

Article

Nitrate Contamination in Groundwater: Evaluating the Effects of Demographic Aging and Depopulation in an Island with Intensive Citrus Cultivation

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Abstract: Despite rapid population aging and depopulation in Japan, groundwater nitrate contamination still poses serious environmental problems. One of the main factors contributing to elevated nitrate levels in Japanese groundwater sources is agricultural intensification, frequently because of increased fertilizer use. We investigated the impact of population aging and depopulation on groundwater nitrate contamination on a western Japanese island that has extensive citrus farming. In comparison to Ocho village, where the average age of farmers is 73 years, Kubi village's farmers are slightly older on average, at 76 years, and agricultural land has decreased by 46% over the past ten years, from 2005 to 2015. Ocho had 830 residents, which was twice as many as Kubi. In comparison to Ocho (4.8 mg/L), Kubi village had higher average $\text{NO}_3^- - \text{N}$ concentrations (6.6 mg/L). $\text{NO}_3^- - \text{N}$ contamination sources in Kubi and Ocho were determined using stable nitrogen isotopes and a Bayesian isotope mixing model. These source distributions were more strongly associated with social and land use factors. It was believed that the older farmers in Kubi employed a significant quantity of chemical fertilizers, which caused inefficient nitrogen uptake by plants, leading to increased leaching and more groundwater contamination than in Ocho.

Keywords: aging; depopulation; farmer activity; fertilizer; osakishimajima island; nitrogen isotope



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1. Introduction

In recent years, demographic trends have raised concerns with respect to the effects of population growth on water resources. Despite rapid global population growth, population densities are declining in some regions and the proportion of aged people in most developed countries is rising. However, Japan has experienced this demographic transition faster than most Western and Asian countries, with an increasing number of citizens over the age of 65 [1]. However, despite these changes in its demographics, it still faces serious environmental problems related to groundwater pollution, with nitrates being one of the more serious groundwater contaminants [2–4].

Agriculture-related nitrate contamination of groundwater is a widespread problem in many countries, and numerous studies have demonstrated the correlation between poor agricultural practices and high nitrate concentrations in groundwater [5–7]. Groundwater contamination occurs when nitrate (NO_3^-) input into the soil exceeds the nitrate consumption capacity of plants, resulting in nitrogen loss to the environment [8,9]. In Japan, use of chemical fertilizers has steadily increased since the 1960s [9]. As a result, the

effectiveness of nitrogenous fertilizers has diminished, and the nitrogen remaining in the soil after absorption by crops has leached into the groundwater in the form of nitrates. Demographic aging is a major socioeconomic problem in many regions of Japan [1] and has led to the increase in usage of chemical fertilizers to maximize production. Previously, high NO_3^- levels have been found in the groundwater in Japanese agricultural islands [1,10,11], which was associated with intensive cultivation methods. The widespread use of fertilizers by farmers was believed to be the primary source of groundwater contamination; however, agricultural farmland has varied sources of contamination input. To effectively manage and control NO_3^- pollution, it is important to identify its sources [12]. Sources of NO_3^- in agricultural fields can be classified into four groups: chemical fertilizers, nitrogen present in soil, atmospheric deposition of nitrogen, and manure and sewage [13–20]. Thus, examination of the different sources of NO_3^- in groundwater is crucial, especially for implementation of groundwater conservation measures [21].

In the past, conventional methods for determining the sources of groundwater NO_3^- relied on the association between types of land use and variations in groundwater chemical composition [22]. Based on this method, most nitrate sources were identified with a high level of uncertainty. Therefore, a technique has been proposed for identifying NO_3^- sources using N and O isotopes [23–25]. Different NO_3^- sources are characterized by their isotopic signatures, which provide a means of tracing point and nonpoint sources of contamination in ground and surface waters. However, a concern arose in relation to overlapping ranges of the $\delta^{15}\text{N}\text{-NO}_3^-$, which might lead to identification of inaccurate nitrate sources, thus compromising the usefulness of these isotopes alone. As a result, it was determined that $\delta^{18}\text{O}\text{-NO}_3^-$ could provide additional information for distinguishing nitrate from chemical fertilizers and atmospheric deposition because of its distinctive values compared to those of the overlapping N isotopes [25]. The isotopic compositions of N and O vary among different nitrate sources. Analysis of these isotopic compositions along with the NO_3^- content is an effective indicator for tracing the source of groundwater nitrate [15]. The typical ranges of $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ for various sources of NO_3^- pollution have been previously reported, following which the double isotope technique has been used to identify the sources of NO_3^- pollution in surface and groundwater [13,25–29]. Using these dual isotopes along with conventional tracing methods yields accurate results [30]. Overall, analysis of the isotopic composition of nitrates in groundwater can help in recognizing their sources such as synthetic or organic fertilizers, human waste or septic system effluents, and soil organic matter.

The Bayesian isotope mixing model has been used to calculate the proportionate contributions of the main nitrate sources in groundwater [16,31–35]. Previous studies have successfully used the $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ and the Bayesian isotopic mixing model to calculate the proportional contributions of the main sources of nitrates in groundwater samples [12,16,36]. The results have revealed that by using a Bayesian “fingerprint” for assessment of pollutants, the stable isotope analysis in R (SIAR) model could predict the proportional contributions of the probable NO_3^- sources. Nitrogen and oxygen isotopes can be used in conjunction with traditional methods to identify the sources of nitrates, and the SIAR model can be used to quantify the contributions of these sources of nitrate contamination in the groundwater to protect the ecosystem in intensive agricultural areas [12,35]. Nitrate contamination of groundwater and surface water in Osakishimojima Island is a cause for concern, as a previous study [11] has linked the elevated nitrate concentrations in water sources to the nitrogenous fertilizers used in citrus farms. Sometimes, the nitrate levels have been observed to exceed the World Health Organization’s [37] recommended guideline for maximum NO_3^- (50 mg/L) in drinking water or Japan’s recommended guideline for maximum NO_3^- –N concentration (10 mg/L) in water supplies. Hence, exploring the spatial variation of NO_3^- and its sources in two study sites with different extents of areas under cultivation could provide insights into the sources contributing to NO_3^- pollution on this island, which would help in the effective management of groundwater sources, particularly considering that the island has a declining and aging population.

The aims of this investigation were: (1) to demonstrate how the dual isotope approach ($\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$) can be used to determine the dominant sources of nitrates in the shallow groundwater of a small island and (2) to evaluate the influence of social aspects such as population aging and depopulation on NO_3^- concentrations in groundwater.

2. Description of Study Site

This study was conducted in Osakishimojima (34°10'24" N, 132°50'3" E), a small island located in the Seto Inland Sea in Hiroshima Prefecture, western Japan (Figure 1), approximately 20 km WSW of Kure City. Groundwater samples from two neighboring villages and watersheds, Ocho in the eastern part of the island and Kubi in the northern part, were analyzed. The population sizes of Kubi and Ocho were approximately 413 and 830, respectively, in 2021 [38], and the average age of farmers was 76 and 73, respectively [39]. Osakishimojima has a warm temperate climate with all four seasons characterized by cold winters and hot summers. The average annual temperature is 15.6 C° and the average annual precipitation is approximately 1100 mm.

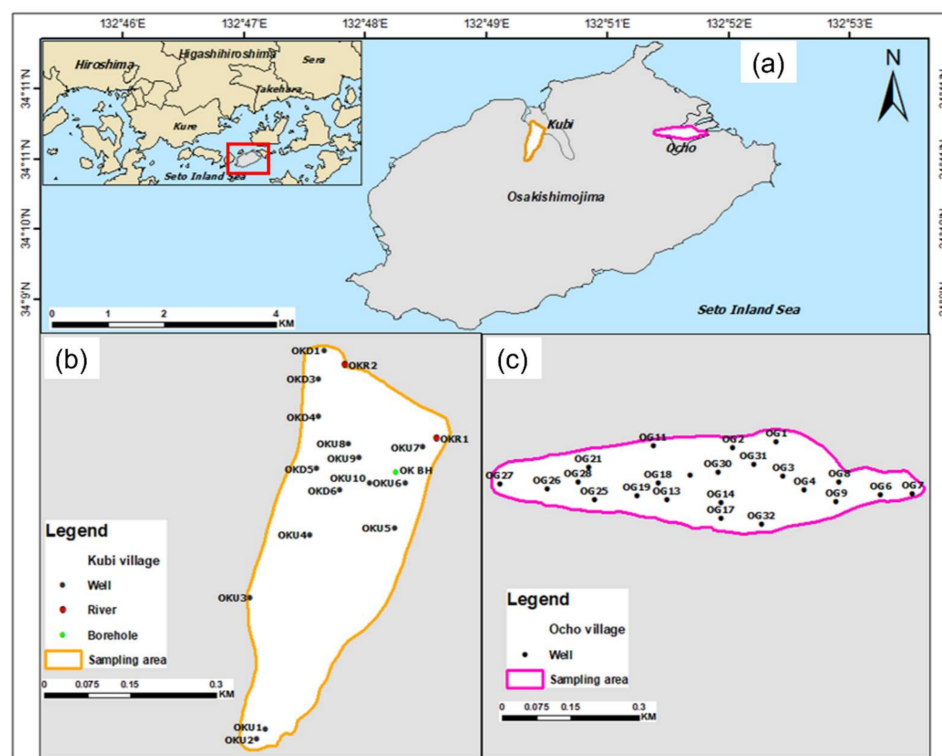


Figure 1. (a); Location map of Osakishimajima Island in the Seto Inland Sea showing the sampling points in (b); Kubi village and (c); Ocho village.

The land use of Osakishimajima Island includes areas allocated to citrus orchards, pine forests, residential areas, paddy weeds, and water bodies, and the proportions of these areas were 56.69, 36.46, 5.56, 0.82, and 0.49%, respectively [11]. Land use data were obtained from the Ministry of Land, Infrastructure, Transport, and Tourism of Japan [40] with a spatial resolution of 100 m, and detailed classification of land use was carried out using Google Earth to suit the purposes of this research. The agricultural land area in Ocho and Kubi was approximately 1.6 and 0.6 km², respectively, which has decreased by 37 and 46%, respectively, in 10 years [40]. Further, citrus orchards and residential areas in the lowlands of Ocho and Kubi comprised 35.2 and 56.7% and 45.4 and 43.3%, respectively (Figure 2). The residential areas in these regions mainly consisted of scattered villages with low urbanization levels and substandard sewage treatment facilities. In addition, Ocho village has higher building density and larger surface area than Kubi village (low housing density, random distribution). General information about the farmers' choice of fertilizers

and agricultural practices in each village was determined based on oral discussions with the farmers and the employees of the agricultural companies in these areas; however, no formal interviews were conducted at the study sites during the survey.

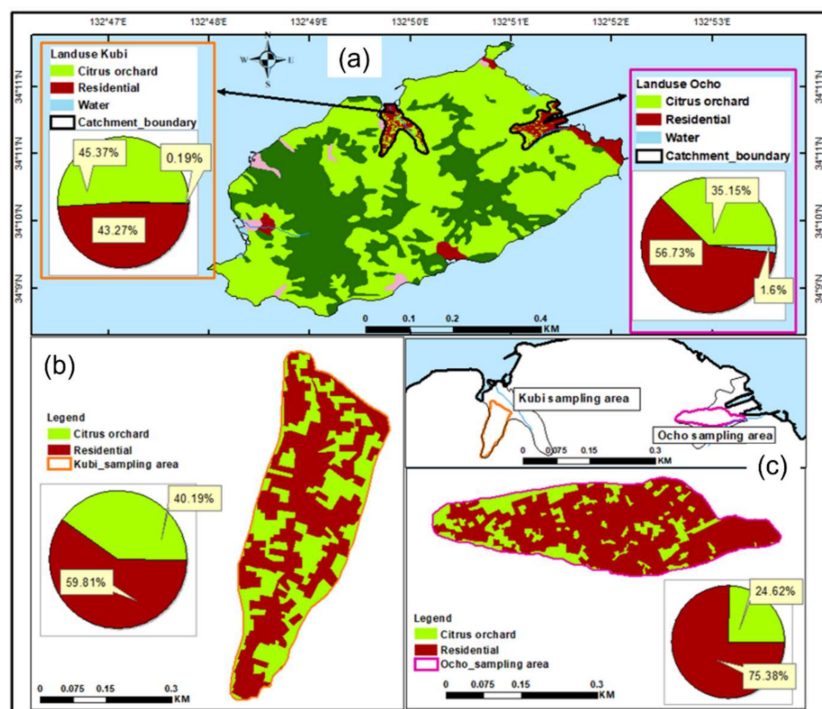


Figure 2. Land use of Osakishimojima, showing proportions of citrus orchards and residential areas in (a); Kubi and Ocho lowland areas, (b); Kubi sampling area, and (c); Ocho sampling area.

Hydrogeological data for the study sites were unavailable; thus, only the geological outcrops were examined. The main geological features of Osakishimojima Island are Late Cretaceous non-alkaline felsic volcanic rocks and rhyolites (Figure S1). They are found on mountain slopes, and Late Pleistocene to Holocene marine and non-marine formations cover the basement rocks in the lowland.

3. Materials and Method

3.1. Sample Collection

Fifty-two water samples were collected in the study area in October 2021, which included 32 sites comprising 2 springs and 30 shallow wells in the Ocho area and 20 sites in the Kubi area consisting of 1 observation borehole, 2 rivers, and 17 shallow wells (Figure 1). The sampling location, depth, and utilization information for each sampling site were determined from GPS coordinates. All wells chosen for groundwater sampling were commonly used for domestic and/or agricultural purposes; these wells had a mean depth of 10.8 m and 4.84 m in the Kubi and Ocho villages, respectively. The groundwater pH, temperature, electrical conductivity (EC), dissolved oxygen (DO), and oxidation-reduction potential (ORP) were measured on-site using a portable multiparameter water quality meter (pH/COND Meter D-54, HACH LD0101, ORP Meter RM-20P). All samples were collected from a 0.5–1 m depth below the water level in the wells using a high-density polyethylene sampler and filtered through a 0.2 µm membrane into one 250 mL, three 10 mL, and one 100 mL high-density polyethylene sampling bottles. After filtration, the samples were stored at 4 °C and subsequently transported to the laboratory, where they were frozen at −4 °C until further hydrochemical and isotopic analyses. The concentrations of the major cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) and anions (Cl^- , NO_3^- , and SO_4^{2-}) were analyzed by ion chromatography with conductivity detection on ICS-2100 (Dionex integrion, Thermo Fisher Scientific, Waltham, MA, USA). Analytical precisions for cations were set at <0.2%

for Na^+ and $<0.1\%$ for Ca^{2+} , Mg^{2+} , and K^+ , while for anions, they were $<0.1\%$ for NO_3^- and Cl^- and $<0.2\%$ for SO_4^{2-} . HCO_3^- was analyzed within 12 h of sample collection by acid titration using 0.02 N H_2SO_4 , which was added to the sample until it reached the endpoint at pH 4.5. Dissolved organic carbon (DOC) was determined using a total organic carbon analyzer (Total Organic Carbon analyzer, SHIMADZU, Hiroshima University, Japan). The analyses of major ions and DOC were conducted at the Biogeochemistry Laboratory, Hiroshima University, Japan.

Isotope analyses were performed at the Institute of Geosciences, Yamanashi University, using a stable isotopic ratio mass spectrometer (MAT 253, Thermo Fisher Scientific, Waltham, MA, USA). Chemical reduction (cadmium and azide reduction) was used to quantify $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$, respectively [41,42]. Briefly, to eliminate nitrite, the samples were treated with a 2.5 mmol/L sulfamic acid solution. The NO_3^- in the samples was then quantitatively converted to gaseous nitrous oxide (N_2O) using a two-step reduction process. First, NO_3^- was reduced to nitrite with spongy cadmium, then nitrite was converted to nitrous oxide with an azide/acetic acid buffer, and finally, the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of N_2O were determined. The stable isotope ratios of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ were given in delta value (δ) and per mil (‰) notation in comparison to international standards as follows [13]:

$$\delta_{\text{sample}}(\text{‰}) = \left[\left(R_{\text{sample}} / R_{\text{standard}} \right) - 1 \right] \times 1000 \quad (1)$$

where R_{sample} and R_{standard} are the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of the samples and standards for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively. The $\delta^{15}\text{N}$ values were reported relative to N_2 in atmospheric air (AIR) and the $\delta^{18}\text{O}$ values relative to Vienna Standard Mean Ocean Water (VSMOW). The precision values for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ were $\pm 0.3\text{‰}$ and $\pm 0.4\text{‰}$, respectively. Two representative samples of organic and chemical fertilizer were collected from local farmers in Kubi village in January 2022 for analysis as end-member samples. The solid samples were transported to the laboratory for air-drying and then fully ground for chemical and isotopic analyses. The solid samples were converted to N_2 by high-temperature redox reactions, and $\delta^{15}\text{N}$ - N_2 was measured using an isotopic ratio mass spectrometer. The precision for $\delta^{15}\text{N}$ was $\pm 0.3\text{‰}$.

3.2. Source Apportionment Calculation

The Stable Isotope Analysis in R (SIAR) software program was used to develop the mixing model. The system model used in SIAR can be expressed by defining a set of N mixture measurements on J isotopes with K source contributors, and the mixing model can be expressed as follows [25]:

$$\begin{aligned} X_{ij} &= \sum_{k=1}^K P_k (P_{jk} + C_{jk}) + \varepsilon_{jk} \\ S_{jk} &\sim N(\mu_{jk}, \omega_{jk}^2) \\ C_{jk} &\sim N(\lambda_{jk}, \tau_{jk}^2) \\ \varepsilon_{jk} &\sim N(0, \sigma_j^2) \end{aligned} \quad (2)$$

where X_{ij} is the isotope value j of mixture i , in which $i = 1, 2, 3, \dots, I$ and $j = 1, 2, 3, \dots, J$; S_{jk} is the source value k of isotope j ($k = 1, 2, 3, \dots, K$) and is normally distributed with a mean value μ_{jk} and a standard deviation ω_{jk} ; P_k is the proportion of source k , which was estimated using the SIAR model; C_{jk} is the fractionation factor for isotope j of source k and is normally distributed with a mean value λ_{jk} ; τ_{jk} is the standard deviation; and ε_{ij} is the residual error representing the additional unquantified variation between individual mixtures and is normally distributed with a mean value of 0 and a standard deviation σ_j . Details of this model have been described in previous studies [8,43].

A Bayesian model was applied to determine the potential NO_3^- contribution from each of four sources for Kubi and Ocho villages: $\delta^{15}\text{N}-\text{NO}_3^-$ in manure and sewage (M&S), chemical fertilizer (CF), and organic fertilizer (OF); and soil nitrogen (SN) $\times (k = 4)$. The end-member isotopic compositions for the three sources were used ($j = 3$) in the model setup. SN and M&S samples were not analyzed in the study area, so the SN values [25,33–35] were compared with the N present in the CF samples, and because similar values were obtained, they were considered as a single source (CF_SN) of N in this study area. The M&S values were obtained from the published literature and used in the model as an additional source. We considered M&S to be a suspension of water and solid waste from humans and animals transported by sewers and OF exclusively to be a mixture of chicken litter and sawdust. Although discrete samples of individual $^{15}\text{N}_{\text{NO}_3}$ sources in the study area were measured, the limited number obtained may induce a biased model outcome. Alternatively, the mean values of $\delta^{15}\text{N}-\text{NO}_3^-$ isotopes (μ_{jk}) and associated SDs (ω_{jk}) of different M&S were acquired by consulting previously published data [25,33–35], whereas CF and OF were obtained from the Kubi area.

3.3. Statistical Method

Statistical analysis was performed to determine the NO_3^- –N relationship with DOC and the major ions using a scattered plot, which was demonstrated by the coefficient of determination (R^2). In addition to correlation analysis, principal component analysis (PCA) was used to analyze groups of ions based on similarities or differences in concentrations. SPSS® ver. 23.2 (SPSS Inc., Chicago, IL, USA) was used to analyze the groundwater chemical data. PCA can explain most of the variability in a dataset with fewer variables than the original dataset, so parameters with similar loadings in the same principal component (PC) group may have similar contributory sources or geochemical behaviors [44,45]. PCA was used to identify the primary groundwater contamination indicators using the Kaiser varimax rotation method, which only accepts PCs with eigenvalues greater than one. An inverse distance weighting method (IDW) was also performed using ArcMap 10.6 to show the spatial distribution of NO_3^- –N and $\delta^{15}\text{N}-\text{NO}_3^-$ in Kubi and Ocho groundwaters.

4. Results and Discussion

4.1. General Hydrochemistry

The hydrochemical compositions of Kubi and Ocho are summarized in Table 1. The results showed that the pH of groundwater was near neutral in Kubi (6.4 to 7.5, mean pH 6.8). The pH values of the river water sample were neutral to alkaline (7.9 to 8.6) and higher than the groundwater pH values, which may be due to the strong evaporation of the surface water. In Ocho village, groundwater was slightly acidic to alkaline with pH values ranging from 6.2 to 8.5 with a mean of 6.7. All samples had moderate EC values varying from 106.3 to 472 $\mu\text{S}/\text{cm}$, (mean 306.7 $\mu\text{S}/\text{cm}$) in Kubi and 164.9 to 479 $\mu\text{S}/\text{cm}$ (mean 308.5 $\mu\text{S}/\text{cm}$) in Ocho. The concentrations of total dissolved solids (TDSs) were estimated from the EC values using the equation mentioned by Evangelou [46] and are shown in Table 1. The DOC levels of groundwater in Kubi ranged from 2.5 to 13.33 mg/L (mean 5.1 mg/L), while those in Ocho ranged from 1.6 to 7.0 mg/L (mean 3.5 mg/L). The DO ranged from 1.1 mg/L to 8.6 mg/L with a mean of 4.9 in the wells in Kubi, while those in Ocho ranged from 0.8 mg/L to 9.1 mg/L with a mean value of 3.4 mg/L. All but one sample from Kubi had DO values above 2 mg/L, whereas in Ocho, nine samples had values less than 2 mg/L. Additionally, observed DO levels were higher in naturally occurring springs (mean 9.2 mg/L in Kubi and 8.6 mg/L in Ocho). Hence, groundwater samples in Ocho had the potential to undergo denitrification processes as opposed to those in Kubi.

Table 1. Statistical characteristics of the hydrochemical compositions of the groundwater and surface water sources in Kubi and Ocho village. For values of individual samples, see Table S1 of Supplementary Materials.

Parameters	Kubi Village											Ocho Village										
	Spring (<i>n</i> = 1)	River (<i>n</i> = 2)					Wells (<i>n</i> = 17)					Borehole (<i>n</i> = 1)	Spring (<i>n</i> = 2)					Wells (<i>n</i> = 30)				
	Min/Max	Min.	Max.	Ave.	Med.	SD	Min.	Max.	Ave.	Med.	SD	Min/Max	Min.	Max.	Ave.	Med.	SD	Min.	Max.	Ave.	Med.	SD
pH	7.3	7.9	8.6	8.3	8.3	0.5	NM	7.4	6.8	6.7	0.4	7.5	7.5	7.5	7.5	7.5	0	6.2	8.5	6.8	6.7	0.5
Temp	19.1	23.7	24.7	24.2	24.2	0.8	18.1	26.7	21.2	20.7	2.4	19	17.6	23.6	20.6	20.6	4.3	19.2	28.3	22.3	22.3	1.7
EC	185.7	206	274	240	240	48.1	107	465	314.8	321	94.2	472	133	217	175	175	59.4	165	479	308.5	317.5	72.7
TDS	118.9	131.9	175.4	153.6	153.6	30.8	68.5	297.6	201.5	205.5	60.3	302.1	85.2	138.9	112	112	38.1	105.6	306.6	105.6	203.2	46.5
DO	9.2	8.3	9	8.7	8.7	0.5	1.1	8.7	5	4.7	2.1	6.1	7.7	9.5	8.6	8.6	1.3	0.8	9.1	3.5	3	2.3
DOC	3.6	3.8	5.3	4.6	4.6	1.1	2.5	13.3	5.1	4.1	3.1	4.1	NM	3.5	3.5	3.5	0	NM	7	3.3	3.2	1.4
Cl [−]	14.7	9.4	11.1	10.3	10.3	1.3	7.6	34	11.9	9.9	6.2	13.4	4.6	10.9	7.8	7.8	4.5	4.1	37.5	11.9	11.2	6.4
SO ₄ ^{2−}	22.9	30.5	50.4	40.5	40.5	14.1	22.1	75.3	44.4	38.8	16.6	80.7	4.5	22.9	13.7	13.7	13.1	—	145.1	37.7	27	28.2
NO ₃ [−]	7.1	12.4	34.2	23.3	23.3	15.5	14.9	74.5	41.5	35.5	19.3	70.3	2.7	13.7	8.2	8.2	7.8	3.5	66.4	21.7	19.7	13.4
NO ₃ [−] –N	1.7	2.9	7.8	5.4	5.4	3.5	3.4	16.9	9.5	8.1	4.4	15.9	0.7	3.1	1.9	1.9	1.7	0.8	15.1	5	4.5	3.1
HCO ₃ [−]	7.2	50.6	61.2	55.9	55.9	7.5	—	121.6	48.6	45.3	24.5	39.1	4	9.3	6.7	6.7	3.8	4.5	150.2	64.2	69.7	45.4
Na ⁺	21	16.3	18.3	17.3	17.3	1.5	9.4	32.5	15.7	13.7	7	31.4	—	5.5	2.8	5.5	3.9	9.4	57.6	18.6	16.7	9.2
K ⁺	2.2	3.2	3.6	3.4	3.4	0.3	0.7	6.9	4.1	4.3	1.9	1	3.2	8.4	5.8	5.8	3.7	0.3	10.5	4.1	4	2.9
Mg ²⁺	9.8	8.2	10.7	9.5	9.5	1.8	7	17.8	11.5	11	3.2	17.8	1.4	25.8	13.6	13.6	17.3	4.9	22.2	10	7.9	5
Ca ²⁺	24.6	22.3	30	26.2	26.2	5.5	20.4	48.4	31.7	30.6	9.1	44.8	—	4.6	4.6	4.6	0	—	50.8	28.8	28	11.6

Note: *n* = number of samples; SD = standard deviation; — = below detection limit; NM = not measured; ionic concentrations, DOC, and DO = mg/L; EC = μ S/cm; Temp = °/C.

Calcium was the most dominant cation in both study areas and ranged from 7.8–38.1 mg/L in groundwater samples and from 9.8 mg/L–35.5 mg/L in surface water samples in Kubi while in the Ocho area, concentrations ranged from 0.5 mg/L–4.6 mg/L in surface water and from 8.8 mg/L–50.8 mg/L in groundwater samples. Magnesium concentrations ranged from 1.6 mg/L–15.3 mg/L in groundwater samples and 4.5–14.4 mg/L in surface water in Kubi whereas in Ocho village, these concentrations were much lower, varying from 4.9 mg/L–22.2 mg/L in groundwater samples (Table 2). Calcium and magnesium can contaminate groundwater through ion exchange when minerals dissolve in rocks or when fertilizers run off and leach into the groundwater. According to Earle [47], soils containing CaCO_3 and CaSO_4 have high levels of Ca^{2+} in the groundwater because of leaching, and Keesari et al. [48] suggested that agricultural runoff and sewage disposal may lead to high Mg^{2+} levels in the groundwater. The most abundant anion detected in the water samples from both villages was HCO_3^- . In the Kubi area, concentrations of HCO_3^- in the river samples ranged from 50.6–61.2 mg/L with a mean value of 55.9 mg/L, while HCO_3^- concentrations in wells ranged from 14.2–121.6 mg/L with a mean value of 45.3 mg/L (Table 1). Bicarbonate concentrations in Ocho ranged from 4.5 to 64.2 mg/L in the wells and from 4 to 9.25 mg/L in the spring samples. The dissolved species in the samples obtained from both villages (arranged in sequence from highest to lowest average concentrations) were $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ cations and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ anions. The chemical compositions of the water samples from Kubi and Ocho villages were examined and classified using trilinear plots (Figure 3).

Table 2. Principal component (PC) loadings of 11 chemical variables for groundwater samples in Kubi and Ocho villages.

PCs Kubi Village (21 Samples)				PCs Ocho Village (32 Samples)			
Variables	PC1	PC2	PC3	Variables	PC1	PC2	PC3
pH	−0.098	0.396	0.663	pH	−0.088	−0.242	0.768
TDS	0.783	−0.379	0.309	TDS	0.542	0.686	0.141
DO	−0.209	0.766	0.105	DO	0.035	−0.726	0.382
$\text{NO}_3^- - \text{N}$	0.903	−0.05	−0.119	$\text{NO}_3^- - \text{N}$	0.815	0.058	−0.033
Cl^-	0.407	0.398	−0.528	Cl^-	0.376	0.723	0.067
SO_4^{2-}	0.914	−0.018	−0.001	SO_4^{2-}	0.922	0.041	−0.067
HCO_3^-	−0.117	−0.603	0.574	HCO_3^-	−0.131	0.798	−0.002
Na^+	0.823	0.394	0.117	Na^+	0.683	0.517	−0.047
K^+	−0.167	−0.747	−0.375	K^+	−0.109	−0.144	−0.787
Mg^{2+}	0.917	−0.099	−0.13	Mg^{2+}	0.719	0.124	0.055
Ca^{2+}	0.673	−0.051	0.29	Ca^{2+}	0.754	−0.023	0.102
Eigen value	4.5	2.2	1.5		4.3	2	1.3
EV	40.9	19.5	13		38.2	18	11.7
CV	40.9	60.3	73.2		38.2	56.2	67.8

EV: explained variance (%); CV: cumulative% of variance; bold and italicized numbers: maximum absolute PC loading of one parameter.

The two groundwater facies in the Kubi area were $\text{Ca}-\text{HCO}_3$ and $\text{Ca}-\text{SO}_4$ water types, comprising 55 and 45% of the water samples, respectively. Meanwhile, the trilinear analysis for Ocho village suggested that 58.7% of the water samples were composed of $\text{Ca}-\text{HCO}_3$ water type, while 41.3% of the water samples were plotted in the zones of $\text{CaMg}-\text{SO}_4$ or $\text{CaMg}-\text{Cl}$ water types. Groundwater samples from both areas showed high percentages of freshwater signatures in the $\text{Ca}-\text{HCO}_3$ zone; however, they showed susceptibility to anthropogenic contamination as they were placed between $\text{Ca}-\text{HCO}_3$ and $\text{CaMg}-\text{SO}_4$ or $\text{CaMg}-\text{Cl}$ types in the trilinear plots.

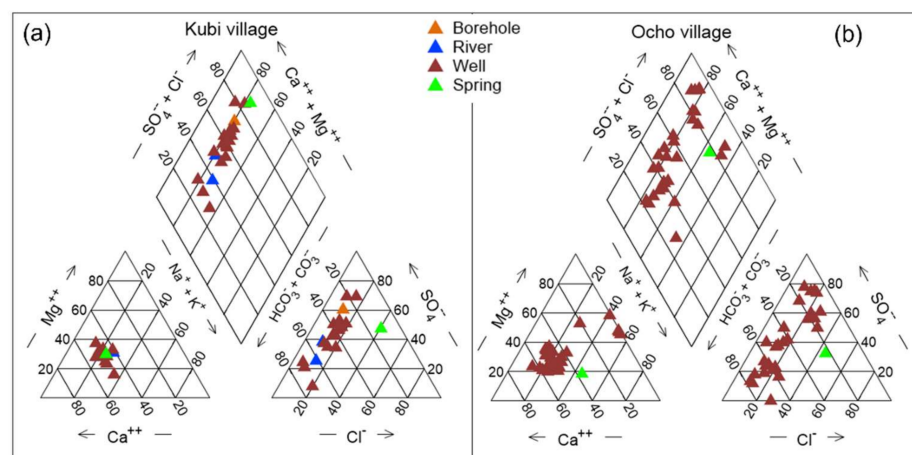


Figure 3. Piper diagram of surface water and groundwater in (a) Kubi and (b) Ocho (adapted from Piper [49]).

4.2. Spatial Variations in the NO_3^- –N Concentration

When the nitrate nitrogen (NO_3^- –N) concentration exceeds the threshold value of 3 mg/L, it is deemed to be affected by human factors [24,50]. NO_3^- –N concentrations were calculated by converting NO_3^- to NO_3^- –N using the equation documented by Kimbi et al. [11]. A mean value of 6.6 mg/L and a median value of 6.5 mg/L were observed in Kubi, with NO_3^- –N concentrations ranging from 0.5–13 mg/L (Table S1). Approximately 33.3% of the groundwater samples had NO_3^- –N concentrations below 5 mg/L, 47.7% of the samples had concentrations ranging between 5–10 mg/L, and 19% of the samples had concentrations above 10 mg/L. Meanwhile, NO_3^- –N concentrations in Ocho varied from 0.7–15.1 mg/L with mean and median values of 4.8 and 4.5 mg/L, respectively. These concentrations were much lower than those of Kubi. In Ocho village, over 62.5% of the groundwater samples had NO_3^- –N concentrations less than 5 mg/L, 31.3% of the samples had concentrations between 5 and 10 mg/L, and 6.2% of the samples had NO_3^- –N concentrations above 10 mg/L. As shown in Figure 4b, most of the samples showing higher concentrations of NO_3^- –N were collected from sites located upstream of the lowland area, which was directly below the upland citrus cultivation zone.

Leaching of chemical fertilizers into the groundwater, which are subsequently transported downstream, could be responsible for the elevated NO_3^- –N concentrations in Kubi. In contrast, Ocho village had lower NO_3^- –N concentrations, with some sampling points showing relatively high NO_3^- –N concentrations, including upstream, midstream, and downstream sampling points (Figure 4c). Groundwater contamination was likely caused by organic fertilizer inputs or leakages from the septic systems. The NO_3^- –N concentration was observed to be between 3 and 8 mg/L at well depth between 4 and 6 m (Figure 5).

A pattern could be observed in Kubi, where groundwater NO_3^- –N concentrations gradually increased from deep to shallow water depths, but in some samples, high concentrations were observed in the samples collected from deep water layers. These results indicate variations in NO_3^- –N residence time in the groundwater system. The topography and hydrogeological properties of the aquifer might equally be influencing the distribution of groundwater contaminants [51]; however, this relationship could not be confirmed in this study because of unavailability of data. In Ocho, NO_3^- –N concentrations did not change significantly with depth, and results for most samples were plotted at 5 m depth.

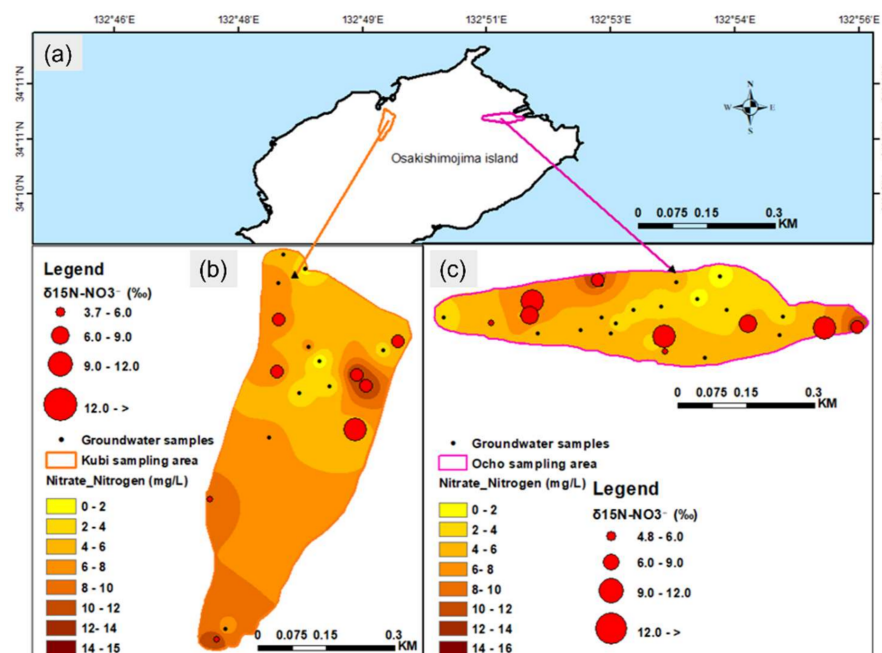


Figure 4. (a) Osakishimojima Island, Spatial variation of $\text{NO}_3^- - \text{N}$ and $\delta^{15}\text{N} - \text{NO}_3^-$ concentrations in groundwater of (b) Kubi and (c) Ocho villages.

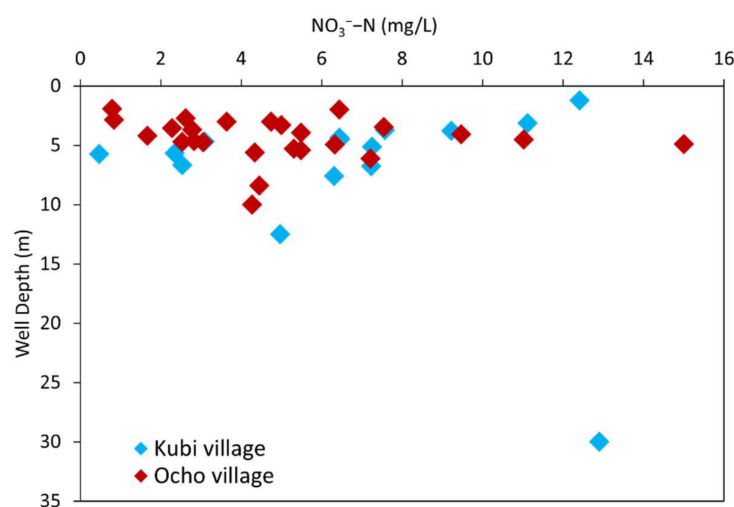


Figure 5. $\text{NO}_3^- - \text{N}$ concentration vs. well depth in shallow wells in the study area.

4.3. Relationship between $\text{NO}_3^- - \text{N}$ and Water Chemical Parameters

A correlation matrix table is presented in Table S2 for all samples. The relatively high concentration of $\text{NO}_3^- - \text{N}$ in the Kubi groundwater is consistent with the significantly elevated concentrations of Mg^{2+} , Ca^{2+} , and SO_4^{2-} (Figure 6). There was a weak positive association among $\text{NO}_3^- - \text{N}$, DOC, and Cl^- in both Kubi and Ocho villages. In the absence of a geological chloride source, nitrate and chloride are frequently utilized as indicators of anthropogenic groundwater contamination because of their positive correlations. While chloride is a conservative tracer that does not normally undergo biological transformation in groundwater, the denitrification process can reduce the nitrate concentration in groundwater [52,53]. Thus, the presence of this process in the groundwater samples from Kubi and Ocho might have reduced the degree of correlation between the parameters shown in Figure 5. Furthermore, the positive relationship between $\text{NO}_3^- - \text{N}$ and SO_4^{2-} could be due to the use of chemical fertilizers such as $(\text{NH}_4)_2\text{SO}_4^{2-}$ [50]. A positive relationship has been suggested among NO_3^- , Mg^{2+} , and Ca^{2+} [34], indicating that they are

derived from chemical fertilizers, such as CaCO_3 and MgCO_3 . In Kubi, concentrations of $\text{NO}_3^- - \text{N}$ showed strong significant positive correlations with SO_4^{2-} ($R^2 = 0.76$, $p < 0.01$) as opposed to Ocho, which presented a weak significant positive relationship ($R^2 = 0.45$, $p < 0.01$). These results are corroborated by the findings of earlier studies [54,55], which have reported correlations between SO_4^{2-} and NO_3^- concentrations in groundwater.

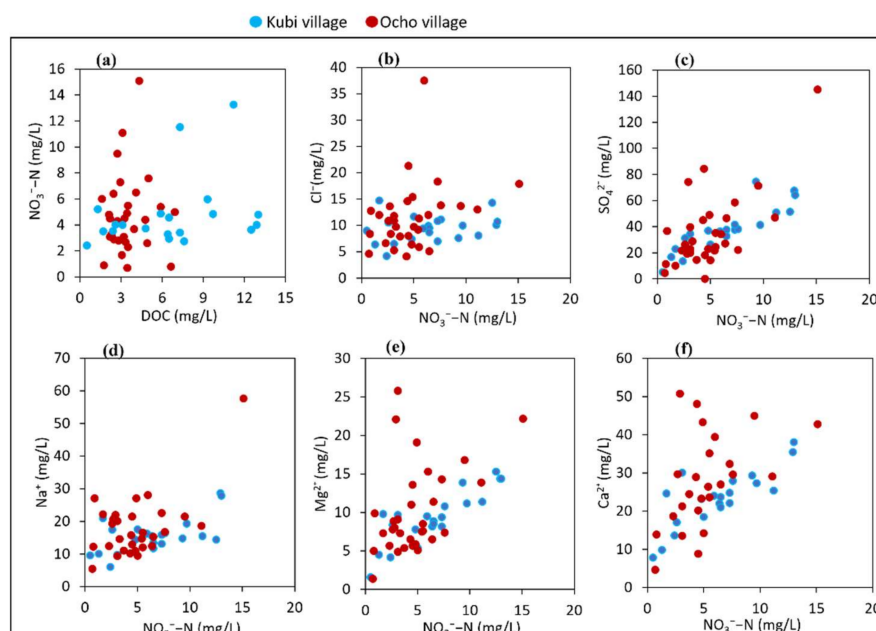


Figure 6. Relationship between $\text{NO}_3^- - \text{N}$ and (a), DOC, (b), Cl^- , (c), SO_4^{2-} , (d), Na^+ , (e), Mg^{2+} , and (f), Ca^{2+} in groundwater samples of Kubi and Ocho villages.

More chemical fertilizers may be used in Kubi since the chemical fertilizer derived component was higher in Kubi than Ocho. These results are corroborated by the findings of earlier studies [54,55], which have reported correlations between SO_4^{2-} and NO_3^- concentrations in groundwater, indicating that locations with high SO_4^{2-} concentrations also have high NO_3^- concentrations. Another study [56] found that the application of CaCO_3 fertilizer generated a positive relationship between NO_3^- and Ca^{2+} . Similarly, in Kubi village ($R^2 = 0.63$, $p < 0.01$), there was a considerable positive correlation between $\text{NO}_3^- - \text{N}$ and Ca^{2+} compared to that in Ocho ($R^2 = 0.22$, $p < 0.01$), confirming inputs from chemical fertilizers. K^+ showed no correlation with $\text{NO}_3^- - \text{N}$ in both study sites.

4.4. Principal Component Analysis Results

A three-factor model controlled the groundwater chemistry in Kubi, and the cumulative variance of the three PCs was 73.2% (Table 2). In Kubi, PC1 explained 40.9% of the total variation, with positive loadings of six variables in the order $\text{Mg}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- - \text{N} > \text{Na}^+ > \text{TDS} > \text{Ca}^{2+}$ (Table 2). A strong positive loading of Mg^{2+} and SO_4^{2-} and a moderate positive loading of Ca^{2+} and TDS suggests a high level of mineralization of groundwater from natural sources, whereas a strong positive loading of $\text{NO}_3^- - \text{N}$ indicates anthropogenic pollution because of agricultural activities, such as fertilizer and manure usage and land use [57]. Several studies [44,47,58] have linked domestic sewage and agricultural fertilizers to the presence of Na^+ , Mg^{2+} , K^+ , SO_4^{2-} , NO_3^- , and Cl^- in groundwater. Thus, PC1 was denoted by the infiltration of agricultural fertilizers and domestic sewage. PC2, accounting for 19.5% of the total variance, showed a moderate positive loading for DO and a moderate negative loading for K^+ . PC3 explained 13% of the total variance, with a moderate loading of pH. The groundwater chemistry of Ocho was also studied using a three-factor model, and the cumulative variance explained by the three PCs was 67.8%

(Table 2). PC1, accounting for 38.2% of the total variance, showed strong loadings for SO_4^{2-} and $\text{NO}_3^- - \text{N}$ and moderate loadings for Ca^{2+} , Mg^{2+} , and Na^+ .

Although these variables can be interpreted as anthropogenic contamination from agricultural fields, these loadings were lower in comparison to the loadings of PC1 in the Kubi area, possibly because of differences in the rates of leaching and residence times of contaminants in the groundwater systems. PC2 explained 18% of the total variance with moderate positive loadings of three variables (HCO_3^- , Cl^- , and TDS) and a negative loading of DO. We believe that the dissolution of carbonate rocks due to water–rock interactions was responsible for the loading of HCO_3^- , while domestic sewage was the source of Cl^- . The third PC, which accounted for 11.7% of the total variance in Ocho village, had moderate positive and negative loadings for pH and K^+ , respectively. The results of the PC analysis indicate that natural processes involving mineral components and anthropogenic contamination because of fertilizers and domestic sewage are the main processes affecting the groundwater chemistry in Kubi and Ocho.

4.5. Distribution Characteristics of Stable Isotopes

Ten samples from Kubi (one river and nine well samples) and nine well samples from Ocho were analyzed for $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ (Table S3). Samples were selected primarily on the bases of nitrate levels and spatial distribution to represent each study site. The $\delta^{15}\text{N}-\text{NO}_3^-$ values of Osakishimajima Island showed high variability in the Kubi and Ocho villages (Figure 3). In Kubi village, the $\delta^{15}\text{N}-\text{NO}_3^-$ values of groundwater samples ranged from 3.7‰ to 13.3‰, with a mean value of 6.7‰, and the $\delta^{18}\text{O}-\text{NO}_3^-$ values ranged from −1.0‰ to 2.8‰, with a mean value of 1.5‰. Similarly, in Ocho village, the $\delta^{15}\text{N}-\text{NO}_3^-$ values ranged from 4.9‰ to 26.0‰, with a mean value of 11.4‰, and the $\delta^{18}\text{O}-\text{NO}_3^-$ values ranged from 0.1‰ to 14.9‰, with a mean value of 5.3‰ (Table S3). A relatively high value of $\delta^{15}\text{N}-\text{NO}_3^-$ (26‰) in sample OG6 may suggest other controlling processes in the catchment area, such as denitrification; however, since the sample size was small, it was excluded from further analysis to avoid bias estimation, especially in the SIAR model. The mean values of $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ in Kubi village were significantly lower than those in Ocho village. This was contrary to the spatial distribution of $\text{NO}_3^- - \text{N}$ concentrations (Figure 3). The reason for this is that more chemical fertilizers with lower isotopic values and faster leaching rate were used for citrus cultivation in Kubi than in Ocho. In general, the leaching rate is determined by the degree of water solubility of a fertilizer in combination with the amount of soil water at any time, soil type, porosity, and compaction [59]. Kubi and Ocho have the same soil type and soil properties, but due to the differences in their choice of fertilizer, variations in $\text{NO}_3^- - \text{N}$ concentrations may arise. Highly soluble fertilizers dissolve quite rapidly into the soil and since plants can only absorb a certain amount of nutrition at a time, a greater percentage of the fertilizer simply leaches through the soil into the groundwater. The nitrate sources were identified from the cross-plot of $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ (Figure 7). Most of the data points were plotted in the range of synthetic fertilizer and soil nitrogen in Kubi village, while in Ocho village, points were plotted mainly in the manure and sewage domain. This suggests that the major inputs of NO_3^- are from synthetic fertilizer in Kubi, whereas in Ocho, they are mainly from organic fertilizer. The groundwater chemistry in Figure 5 indicates that more chemical fertilizer was used in Kubi than in Ocho, which explains the significant differences in the isotopic values between the sites. Additionally, higher $\delta^{15}\text{N}-\text{NO}_3^-$ concentrations may have been derived from sewage systems, whose end-member samples were not measured in this study.

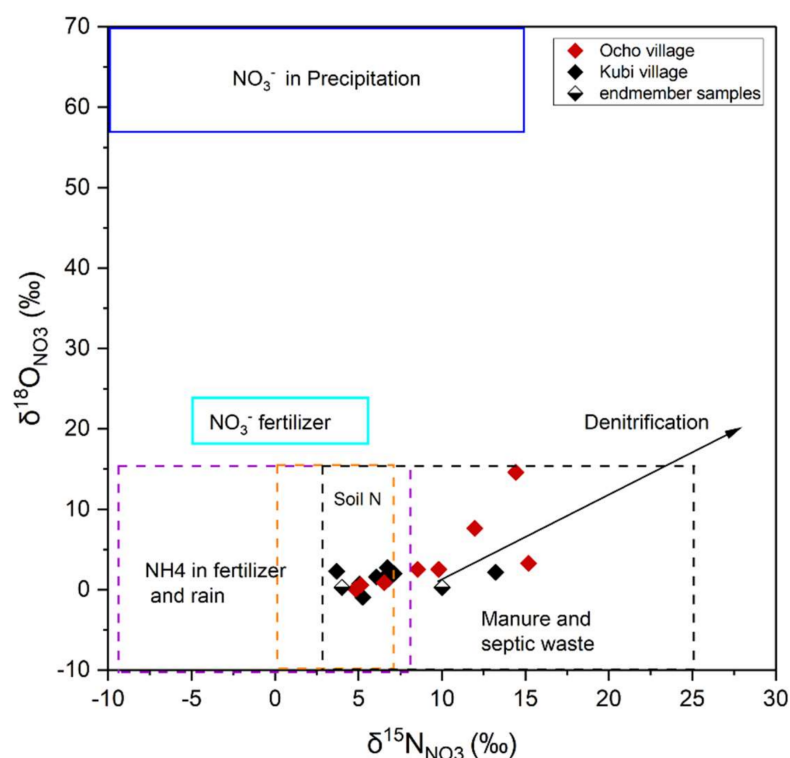


Figure 7. Nitrate isotopic signatures for sampling points in Kubi and Ocho with typical nitrate endmembers (adapted from Kendall et al. [25]).

Ocho has a higher housing density than Kubi (Figure 2), and since the area is a rural depopulating and aging community, the sewage system was poorly managed, and contamination of the groundwater system could have occurred because of leakages through worn-out pipes. According to the Kure City Water Works and Sewerage Bureau [60], Kubi has a local wastewater treatment plant, whereas Ocho depends solely on septic treatment tanks. Considering the housing density in Ocho, sewer discharge into the groundwater is more likely. The difference in the age structure and population size influences farming practices, such as the method of fertilizer and pesticide application and the application schedule, which are important processes for quality crop yields. Chemical fertilizers are water soluble which makes them readily available for plant uptake than organic fertilizers; thus, aged farmers prefer to use chemical fertilizers that are more cost-effective, less time consuming, and more convenient for maximum crop yield. However, because the nutrient requirements for plant growth, productivity, and fruit quality fluctuate seasonally, the split fertilization method is commonly utilized in citrus farming [61]. While this strategy is acceptable and reduces inorganic N leaching while boosting N use efficiency [62], it necessitates the utilization of an additional labor force, which is unsuitable for Kubi and Ocho as the population is both declining and aging [37,38] with a limited crop production labor force. In studies conducted in China by [62,63], the association between fertilization application methods, population aging, and restricted labor force has been observed. However, the fact that Kubi farmers tend to use more fertilizer may possibly be because of their lower population size when compared to Ocho [38].

Additionally, the proportion of area under cultivation may influence the quantity of fertilizer applied, subsequently contributing to elevated $\text{NO}_3^- - \text{N}$. As observed in Figure 2, Kubi has approximately 40.2% of its total area occupied by orchard fields, which is twice the coverage area than that of Ocho village, and even though at the catchment scale, Ocho has almost thrice the agricultural land than Kubi [40], the pathways of nitrate in the two study sites may be different. Nevertheless, the overlapping $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values of the different sources hinder the quantitative estimation of their contributions. Furthermore, a previous study reported related investigations and concluded that the link

among $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and NO_3^- is a complex web in which all environmental settings should be considered to accurately distinguish between different biogeochemical processes [16]. Hence, biological and geochemical processes may occur simultaneously in Ocho village, resulting in a shift in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ levels.

4.6. Source Apportionment of NO_3^-

The proportional contributions of NO_3^- sources in groundwater were identified using the SIAR model. Two isotopes ($J = 2$) ($\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$) and three potential sources ($K = 3$) (OF, CF_SN, and M&S) were used to estimate the contributions of NO_3^- sources in Kubi and Ocho village. The $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ of groundwater samples (Table S3) and sources (both mean and SD in Table 3) were input into the SIAR model.

Table 3. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of various nitrate sources.

Source	$\delta^{15}\text{N}$ (‰)		$\delta^{18}\text{O}$ (‰)	
	Mean	SD	Mean	SD
^b Soil nitrogen (SN)	4.4	0.7	2.85	0.2
^a Chemical fertilizer (CF)	4	0.3	2.85	0.4
^{a,b} Chemical fertilizer_Soil nitrogen (CF_SN)	4.2	0.5	2.9	0.3
^a Organic fertilizer (OF)	10	0.3	2.85	0.4
^b Manure and sewage (M&S)	19	0.3	−12.51	0.4

^a The theoretical values analyzed and ^b data sources [25,33–35].

Sewage was not measured in the study area; however, considering the residential area in one of the study sites, we applied the literature value for the model, while atmospheric deposition was not considered. Furthermore, the fractionation factor C_{jk} was set to zero because we did not investigate to determine its value. The results of source apportionment are shown in Figure 8.

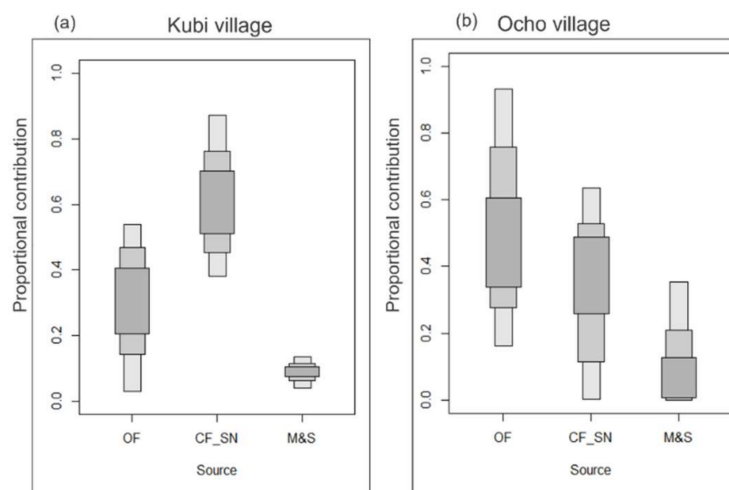


Figure 8. Spatial proportional contributions of NO_3^- sources estimated using SIAR in (a); Kubi and (b); Ocho village. Boxplots illustrate the 50th, 75th, and 95th percentiles from dark to light.

The source contributions showed significant spatial variation under similar cropping systems with different land use proportions. The dominant source of NO_3^- pollution in Kubi village was CF_SN, which contributed 60.1%, followed by OF, which contributed 30.1%, and M&S, which contributed 9.8%. An increase in the fertilizer source contribution in the research area could also be due to the irrigation system. According to another study conducted by [29], higher yields from irrigated crops are generally associated with higher nitrogen fertilizer applications, increasing the risk of N loss to the environment.

For Ocho village, the proportional contribution decreased in the following order: M&S (10.9%) < CF_SN (38.4%) < OF (50.7%). The results of NO_3^- source apportionment with SIAR in Ocho corresponded with our field investigation and the land use distribution shown in Figure 2. Residential areas in Ocho are more concentrated than those in Kubi and have a low urbanization level due to depopulation. Contamination from old and poorly maintained drainage systems is highly probable. According to the Kure City Water Works and Sewerage Bureau [60], 70% of the wastewater generated in Kubi is treated in a local wastewater treatment plant, while the remaining 30% is treated in septic tanks, whereas in Ocho, all the waste is treated by septic tanks. The differences between the waste management systems may explain the differences in the NO_3^- –N concentrations in each area.

In summary, chemical fertilizers are mainly used in Kubi and organic fertilizers are used in Ocho (Figure 7). Due to differences in the wastewater treatment systems, Ocho has higher values of sewage and manure contribution than Kubi [60], but its impact is not as high as that of organic fertilizer input; therefore, we concluded that the main source of nitrate pollution is organic fertilizers. Additionally, large quantities of manure, sewage, and chemical fertilizers are used in Kubi, suggesting a high rate of leaching, resulting in a higher concentration of nitrates in the groundwater system. Table 4 demonstrates the relationship between social factors and groundwater nitrate–nitrogen contamination in Kubi and Ocho villages, with Kubi having a smaller population and agricultural area and a higher concentration of NO_3^- –N levels, primarily due to chemical fertilizers. Compared to Kubi village, Ocho village had lower NO_3^- –N levels despite having a larger population, and the organic fertilizers used in agricultural areas were the primary source of contamination.

Table 4. A summary of social aspects and groundwater NO_3^- –N contamination status in Kubi and Ocho villages.

Social Information	Units	Kubi Village	Ocho Village	Key References
Population		413	830	[38]
Average farmer age	years	76	73	[39]
Agricultural land	km ²	0.6	1.6	[40]
Sewage treatment coverage	%	70	0	[60]
Summary of NO_3^- –N concentration				Figure 4
Average NO_3^- –N concentration	mg/L	6.6	4.8	
<5	%	33.3	62.5	
5–10	%	47.7	31.3	
>10	%	19	6.2	
Main NO_3^- –N contribution ratio				Figure 8
Chemical fertilizer	%	60.1	38.4	
Organic fertilizer	%	30.1	50.7	
Manure and sewage	%	9.8	10.9	

5. Conclusions

Japan is currently experiencing rapid depopulation in most cities, and this demographic shift has caused both social and environmental impacts. Agricultural intensification is one of the main causes of elevated nitrate levels in the groundwater sources in Japan, often due to increased fertilizer application. However, other factors, such as land use and cultivation and farming methods, may also contribute to pollution. In comparison to Ocho, which had an average NO_3^- –N concentration of 4.8 mg/L (37.5% of water samples >5 mg/L), Kubi village had a higher average NO_3^- –N concentration of 6.6 mg/L (66.7% of water samples > 5 mg/L). Analysis of the proportional contributions of each NO_3^- –N source, calculated using SIAR (end-member method), showed that chemical fertilizers (60.1%) were the main contributing NO_3^- –N source in Kubi, while in Ocho, organic fertil-

izers (50.7%) were the major contributors, with minor contributions observed from sewage. These source distributions were associated with social aspects, such as depopulation and population age, and to a greater extent, land use type. It is suspected that the considerable quantities of chemical fertilizers that are applied by the older farmers in Kubi lead to inefficient nitrogen uptake by the plants, resulting in leaching of N. Thus, the level of contamination of groundwater was higher in Kubi than in Ocho.

There were limited source end-members in this study, and they were not fully representative of both study sites; therefore, some sources may have been underestimated or overestimated. For the sustainable development of local agriculture, improved fertilizer utilization efficiency is crucial considering the characteristics of intensive cultivation areas. To overcome the limitations of this research, further research could include detailed demographic and time-series studies.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w14142277/s1>, Figure S1: Outcrop geology of Osakishimojima Island; Table S1: Hydrochemical compositions of the groundwater and surface water sources in Kubi and Ocho village for the 2021 sampling campaign, Table S2: Correlation matrix of physiochemical data of groundwater samples collected from Kubi and Ocho village, Table S3: Isotopic data (‰) of sampled groundwater and surface water sources in Kubi and Ocho village.

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