



# Article Assessment of Ammonium–N and Nitrate–N Contamination of Shallow Groundwater in a Complex Agricultural Region, Central Western Taiwan

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Abstract: The characteristics of nitrogen contamination of shallow groundwater were evaluated through current status analysis and trend detection of ammonium-N and nitrate-N concentrations under various cropping patterns to assess the effectiveness of rational fertilization in the Choushui River alluvial fan, central Western Taiwan. The influence of cropping patterns on both ammonium-N and nitrate-N contamination associated with redox conditions/dissolved oxygen (DO) in shallow groundwater was also discussed in this study. The analysis revealed that shallow groundwater beneath double rice cropping and rotational cropping regions is still characterized by high ammonium-N concentration despite rational fertilization promotion. However, very few monitoring wells showed an upward trend of ammonium-N/nitrate-N concentrations, indicating that shallow groundwater is not further deteriorated by nitrogen pollution in most parts of the study area. Therefore, the remediation of nitrogen contaminated groundwater will be a long-term process and more effort must be invested. Moreover, the strict redox conditions defined by a single DO threshold value may not account for groundwater nitrogen pollution in the study area. It is difficult to determine the redox conditions and predominant nitrogen pollution patterns of shallow groundwater purely from cropping patterns. Instead, contamination may have resulted from an integrated process governed by several other factors. Tracing the potential sources of nitrogen pollution and establishing a more integral monitoring network should be implemented to formulate a more comprehensive nitrogen pollution control strategy in this area.

**Keywords:** groundwater; trend detection; rational fertilization; ammonium–N; nitrate–N; cropping pattern

# 1. Introduction

Nitrogen is an indispensable nutrient for planting crops, and its efficient use is key to the trade-off between crop yield, economic profit, and environmental protection. Improper application of fertilizers has become one of the primary sources of non-point source pollution in agricultural areas [1,2]. Due to the complex nitrogen cycle transformations in farmland [3,4], low nitrogen use efficiency has become a challenge for crop production [5,6]. This often led to excess fertilizer applied by farmers in an attempt to increase crop yields, which was responsible for the higher cost of crop planting and increased environmental pollution potential. A large amount of nitrogen fertilizer applied to crops is lost to the environment via denitrification, volatilization, surface runoff, and leaching [7]. Among these pathways, excess nitrogen can result in groundwater pollution through leaching, mainly in the form of nitrate or ammonium.

In comparison, nitrate is more easily leached into groundwater due to its high solubility and low soil adsorption capacity [3,8]. Because of its high potential risk to human health in drinking water [9–12], numerous surveys and analyses of soil nitrate leaching or nitrate contamination in groundwater caused by various agricultural activities have been



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). widely reported e.g., [13–20]. Unlike nitrate, ammonium has very low toxicity to human health, and due to its low mobility in soil-water or aquifer systems [3,21], relatively few related studies have focused on evaluating ammonium contamination in aquifers from natural sources or anthropogenic activities [22–26]. However, ammonium in aquifers can degrade groundwater quality and affect its usability; and it can also be a potential source of nitrogen in surface water bodies receiving discharge from groundwater [21]. Therefore, from the sustainable utilization of groundwater resources, both nitrate and ammonium contamination must be considered.

High inputs of nitrogen and related soil anaerobic–aerobic conditions in flooded or upland conditions may result in differences in nitrogen leaching. A series of complex physical, chemical, and biochemical reactions in aeration layer and aquifer will jointly determine the main nitrogen pollution pattern of groundwater. Nitrogen loading from intense chemical fertilizer application to upland crops has been identified as a major source of high nitrate concentrations in groundwater [14,20,22,27,28]. On the contrary, regional investigation revealed that groundwater under flooded paddy fields is rarely polluted with nitrate [14,22], even though some studies have pointed out that nitrate is dominant in the leaching water of rice paddies [29,30] and paddy-wheat rotation systems [31–34]. However, some field experiments have shown that ammonium is the main form of nitrogen in the leaching water during the rice-planting season [35,36]. Du et al. [25] also reported that ammonium is most likely to accumulate in shallow groundwater beneath the paddy fields. The discrepancy in the above findings highlights that agricultural land use or crop patterns may not be the decisive factor in determining the dominance of nitrate or ammonium contamination in aquifers; instead, it may result from a more complex integrated process.

In addition to understanding contamination levels for the current state, identifying trends in contamination and reversing significantly increasing trends is critical to the sustainable use of groundwater resources. Among the different trend test methods, the non-parametric Mann–Kendall (MK) test [37,38] with the advantages of no particular distribution needs to be confirmed, and non-detect records are available by assigning them a smaller value compared to the smallest measured value in the data set. It has been widely used to identify trends in hydro-meteorological time series and water quality of various water bodies e.g., [39–48]. However, directions can be different or, on the contrary, depending on the period length of a data set, and the test of stability over time of the time series to identify the "recent" trend will be of particular interest from a management or scientific standpoint [49]. As suggested by Pettit [50], change point analysis helps evaluate abrupt changes in observation records [51] and for detecting recent trends. After determining trends, the Sen slope estimate [52], owing to its high precision in the presence of skewed data [53], can be coupled to quantify the trend slopes.

The Choushui River alluvial fan, located in central Western Taiwan, is an important agricultural area with complex irrigation and cropping patterns. Groundwater has long been regarded as one of the main sources of water supply. Long-term excess application of chemical nitrogen fertilizers has resulted in a negative impact on groundwater quality in this area [28,54]. To reduce the use of chemical fertilizers, the Committee of Agriculture, Taiwan (Taiwan COA) has been promoting a series of rational fertilization policies since the late 1990s. However, such policies or advocacy are not compulsory, and their effectiveness is mainly dependent on farmers' awareness and economic benefit considerations. To evaluate the effect of a rational fertilization policy on nitrogen pollution control, not only the current status, but also the variation trends of nitrogen concentrations in groundwater should be examined. Moreover, because of the complexity of farming patterns in this area, different agricultural environments may lead to different types of nitrogen pollution, and the impact of different farming patterns on groundwater nitrogen pollution must be further understood and differentiated. Therefore, the aims of this study were to examine the current status of ammonium and nitrate contamination, identify trends in contaminant concentrations, evaluate the effects of different cropping patterns on nitrogen pollution in shallow groundwater, and assess the success of the rational fertilizer policies of government

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agencies. The influence of cropping patterns on both ammonium–N and nitrate–N contamination associated with redox conditions/dissolved oxygen (DO) in shallow groundwater was also discussed in this study.

# 2. Materials and Methods

## 2.1. Hydrogeological Conditions and Monitoring Wells of the Study Area

The Chuoshui River alluvial fan traverses central Western Taiwan and divides the area into North and South subregions. This alluvial fan occupies an area of approximately 2700 km<sup>2</sup>, and the hydrogeological conditions can principally be partitioned into proximal, mid, and distal fan zones (Figure 1). The mean annual precipitation in the study area was approximately 1387 mm, according to climate statistics for 2000–2020 [55]. The Quaternary unconsolidated sediment underlying this alluvial fan constitutes a complex flow system, including an unconfined aquifer and several confined aquifers, and the eastern proximal fan is a natural groundwater recharge zone for these deeper confined aquifers [56]. Low-permeability topsoil materials are primarily distributed in the mid-fan and distal-fan areas, but the amount of these materials in the proximal fan region is relatively low [56]. Groundwater flows seaward in a pattern similar to that of surface water for these aquifers [54].



**Figure 1.** Spatial distribution of monitoring wells and cropping patterns in the Choushui River alluvial fan in Taiwan.

Water quality records from 38 monitoring wells of the Taiwan Environmental Protection Administration (Taiwan EPA) located in the study area (assigned from N1 to N20 and S1 to S18 for the Northern and Southern subregions, respectively) were used in this study (Figure 1). All monitoring wells partially penetrate the shallow unconfined aquifer according to the groundwater quality monitoring well setting specification of the Taiwan EPA [57], which sets the diameter of the monitoring well to 2 or 4 inches with a 6 m long well screen to cover groundwater level during the high and low water level periods, and at least 1 m of well screen must be placed below the groundwater surface during the low water level period. Unlike the entirely penetrating and full-screening monitoring wells set up by other institutions, the monitoring wells of the Taiwan EPA screen shallow water in the groundwater flow system and are generally more vulnerable to contamination from agricultural activities. The shallow groundwater table is very close to the ground surface in this area. Figure 2 shows the range of depth to the water table for each monitoring well from 2018 to 2020 in the study area. The maximum water table depth (>15 m) was found in S7, located in the proximal fan; while the water table depth of the monitoring wells in the distal fan was mostly below 4.5 m.



Figure 2. Range of depth to water table for each monitoring well from 2018 to 2020 in the study area.

## 2.2. Cropping Patterns

Because of the rather distinctive dry season followed by the wet season, the main cropping periods are classified into the first and second cropping seasons in Taiwan. In the command areas of irrigation associations, the crop patterns have been developed over the long term to adapt to local farmland production environments including climatic and hydrologic conditions, topography, soil textures, crop species, availability of irrigation water resources, and applicable crop planting techniques [58]. The main cropping patterns commonly practiced in the study area are as follows:

- (i) Double rice cropping: farms in which rice crops are grown and harvested twice a year.
- (ii) Single rice cropping: farms in which rice crops are grown and harvested the first or second rice crop in a year.

- (iii) Rotational cropping: farms in which rice crops are grown and harvested every two years (type I). Other farms grow and harvest either a single season or twice the paddy rice crop at an interval of three years (type II and type III).
- (iv) Sugarcane: farms that mainly grow and harvest sugarcanes all year.

The cropping patterns in the northern subarea are mainly dominated by double rice cropping, while rotational and rice cropping systems are utilized in the southern subarea (see Figure 1). In the rotational cropping areas, various upland crops are planted during non-rice cropping seasons. This study focused on assessing the effects of large-scale primary cropping patterns on nitrogen pollution of regional shallow groundwater, although some different small-scale cropping patterns or fallow fields may exist in these primary cropping regions.

#### 2.3. Data Analysis

Seasonal or semi-annual ammonia–N and nitrate–N concentration data for 38 monitoring wells obtained from the Taiwan EPA [59] were used in this study. As the monitoring network is still being constructed and improved, the monitoring period of each well is not completely consistent. The length of the observation period refers to the length of the observation period from the beginning of the observation to the end of 2020. Figure 3 shows a histogram of the lengths of the data series. The monitoring period of 21 years is the majority, and only a few monitoring wells (N20, S1, S7, and S14) have monitoring periods of less than 10 years.



Figure 3. Histograms of lengths of the data series.

Details of the water quality sample collection protocol and laboratory analysis are described in the Taiwan EPA [60]. Non-detection records were made available by assigning half of the detection limits to conduct a trend test. It is worth noting that the measured ammonia–N was analyzed using the phenate method, and as such, misinterpretations of what is being measured may occur. In fact, ammonia–N (un-ionized form) and ammonium–N (ionized form) may both be present in aquatic environments at an equilibrium point that is governed mainly by pH and temperature [61]. To understand the predominant species for both, we inspected the average pH values of the monitoring wells over a 3-year period (2018–2020) and found that there were 33 wells with pH < 7 and only five wells with pH > 7 in the study area. The overall average was 6.88 with a minimum of 6.45, and a maximum of 7.36. According to the calculation method developed by Emerson et al. [62], the percentage of un-ionized aqueous ammonia solutions at different pH values was determined and used to calculate ammonium–N concentrations. Theoretically, ammonium is the predominant

species at a pH of approximately 7.0, and ammonium–N was used instead of ammonia–N in this study to avoid misunderstanding.

To understand the current state of nitrogen pollution, the mean water quality averaged over a 3-year period (2018–2020) was calculated to minimize the potential effects of interannual hydroclimatic and cropping variability. The Taiwan EPA's classification criteria for groundwater quality, drinking water quality standards, and World Health Organization drinking water quality standards were used to assess the nitrogen pollution of groundwater.

# 2.4. MK Test and Slope Estimation

The non-parametric MK test is insensitive to outliers and does not require data to be normally distributed, thus, has been one of the most popular methods for detecting trends in hydro-meteorological and water quality time series. In this test, each value in the time series is compared with others in sequential order, and the test statistic *S* is given by

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \operatorname{sign}(X_j - X_i) , \qquad (1)$$

where *n* is the number of observation data points,  $X_i$  and  $X_j$  are the *i*th and *j*th (j > i) observations in the time series, respectively, and the function sign ( $X_j - X_i$ ) is defined as:

$$\operatorname{sign}(X_j - X_i) = \begin{cases} +1, & \text{if } (x_j - x_i) > 0\\ 0, & \text{if } (x_j - x_i) = 0\\ -1, & \text{if } (x_j - x_i) < 0 \end{cases}$$
(2)

When n is greater than 10, the distribution of S is approximately normal, and the variance can be calculated as follows:

$$Var(S) = \frac{n(n-1)(2n+5) - \sum_{k=1}^{m} t_k(t_k-1)(2t_k+5)}{18}$$
(3)

where *m* is the number of tied groups and  $t_k$  is the number of ties of extent *k*. The standard normal test statistic *Z* used to detect a significant trend was calculated according to the following equation:

$$Z = \begin{cases} \frac{S-1}{\sqrt{Var(S)}}, & if \ S > 0\\ 0, & if \ S = 0\\ \frac{S+1}{\sqrt{Var(S)}}, & if \ S < 0 \end{cases}$$
(4)

The null hypothesis ( $H_0$ ) is accepted at the  $\alpha$  significance level for  $|Z| \leq |Z_{1-\alpha/2}|$  in a two-tailed test. Otherwise, the null hypothesis is invalid, and the statistically significant trend is identified at the  $\alpha$  significance level. In this way, a positive Z value indicates an upward trend, while a negative value indicates a downward trend. In this study, the calculated standard values of Z at 5% significant levels ( $\alpha = 5\%$ ) were used for detecting trends in observed ammonium–N and nitrate–N data sets.

The MK trend test can only determine whether the trend is rising, falling, or not statistically significant, but cannot show magnitude. Because of this, slope estimates for the importance of the direction were calculated using the Theil–Sen estimator [52,63], which is the median slope of all ranked regression slopes and appears to be robust, even when outliers are present [53]. The MK test coupled with the Theil–Sen slope estimation can determine the magnitudes of those with significant trends.

#### 2.5. Significant Change Point and Recent Trends

Recent trends are those established over the last time series period, with no trend reversal or break. The last period can be defined as starting at the change point in the time series and ending with the most recent monitoring record [49]. Pettitt [50] showed that a nonparametric approach makes it possible to detect a significant change in the evolution of

time-series means. In this approach, if a change point at *t* is exhibited in a time series of observed data  $x_1, x_2, x_3, ..., x_n$ , then the probability distribution function  $F_1(x)$  of the first part of the series  $x_1, x_2, ..., x_t$  will be different from the distribution function  $F_2(x)$  of the second part of the series  $x_{t+1}, x_{t+2}, x_{t+3}, ..., x_n$ . The non-parametric test statistics  $U_t$  for this test can be described as follows:

$$U_{t} = \sum_{i=1}^{t} \sum_{j=t+1}^{n} \operatorname{sign}(x_{t} - x_{j}) , \qquad (5)$$

$$\operatorname{sign}(x_{t} - x_{j}) = \begin{cases} 1, if(x_{i} - x_{j}) > 0\\ 0, if(x_{i} - x_{j}) = 0\\ -1, if(x_{i} - x_{j}) < 0 \end{cases}$$
(6)

The test statistic *K* and associated probability of exceedance  $\rho$  for the time-series length *n* can be described as follows:

$$K = Max|U_t| \quad , \tag{7}$$

$$\rho = \exp\left(\frac{-K}{n^2 + n^3}\right). \tag{8}$$

The null hypothesis is rejected when  $\rho$  is less than the specific significant level, and the series can be segmented into two subseries at the location of the change point. Otherwise, the null hypothesis is valid and no statistically significant change point exhibited in the series. The approximate significance probability p for a change point in a time series is defined as

$$p = 1 - \rho . \tag{9}$$

In this study, the critical values of *K* at a 5% significant level were used to detect a significant change point in the observed ammonium–N and nitrate–N datasets. Once the change point has been determined, the recent trend and its magnitude after the change point can be detected using the MK test coupled with Theil–Sen slope estimation.

# 3. Results

#### 3.1. Groundwater Quality Standards and Current Status of Nitrogen Pollution

According to the groundwater pollution monitoring standards of the Taiwan EPA [64], groundwater quality is classified into two categories. Category one refers to groundwater in the drinking water source protection areas, which sets the threshold of anthropogenic groundwater pollution for the ammonium–N and nitrate–N to be 0.05 mg/L and 5.0 mg/L, respectively; category two refers to groundwater other than that under the first category, with threshold values of 0.25 mg/L and 25 mg/L for ammonium–N and nitrate–N, respectively. The above standards can be used to judge whether the groundwater quality has been affected by anthropogenic activities. However, Chen and Liu [54] suggested that a nitrate–N of 0.5 mg/L can be served as the threshold of anthropogenic groundwater pollution in the study area. In addition, according to the drinking water quality standards of the Taiwan EPA [65], the threshold values of ammonium–N and nitrate–N are 0.1 mg/L and 10 mg/L, respectively. The WHO drinking water quality standard does not set a limit for ammonium–N; however, the threshold value for nitrate is 50 mg/L (11.3 mg/L for nitrate–N) [66]. In the European Union, the allowable limit of ammonium in groundwater is 0.5 mg/L to maintain disinfection efficiency [67].

According to the above standards, we can evaluate the nitrogen pollution levels using the 3-year (2018–2020) average ammonium–N and nitrate-N concentrations of the groundwater in the study area. Table 1 shows the distribution of ammonium–N and nitrate–N in different concentration ranges in all monitoring wells under various cropping patterns, and Figure 4 shows their spatial distribution in the study area. The 3-year average ammonium–N concentrations in the 38 monitoring wells ranged from ND to 5.41 mg/L, while nitrate–N concentrations ranged from ND to 11.17 mg/L. Ammonium–N concentrations exceeding 0.25 mg/L were observed in 23 monitoring wells (about 60% in

total), which does not meet the Taiwan EPA category two groundwater pollution monitoring standard. Only five wells met the category one criteria of the groundwater pollution monitoring standard (ammonium–N < 0.05 mg/L). In addition, only six monitoring wells met Taiwan's drinking water quality standard (ammonium–N < 0.1 mg/L).

Concentration	Double Rice Cropping	Rotational Cropping II	Rotational Cropping III	Others	Total
(IIIg/L)		$NH_4^+ - N$	I		-
< 0.05	S4, S7	S5	S11, S17	-	5
0.05 - 0.1	-	-	S18	-	1
0.1-0.25	N6, N9, N13, S6, S12	-	S9	N3, N14, N20	9
	N1, N5, N7, N10, N12,				
0.25-1.5	N15, N16, N18, N19,	S2, S13, S14	S10	-	15
	S3, S15				
>1.5	N2, N4, N11, N17	S1, S8, S16	-	N8	8
Total	22	7	5	4	38
		$NO_{3}^{-} - 1$	N		
	N1, N2, N4, N6, N7,				
-0 F	N10, N11, N12,	S1, S2, S8,	S9, S10, S17,	N3, N8, N14,	20
<0.5	N13, N16, N17, N18,	S13, S14, S16	S18	N20	29
	N19, S3, S15				
0.5-2.5	N5, N9, N15, S12	-	-	-	4
2.5–5	S4, S6	-	-	-	2
>5	S7	S5	S11	-	3
Total	22	7	5	4	38

**Table 1.** The distribution of ammonium–N and nitrate–N in different concentration ranges of all monitoring wells under various cropping patterns.

Nitrate–N contamination in shallow groundwater appeared to be less severe than ammonium–N contamination in this area. Only three wells exceeded the threshold value of 5.0 mg/L for Category one of the Taiwan EPA groundwater monitoring standard, and no monitoring exceeded 25 mg/L for Category two. These concentrations are also relatively low compared with the WHO standard of 11.3 mg/L. However, when a more stringent standard suggested by Chen and Liu [54] was adopted to identify anthropogenic groundwater pollution, nitrate–N concentrations exceeding 0.5 mg/L were observed in nine monitoring wells (about 24% in total). Overall, ammonium–N contamination of shallow groundwater is currently more serious than nitrate–N contamination in this area.

# 3.2. Influence of Cropping Patterns on Nitrogen Pollution

It is of interest to evaluate the influence of various cropping patterns on different nitrogen pollution levels. From Table 1, we can see that almost all monitoring wells located in the double-rice cropping region exceeded the threshold value of 0.05 mg/L for ammonium– N, except for two monitoring wells (S4 and S7). Moreover, it is worth noting that in the rotational cropping regions, many monitoring wells also have excessive ammonium–N concentrations, especially for rotational cropping II. In contrast, the ammonium contamination of the groundwater in rotational cropping III was not as serious as that of rotational cropping II.

Compared with ammonium–N, nitrate–N contamination of groundwater occurred less frequently in double-rice cropping regions (68% monitoring wells < 0.5 mg/L), even though higher concentrations of nitrate–N were found in some monitoring wells, including S4 and S6 ranging from 0.5 to 5.0 mg/L, and S7 exceeding 5.0 mg/L. Similarly, high nitrate–N concentrations also occurred in the rotational cropping II and rotational cropping III regions, where two monitoring wells (S5 in rotation cropping II and S11 in rotational cropping III) were found to have nitrate–N concentrations exceeding 5.0 mg/L. Overall, relatively high



nitrate–N concentrations were mainly distributed along the southern bank of the Chuoshui River (Figure 4).





**Figure 4.** Spatial distribution of (**a**) ammonium–N and (**b**) nitrate–N in different concentration ranges in all observation wells under various cropping patterns.

It is evident that the high ammonium–N concentrations not only occurred in the double rice cropping regions but also in various rotational cropping regions where upland crops dominate. Therefore, cropping pattern is not the sole factor determining ammonium–N or nitrate–N contamination in groundwater of the study area; instead, it may be an integrated process governed by several other factors that need to be further determined.

# 3.3. MK Test for the Entire Period of the Data Set

To identify the long-term trends for both ammonium–N and nitrate–N concentrations, the MK trend test was performed using the entire period of the data sets. Among all monitoring wells, only a few monitoring wells (N20, S1, S7, and S14) had a monitoring period of less than 10 years, and their entire-period MK trends cannot be regarded as long-term trends. Table 2 and Figure 5 show the entire-period MK trends of the ammonium–N and nitrate–N concentrations for each monitoring well in the study area. Upward, downward, and no statistically significant trend in ammonium–N can be found in five, 15, and 18 monitoring wells, respectively. As for the nitrate–N concentration, upward trends were found in six wells, downward in 25 wells, and the remaining seven showed no statistically significant trend. In comparison, nitrate–N showed a more evident (upward or downward) trend than ammonium–N in the study area. Four of the five wells with an upward trend in ammonium–N were mainly distributed in the northern double-rice cropping region. As for the wells with an upward trend in attrend in the double rice cropping region, and the other half were distributed in the rotational cropping regions.

Trend	Double Rice Cropping	Rotational Cropping II	Rotational Cropping III	Others	Total		
		$\mathbf{NH}_{4}^{+}-\mathbf{N}$	[		-		
Upward	N4, N10, N16, N17	S8	-	-	5		
No significant trend	N2, N5, N7, N11, N12, N13, N19, S3, S4, S15	S1, S2, S5, S14	-	N3, N8, N14, N20	18		
Downward	N1, N6, N9, N15, N18, S6, S7, S12	S13, S16	S9, S10, S11, S17, S18	-	15		
Total	Total 22		5	4	38		
	$NO_3^ N$						
Upward No	N9, N15, S6	S5	S11	N14	6		
significant trend	N11, S4, S7, S12	-	S9, S10	N20	7		
	N1, N2, N4, N5, N6,						
Downward	N7, N10,N12, N13, N16, N17, N18, N19, S3, S15	S1, S2, S8, S13, S14, S16	S17, S18	N3, N8	25		
Total	22	7	5	4	38		

**Table 2.** The entire-period Mann–Kendall (MK) trends of ammonium–N and nitrate–N concentrations for each monitoring well in the study area.

A cross-comparison of trends between ammonium–N and nitrate–N concentrations in all monitoring wells was also carried out, as shown in Table 3. Simultaneous increases in ammonium–N and nitrate–N concentration trends were not observed. When one of the two showed an upward trend, the other showed a downward trend (or no significant trend). Both concentrations showed no significant trends in the three monitoring wells. It is worth noting that both concentrations simultaneously showed a downward trend in seven monitoring wells, which may result from the reduction in surface nitrogen sources after the implementation of rational fertilization policies.



(a)



(b)

**Figure 5.** Spatial distribution of entire-period Mann–Kendall (MK) trends of (**a**) ammonium–N and (**b**) nitrate–N concentrations for each monitoring well in the study area.

$\mathbf{NH}_{4}^{+}-\mathbf{N}$	$NO_3^ N$	Well NO.	Total
Upward	Upward	_	0
Upward	Downward	N4, N10, N16, N17, S8	5
Upward	No significant trend	_	0
Downward	Upward	N9, N15, S6, S11	4
Downward	Downward	N1, N6, N18, S13, S16, S17, S18	7
Downward	No significant trend	S7, S9, S10, S12	4
No significant trend	Upward	N14, S5	2
Ū.	*	N2, N3, N5, N7, N8,	
No significant trend	Downward	N12, N13, N19, S1, S2, S3, S14, S15	13
No significant trend	No significant trend	N11, N20, S4	3

 Table 3. Cross-comparison of trends between ammonium–N and nitrate–N concentrations in all monitoring wells.

The promotion of rational fertilization by governmental agencies seems to have achieved a preliminary goal of improving groundwater quality in the study area. However, when the result of the MK trend test is coupled with the Theil–Sen slope estimation, the effectiveness of this policy needs to be further reviewed. Although many observation wells showed significant trends in the MK test, the magnitudes of the trends were relatively small, which may result in misleading pollution levels. Lopez et al. [49] indicated that due to the analytical uncertainty in the nitrate concentration determination, trend magnitudes ranging from -0.1 to 0.1 mg/L/year are considered to be stable. The above classification was adopted in our study to redefine the trend of the nitrate–N concentration based on the MK test. As for ammonium–N, due to its low pollution threshold, the stable condition is defined between -0.01 mg/L/year and 0.01 mg/L/year in this study.

The MK test results coupled with slope estimation under various classifications, including stable conditions, are listed in Table 4, and their spatial distributions are shown in Figure 6. For ammonium–N, upward trends reduced from five to four, downward trends reduced from fifteen to ten, and the remaining six were classified as stable owing to their weak evolution. As for nitrate–N, the upward trend decreased from seven to four, the downward trend dropped dramatically from 25 to one, and 26 wells were classified as stable. The introduction of stable classification inevitably resulted in a reduction in the upward and downward trends for both ammonium–N and nitrate–N. If the stable level range of the ammonium–N concentration is set to be the same as that of nitrate–N, the number of monitoring wells with stable ammonium–N will also increase significantly.

Entire-period trend analysis can provide guidance on priority remediation targets, especially for those with upward trends and high concentrations, such as N4, N16, N17, and S8 for ammonium–N; and S5, S6, and S11 for nitrate–N. Moreover, trend analysis coupled with classification also highlights that although groundwater quality degradation by nitrogen pollution has almost been controlled, more efforts should be made to further improve water quality.

Trend (mg/L/yr)	Double Rice Cropping	Rotational Cropping II	Rotational Cropping III	Others	Total		
(mg/L/y1)	NH4 <sup>+</sup> -N						
Upward (0.01 < Trend)	N4, N16, N17	S8	-	-	4		
Stable (-0.01 < Trend < 0.01)	N10, S6, S7	-	S11, S17, S18	-	6		
Downward (Trend < -0.01)	N1, N6, N9, N15, N18, S12	S13, S16	S9, S10	-	10		
No significant trend	N2, N5, N7, N11, N12, N13, N19, S3, S4, S15	S1, S2, S5, S14	-	N3, N8, N14, N20	18		
Total	22	7	5	4	38		
		$NO_3^ N$					
Upward (0.1 < Trend)	N9, S6 N1, N2, N4, N5, N6, N7,	S5,	S11	-	4		
Stable (-0.1 < Trend < 0.1)	N10, N12, N13, N15, N16, N17, N18, N19, S3, S15	S1, S2, S8, S13, S14, S16	S18	N3, N8, N14	26		
Downward (Trend < -0.1)	-	-	S17	-	1		
No significant trend	N11, S4, S7, S12	-	S9, S10	N20	7		
Total	22	7	5	4	38		





(a)

Figure 6. Cont.



**Figure 6.** Spatial distribution of the MK test coupled with slope estimation under various classifications, for (**a**) ammonium-N and (**b**) nitrate-N concentrations.

# 3.4. Recent Trend of Nitrogen Pollution

The change point of the time series was tested based on the Pittett method to determine the time period during which a recent trend should be sought. The MK test coupled with the Sen–slope estimator was applied to the periods following the point breaks for each well. Change points were detected in 23 and 33 wells for ammonium–N and nitrate–N, respectively. The change points for ammonium–N that occurred after 2008 were slightly higher than those before 2008, whereas most of the nitrate–N change points (29 of 33) occurred after 2008.

Recent trends coupled with slope estimation under various classifications, including stable condition, are listed in Table 5, and their spatial distributions are shown in Figure 7. For some monitoring wells without change points, their entire period trends are regarded as recent trends. Temporal recent trends for ammonium–N were upward in two wells, downward in four, stable in four, and there was no statistically significant trend in the remaining 28. As for nitrate–N, upward trends were found in only one well, stable in eight wells, and the remaining 29 wells showed no statistically significant trend. Compared with entire-period trends, it was found that the number of monitoring wells with an upward trend further decreased after recent trend analysis. In addition, recent trends showed more insignificant trends in both nitrogen concentrations, which may be related to the more frequent occurrence of ND values in the monitoring values of both concentrations in many monitoring wells in recent years. For example, Figure 8 shows the entire-period downward trends in the ammonium–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate–N concentration histogram of monitoring well S17 and the nitrate-N concentration histogram of monitoring wells

Trend	Double Rice Cropping	Rotational Cropping II	Rotational Cropping III	Others	Total	
(mg/L/yr)	NH4 <sup>+</sup> -N					
Upward (0.01 < Trend)	N1	-	-	N8	2	
Stable (-0.01 < Trend < 0.01)	N13, S6, S7, S12	-	-	-	4	
Downward (Trend $< -0.01$ )	N17	S2, S13, S16	-	-	4	
No significant trend	N2, N4, N5, N6, N7, N9, N10, N11, N12, N15, N16, N18, N19, S3 S4 S15	S1, S5, S8, S14	S9, S10, S11, S17, S18	N3, N14, N20	28	
Total	22	7	5	4	38	
		NO3	$3^{-} - N$			
Upward (0.1 < Trend)	S6	-	-	-	1	
Stable $(-0.1 < \text{Trend} < 0.1)$	N2, N4, N7, S3	S16	S17	N3, N14	8	
Downward (Trend $< -0.1$ )	-	-	-	-	0	
	N1, N5, N6, N9, N10,					
No significant trend	N11, N12, N13, N15, N16, N17, N18, N19, S4, S7, S12, S15	S1, S2, S5, S8, S13, S14	S9, S10, S11, S18	N8, N20	29	
Total	22	7	5	4	38	



Table 5.	The recent	trend couple	ed with slo	pe estimation	under	various	classifications.



Figure 7. Cont.





**Figure 7.** Spatial distribution of recent trends in (**a**) ammonium–N and (**b**) nitrate–N concentrations for each monitoring well in the study area.



(a)

Figure 8. Cont.



(b)

**Figure 8.** Concentration histograms of (**a**) ammonium–N in monitoring well S17, and (**b**) nitrate–N in monitoring well N18.

It is worth noting that the monitoring wells showing a recent upward trend for ammonium–N (N1 and N8) were not consistent with those with an entire-period upward trend (N4, N16, N17, and S8), whereas the only monitoring well showing a recent upward trend (S6) in nitrate–N also had an entire-period upward trend. Recent trend analysis also provides guidance on priority remediation targets, especially for those with upward trends and high concentrations, such as N1 and N8 for ammonium–N, and S6 for nitrate–N. However, owing to the low detection rate of recent significant trends, the priority of remediation should still be determined in line with entire-period trends to reduce the risk of misjudgment.

# 3.5. Threshold Value of DO and Redox State

The previous analysis shows that the nitrogen pollution in the study area is dominated by ammonium–N. The scatter plot of the recent 3-year average concentrations of ammonium–N vs. nitrate–N at each well (Figure 9) indicates that when one is dominant, the other is in a disadvantaged situation. The redox state of the groundwater may play a key role in the predominance of ammonium–N or nitrate–N. The WHO [66] indicated that high ammonium–N concentrations can be found when anaerobic conditions dominate, whereas the ammonium–N concentration in aquifers is <0.2 mg/L under aerobic conditions. Additionally, Gurdak and Qi [17] pointed out that DO is one of the most important factors in predicting elevated nitrate concentrations. DO greater than 0.5 mg/L has been regarded as the oxic threshold for groundwater in this area [28,54,68]. The categories of oxic (DO  $\ge$  0.5 mg/L), anoxic (DO < 0.5 mg/L), and other redox classifications in aquifers were also applied or examined in other studies [17,69]. It would be interesting to examine the suitability of this threshold in the study area.

Scatter plots of ammonium–N concentration vs. DO and nitrate–N concentration vs. DO are shown in Figure 10. In general, high ammonium–N concentrations not only occurred when DO < 0.5 mg/L but also appeared when DO > 0.5 mg/L. Many high ammonium–N concentrations can be found with their DO ranging from 0.5 mg/L to 0.75 mg/L, and only very few high concentrations of ammonium–N appear with DO > 0.75 mg/L. As for nitrate–N, three wells exceeded the threshold value of 5.0 mg/L for category two of the groundwater monitoring standard of the Taiwan EPA with their DO at high concentrations. However, there were still a few monitoring wells with their nitrate–N concentrations exceeding 0.5 mg/L but with DO concentrations less than 0.5 mg/L. In this regard, considering a DO concentration of 0.5 mg/L as the threshold value of the redox

state cannot fully interpret the exceptional values of the concentration for ammonium–N or nitrate–N, and uncertainty still exists for setting a threshold value of DO to determine the redox state of groundwater in this area.



Figure 9. Scatter plot of recent 3-year average concentrations of ammonium–N and nitrate–N in each well.



Figure 10. Scatter plots of (a) ammonium–N vs. dissolved oxygen (DO) and (b) nitrate–N vs. DO.

# 3.6. Relationship between Groundwater DO and Cropping Pattern

A further check was conducted according to the redox state with a threshold value of 0.5 mg/L DO and other classifications under various cropping patterns. As shown in Table 6 and Figure 11, there are 19 monitoring wells (50% in total) under anaerobic conditions (DO < 0.5 mg/L), which are distributed in some double rice cropping regions and various rotational cropping regions. Because rice is planted under flooding conditions, the root zone of the muddy layer is usually in a reduced state [3]. However, the shallow groundwater beneath the paddy fields is not absolutely in a reduced state as determined by DO < 0.5 mg/L. Among the 22 monitoring wells in the double rice cropping region, 15 wells had ammonium–N concentrations exceeding 0.25 mg/L. Among these 15 wells, only six showed a DO less than 0.5 mg/L. In contrast, the root zone of rotational crops is mainly in an oxidized state most of the time, except during the rice planting period, but there are some monitoring wells that are still in a reduced state. Compared with rotational cropping III, the more reducing state can be found in rotational cropping II.

**Table 6.** Dissolved oxygen (DO) in different concentration ranges of all monitoring wells under various cropping patterns.

Concentration (mg/L)	Double Rice Cropping	Rotational Cropping II	Rotational Cropping III	Others	Total
<0.5	N5 *, N7 *, N9, N10 *, N11 *, N12 *, N13, S3 *, S6, S12	S1 *, S13 *, S14 *, S16 *	S9, S10 *	N8 *, N14, N20	19 (* 12)
0.5–1.0	N1 *, N2 *, N4 *, N16 *, N18 *, N19 *, S4	S2 *, S8 *	-	N3	10 (* 8)
1.0-2.0	N6, N15 *, N17 *, S15 *	S5	S11, S17	-	7(* 3)
>2.0	S7	-	S18	-	2 (* 0)
Total	22 (* 15)	7 (* 6)	5 (* 1)	4 (* 1)	38 (* 23)

Note(s): \* indicates an ammonium–N concentration > 0.25 mg/L.



**Figure 11.** Spatial distribution of DO in different concentration ranges for all observation wells under various cropping patterns.

Theoretically, monitoring wells in the anaerobic state may make it easier to reach higher ammonium–N concentrations. However, 23 monitoring wells (about 71% in total) showed ammonium–N concentrations exceeding 0.25 mg/L and did not meet category two of the groundwater pollution monitoring standard by Taiwan EPA. Of the 23, only 12 wells had a DO less than 0.5 mg/L. Eight out of the remaining 11 wells had DO concentrations slightly greater than 0.5 mg/L, ranging from 0.5 to 0.75 mg/L. In other words, if the threshold value of DO can be slightly increased, more monitoring wells with high ammonium–N concentrations can be included in the anaerobic state, as described in the previous paragraph. This analysis showed that strict redox conditions defined by a single DO threshold value may not account for groundwater nitrogen pollution in the study area. Likewise, it is unlikely that the redox conditions of shallow aquifers are purely dependent on cropping patterns or agricultural land use.

#### 4. Discussion

#### 4.1. Nitrogen Pollution Level and Effectiveness of Rational Fertilization Promotion

To reduce the use of chemical fertilizers, the Taiwan COA has promoted a rational fertilization policy since the 1990s. In the initial stage, a series of experiments were conducted, and the results were provided as the basis for publicity. It was not until 2008 that a special project team was formally established to actively promote rational fertilization through publicity lectures, soil fertility testing, establishment of rational fertilization demonstration farms, expansion of organic fertilizer application, and planting of green manure crops during winter fallow periods. According to the results of the experiments, the application of rational fertilization has reduced the amount of chemical fertilizers by an average of 34.6% from 2008 to 2014 across the country [70].

In this study, current status analysis combined with trend analysis has proven to help evaluate the effectiveness of such non-point source pollution control strategies and also provides guidance on priority remediation targets, especially for those with upward trends and high concentrations in groundwater. Although the above-mentioned rational fertilization promotion has been carried out, the shallow groundwater in this area is still characterized by high concentrations of ammonium–N. However, very few monitoring wells show an upward trend of ammonium–N and nitrate–N concentrations in both entireperiod and recent trends, indicating that shallow groundwater is no longer degraded by nitrogen pollution in most parts of the study area. Restoring groundwater contaminated by nitrogen will be a long-term process, and more effort must be invested into it.

Compared with the entire-period trend, recent trends showed a lower significant trend detection rate which may be due to shorter time series data and increased ND records. In addition, nitrate–N concentration has a more significant entire-period trend than ammonium–N concentration and is more consistent with the timing of the government agency's rational fertilization in the change point analysis. This may indicate that the ammonium contamination of the groundwater in this area has a higher uncertainty than that of nitrate.

# 4.2. Effects of Cropping Patterns, Redox Conditions, and Hydrogeological Conditions on Nitrogen Pollution

It is worth noting that paddy fields have long been regarded to function in water quality purification [27,71–73] because their anaerobic environment is valid for the denitrification process [3,74], and thus reduces the risk of nitrate–N contamination of nearby water bodies. In this study, the water purification function of paddy fields is reflected in the nitrate contamination of groundwater in the double rice cropping region not being severe. However, this function is not reflected in preventing ammonium contamination in the groundwater. Similar to the findings of this study, Du et al. [25] also reported high level of ammonium concentrations in shallow groundwater under rice paddies and indicated that ammonium was derived from intensive N fertilization and remained steady in the reducing environment. In contrast to upland farms, rice fields may form a low-conductivity plow

sole beneath the root zone after long-term ponded cultivation, which can retard vertical water and solute movement [75,76]. However, from the perspective of the infiltration path, preferential flows, such as bund percolation or lateral seepage, would also enhance solute transport towards the groundwater [77,78]. The preferential flow associated with the short percolation pathway may be the potential cause of the high concentration of ammonium–N in the double rice cropping region.

On the other hand, our finding also contradicts the conventional idea that nitrate is predominant in rotational cropping regions, where upland crops are mainly planted during the rotational period. The low concentration of nitrate–N is more likely to be the predominant effect of denitrification. Gurdak and Qi [17] indicated that a shallow seasonal water table promotes reduced conditions in aquifers, and fine-grained sediments/clayrich soils can slow nitrate transport, enhance denitrification, and result in low nitrate concentrations. The above-mentioned conditions are consistent with the hydrogeological conditions of the middle and distal-fan zones of the study area, which may explain why the groundwater nitrate–N concentration in these regions is relatively low. Similarly, the reduced conditions in the aquifer are also valid for elevated ammonium concentrations, especially in the distal-fan zone. This may also explain why the ammonium contamination of the groundwater in rotational cropping III is not as serious in rotational cropping II.

In general, cropping pattern is not the sole factor determining which types of nitrogen pollution are dominant in shallow groundwater of the study area. Redox conditions in shallow groundwater may be essential in controlling nitrogen pollution. However, using a single DO threshold value to define redox conditions may not completely account for the groundwater nitrogen pollution in the study area. McMahon and Chapelle [69] suggested that anoxic designation should include other concentrations, such as Mn (IV) and Fe (III), and larger threshold DO concentrations of 2.0 mg/L can be found in some aquifers [79]. In addition, Du et al. [25] applied redox potential (Eh) combined with DO and well depth as the basis for judging the redox state of groundwater and related nitrogen pollution. Such research can provide a reference for redefining the redox conditions in the study area in the future.

# 4.3. Other Factors Inducing High Level Ammonium-N Contamination

The reason for the high ammonium–N groundwater in this area deserves further discussion from other mobile-transformation characteristics and the diverse nitrogen sources. Ammonium is immobile to leaching and is not transported by water flow, except when a large amount of fertilizer is applied [3,80]. Yang et al. [81] proved that the ammonium leaching amount is higher because of the high concentration, which leaves the soil adsorption capacity close to saturation. Ağca et al. [82] also pointed out that ammonium–N is seldom present in excess of 1.0 mg/L in groundwater, unless ammonia fertilizer or wastewater is added to the water supply. In addition, ammonium movement in aquifers may be retarded by various physical, chemical, or biological processes [21] which may lead to much longer aquifer flushing times compared to other more mobile aqueous species [83].

Although no official statistics for the actual fertilization rate are available in the study area, interviews with farmers in this study and other research [84] revealed that nitrogen fertilization rates in many paddy fields were still higher than the official rationalized fertilization rates (120 kg N/ha for the first crop and 110 kg N/ha for the second crop), even up to twice the amount of rationalized fertilization. This over-fertilization has also been reported in related studies in other regions of Taiwan [85]. In addition, because a large number of livestock and poultry farms are located in mid- and distal-fan zones in the study area [86], livestock manure and poultry litter are easily and widely applied to neighboring farmlands, especially for upland crops. This may inevitably become a potential source of ammonium contamination in the groundwater. On the other hand, although high ammonium concentrations in reducing groundwater have been regarded as an indicator of influences from anthropogenic nitrogen sources, the abundance of natural organic matter in the buried peat layer or clay layer may also be a potential cause of elevated ammonium

concentrations which generate a reducing environment in aquifers [23,26]. The high organic matter content found in aquifers of finer grained sand in the study area has been reported by Chen and Liu [54]. This may result in higher DO consumption rate and a reducing environment in mid- and distal-fan zones of the study area.

Generally, anthropogenic sources (i.e., wastewater, chemical fertilizers, livestock manure, and poultry litter) and high organic matter content exhibited in geological formations may be potential sources of high ammonium–N in shallow groundwater. Moreover, after long-term intensive recharge by nitrogen-rich water into the groundwater, it is reasonable for ammonium to accumulate in the reducing aquifer owing to its retardation effect.

# 4.4. Tracing of Nitrogen Sources and Monitoring Network in Study Area

Previous studies have reported groundwater quality issues, with an emphasis on chemical characteristics and metal or nitrate contamination in the Choushui River alluvial fan [28,54,68,74,87]. In contrast, the evaluation of ammonium contamination in shallow groundwater is limited. However, this issue has gradually received attention. A recent study has noted the high concentrations of ammonium in the aquifers in this area and pointed out the risks it poses to different water uses [88]. Considering that the high concentrations of ammonium may be derived from natural or anthropogenic sources, tracing the potential sources and understanding the transport and transformation characteristics of ammonium in shallow groundwater will be helpful in formulating a more comprehensive nitrogen pollution control strategy in this area. Additionally, the monitoring wells of the Taiwan EPA are not evenly distributed in the study area to cover various cropping patterns, especially in the proximal fan, and are relatively rare, which will inevitably affect the possible nitrogen pollution monitoring and related bivariate regression analysis between nitrogen concentrations and other possible impact factors in this area. In fact, in other studies, based on monitoring records from other agencies, a considerable level of nitrate-N contamination was found in the proximal fan zone [28,54,88]. Therefore, it is recommended that the Taiwan EPA increases the number of shallow monitoring wells in specific areas to establish an integral monitoring well network.

# 5. Conclusions

The analysis revealed that ammonium-N contamination of shallow groundwater was much more severe than nitrate–N contamination in the study area. High levels of ammonium-N concentrations were observed in the double rice cropping and rotational cropping regions. Cropping pattern is not the sole factor determining ammonium–N or nitrate-N contamination in groundwater of the study area; instead, it may be an integrated process governed by several other factors. After the governmental agency actively implemented the rational fertilization policy, a significantly upward trend for both nitrogen concentrations were observed in only a few monitoring wells. In general, this policy has achieved a preliminary goal in controlling water quality that no longer continues to deteriorate for both nitrogen concentrations. Restoring groundwater quality will be a long-term process and more effort must be invested. Moreover, using a single threshold value of DO to determine the redox condition in shallow groundwater may be too arbitrary and cause misleading results in a complex agricultural area. Setting a possible range to replace a single threshold could better reflect the real nitrogen pollution conditions. It is suggested that tracing the actual sources of nitrogen pollution, especially ammonium–N contamination in shallow groundwater, should be implemented to formulate a more comprehensive nitrogen pollution control strategy in this area.

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