N}$  into  $\text{N}_2$ . The availability of  $\text{NO}_3\text{-N}$  during the dry season in the reducing environment could be due to denitrification in the presence of  $\text{Fe}^{2+}$  as an electron donor (Equation (6)), also explained by Pathak and Hiratsuka [30], or denitrification by micro-bacteria in the presence of high organic contents in both the clay- and gravel-bearing areas.

The excessive high concentration of  $\text{NO}_3\text{-N}$  rather than  $\text{NH}_4\text{-N}$  in the wet season, provides the insight regarding the various processes in the aquifer system of the studied area.  $\text{NO}_3\text{-N}$  fluctuation varied between gravel- and clay- bearing areas observed in the monthly recorded data. Meanwhile, the variation of  $\text{NO}_3\text{-N}$  in spatially distributed gravel- and clay- bearing areas also corresponded to the similar fluctuation pattern like in monthly recorded data. The excessive increase in  $\text{NO}_3\text{-N}$  (Figure 4a) during the wet season indicates that  $\text{NO}_3\text{-N}$  does not originate entirely from nitrification (Equations (4) and (5)), but rather from other sources as well. The oxidation of  $\text{NH}_4\text{-N}$  due to nitrification process explains the increment of  $\text{NO}_3\text{-N}$  during wet season in Figure 4a. However, the distinctive increment of other remaining  $\text{NO}_3\text{-N}$  in gravel-bearing area, higher than the available  $\text{NH}_4\text{-N}$  is remarkable. A similar increase in  $\text{NO}_3\text{-N}$  was also reported near the leachate [57] and in the study of [55] caused by the rapid groundwater flow carrying  $\text{NO}_3\text{-N}$ . The study [55] also showed that the higher  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  might be due to the mixing from partial nitrification of ammonia and leakage in the sewage pipes. Similarly, the higher levels of  $\text{NO}_3\text{-N}$  were recorded with the excess limit of fertilization in an agricultural area [47]. Furthermore, change in the redox condition by the interaction of oxygenated surface water in changing the nitrification processes in gravel bearing areas near flood plain is well explained by Dwivedi et al. [44]. Various possible phenomenon can be discussed in the increment of  $\text{NO}_3\text{-N}$ , specifically during wet season. Basically,  $\text{NO}_3\text{-N}$  entered into the unsaturated zone are not entirely eliminated during the dry season due to denitrification and it consequently remains there for a certain period of time [43], where the retention time depends upon the permeability and water table level. The groundwater levels during wet season are relatively close to the ground surface which then behaves as a medium in transporting the contaminants in groundwater those were retained in an unsaturated zone especially during wet season. Similar to this study, the fluctuation of  $\text{NO}_3\text{-N}$  can be observed in the area characterized by the local flow system and river water aquifer interacted

area [48]. Additionally, urban flooding during excessive storm period carrying contamination is yet another major problem in this area [64] showing the local flow during wet season. Since,  $\text{NO}_3\text{-N}$  into the groundwater are carried more intensively by the internal and solute movement in soils than surface runoff [6], the higher  $\text{NO}_3\text{-N}$  is possibly due to the loading of leached anthropogenic contamination both from sewage and irrigation return flow.

On the contrary, the  $\text{NO}_3\text{-N}$  contamination in clay-bearing area is greater than  $\text{NH}_4\text{-N}$  as shown in Figure 4b. Nitrification processes in clay-bearing areas might not be fully developed due to the limited  $\text{NH}_4\text{-N}$  occurrence. Since the retention period of contamination depends upon the permeability of the soil material, the dispersion mechanism in clay is slower than that of gravel. Similarly, clay bearing aquifers are limited with dissolved oxygen (DO) than gravel bearing aquifers. This limiting amount of DO prevents nitrification and causes nitrite accumulation [61]. In this context, the higher concentration of  $\text{NO}_3\text{-N}$  is possibly due to the addition of anthropogenic leached contamination during wet season either from the oxidation of septic and sewage leakage or from the agricultural practice which is later accumulated in the clay due to the lack of DO. Bittner [28] reported the existence of a nitrate plume in the study area. The accumulation of  $\text{NO}_3\text{-N}$  in clay-bearing areas than in gravel-bearing areas is relatable with the permeability of the soil properties as well. From all these, it can be attributed that the nitrification and surface loading during wet season are more prevalent than the dilution of chemical concentration along with the constant contamination load throughout the year, which are the major attributable reason in the higher  $\text{NO}_3\text{-N}$  in this study area.

#### 4.6. Factors Controlling $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in Deep Groundwater

The constant  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  concentrations in the deep groundwater demonstrate the occurrence of similar nitrogen processes throughout the year. Thus, the deep groundwater is far below the zone that is affected by the small changes in the surface conditions and is more isolated than the shallow groundwater. As previously reported,  $\text{NH}_4\text{-N}$  is derived from natural sources, and human  $\text{NO}_3\text{-N}$  contamination is nearly absent [21,23] and follows the ammonification process due to the reduced environment.

#### 4.7. Source and Fate of Nitrogen According to Isotopes

The dual isotope ratios ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) from nitrate can be used successfully to trace the fate and source of nitrogen due to their distinct ranges [65]. The range of  $\delta^{15}\text{N}$  typically depends upon the source, where the ranges corresponding to soil nitrogen, commercial fertilizer, and anthropogenic waste are 5‰ to 7‰ [51], −6‰ to 6‰, and 10‰ to 25‰, respectively [63]. The  $\delta^{18}\text{O}$  in nitrate may derive either from atmospheric oxygen or synthetic fertilizers, ranging from 18‰ to 22‰ [66], while the soil nitrogen transformed from onsite  $\text{NH}_4\text{-N}$  by nitrification has a range from −5‰ to 5‰ [67]. The combined dual isotopic range extracted from various sources is shown in Figure 5.

With the lack of sufficient data for the dual isotopes of nitrate throughout the year, the isotope composition variations obtained from the data available from Chyusal and Thimi supports the information regarding the sources of and processes related to nitrogen. The wide range of  $\delta^{15}\text{N}\text{-NO}_3$  from Chyusal (Figure 5) indicates that nitrate in groundwater is derived from multiple sources in two seasons, mainly from precipitation or nitrification of soil nitrogen and anthropogenic waste (sewage and chemical fertilizers). In addition, the values of the two isotopes indicate the occurrence of isotopic fractionation, possibly due to the nitrogen cycle (nitrification and denitrification) in the presence of microbiological activity. Similarly, the samples from Thimi indicate the loading of nitrate from a single source, i.e., anthropogenic waste, throughout the year. The seasonal variations in the isotopic signature were also easily observable in the gravel-bearing area, indicating higher isotopic fractionation than in the clay-bearing area.

#### 4.8. Health Effects

As explained by Warner et al. [21], the selection of drinking water is based upon the taste i.e., those with good taste are considered drinkable although they are highly contaminated.  $\text{Fe}^{2+}$  for taste and  $\text{NH}_4^+$  for smell are considered as the major parameter in governing the physical state of water. Following the study, it can be predicted that the groundwater use in the wet season is higher than in dry season where  $\text{Fe}^{2+}$  and  $\text{NH}_4\text{-N}$  concentrations are lower. This study, from the discussion on general chemistry, predicts the higher risk in nitrogen contamination during wet season than in dry season caused by the higher  $\text{NO}_3\text{-N}$  intake. This study also shows that the people residing in this study seriously need to consider the limit of nitrogen compound concentration before the use.

### 5. Conclusions

The results obtained in this study from chemical and isotopic investigations of the groundwater system in Kathmandu Valley reveal the degrading conditions of the shallow groundwater. No specific cluster of  $\text{NO}_3\text{-N}$  or  $\text{NH}_4\text{-N}$  contamination was found in the spatial distribution, indicating the prevalence of point source pollution of the groundwater in the study area. The data analysis showed that the  $\text{NO}_3\text{-N}$  in Kathmandu Valley is derived from multiple sources of contamination, i.e., anthropogenic sources and nitrogen in the soil.  $\text{NO}_3\text{-N}$  was also found to be added to the groundwater from the nitrification of  $\text{NH}_4\text{-N}$  that was sorbed in unsaturated zones. In general, the dry season acted as the storage for rapidly transported partially nitrified  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$ , which later transformed to  $\text{NO}_3\text{-N}$  with an appropriate environment during wet season. The nitrification seemed higher in the wet season than in the dry season, which could also be due to the addition of dissolved oxygen carried by rain, surface water interaction and irrigation return along with the local flow. Based on seasonal comparison, it was found that the groundwater in Kathmandu Valley is more vulnerable and poses high health risks during the wet season. This study thus helps in assessing the effective management of the shallow groundwater and the future nitrogen contamination vulnerability depending upon the soil type. Furthermore, this study does not cover the effective nitrogen contamination depending upon the land use. The nitrogen source identification in various land use areas will be focused with detail nitrogen contamination modeling in future research. Overall, the approach applied here can also be applicable in other basins with complex point source contamination comparing with the various soil types present.

### 6. Recommendation

For future well establishment; rigorous contamination source identification, i.e., natural and anthropogenic (septic and sewage, agricultural), and regular monitoring of aquifers condition are to be done. Agronomics and nitrogen fertilization education in the agricultural area are to be encouraged. Development of proper guidelines for sealing of newly constructed wells, maintenance of existing groundwater wells and groundwater management rules are suggested. Adequate treatment of groundwater before its use is highly recommended, especially during wet season.

**Author Contributions:** This research was conceptualized by B.M.S. and T.N. B.M.S. and T.K. were involved in the sampling, data collection, and analysis during the study. T.N., T.K., S.D.S., and K.N. supervised this work.

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