Article

Potential Sources of Ammonium-Nitrogen in the Coastal Groundwater Determined from a Combined Analysis of Nitrogen Isotope, Biological and Geological Parameters, and Land Use

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Abstract: The origin of ammonium-nitrogen in Indonesian coastal groundwater has not been intensively examined, meanwhile the elevated concentration remains a concern. This research aims at tracing the potential sources of ammonium-nitrogen in the groundwater of Indramayu, Indonesia where groundwater is vital for livelihood. From results, a combined examination of nitrogen isotope, coliform bacteria, land-use, and geology confirmed the natural and anthropogenic origins of ammonium-nitrogen in the groundwater. In the brackish-water aquaculture region, groundwater has $\delta^{15}\text{N}_{\text{NH}_4}$ values from +1.8 to +4.8‰ signifying that ammonium-nitrogen is derived from mineralization of organic nitrogen to ammonium. Furthermore, ammonium has a significantly positive relationship with sodium indicating the exchangeable ammonium is mobilized to groundwater via cation exchange. Meanwhile ammonium-nitrogen from anthropogenic waste was detected in agricultural and residential region. The groundwater has more varied $\delta^{15}\text{N}_{\text{NH}_4}$ values, from −2.9 to +16.1‰, which implies attenuation of ammonium-nitrogen from several sources namely manure, mineral fertilizer, sewage, and pit latrines. Also, the presence of *E. coli* confirms the indication of human and animal waste contamination. However, since ammonium has no relationship with sodium, cation exchange is not feasible and ammonium-nitrogen flows into the groundwater from anthropogenic sources along with liquid wastes.

Keywords: ammonium-nitrogen; nitrogen isotope; coliform; sodium; alluvial groundwater; Indramayu

Citation: Rusydi, A.F.; Onodera, S.-I.; Saito, M.; Hyodo, F.; Maeda, M.; Sugianti, K.; Wibawa, S. Potential Sources of Ammonium-Nitrogen in the Coastal Groundwater Determined from a Combined Analysis of Nitrogen Isotope, Biological and Geological Parameters, and Land Use. *Water* **2021**, *13*, 25. <https://dx.doi.org/10.3390/w13010025>

Received: 25 November 2020

Accepted: 22 December 2020

Published: 25 December 2020

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1. Introduction

Groundwater as one of the clean water sources is presently experiencing nitrogen contamination because of human activities [1–3]. Ammonium is one form of dissolved inorganic nitrogen that is naturally occurring in low concentrations within groundwater. Generally, under aerobic condition, ammonium-nitrogen (NH_4^+-N) concentration in groundwater is <0.2 mg/L, and it may increase more than ten times under anaerobic environment [4]. The considerably high ammonium groundwater concentrations are indications of anthropogenic contamination from sources such as fertilizer, manure, septic tanks, and sewage [4–6]; therefore, these undesirable concentrations need to be removed [7,8]. Additionally, previous research found that high concentration of ammonium in groundwater is significantly correlated with high contents of more dangerous contaminants, which are dissolved iron and manganese [9].

Several studies in Indonesian coastal alluvial region have reported the groundwater quality issues with emphasis laid on metals and nitrate contaminations [10–12]. Equally, $\text{NH}_4^+ - \text{N}$ was also detected in shallow and deep groundwater with concentrations approximately 7.8 and 12 mg/L, respectively [13]. However, the evaluation of the ammonium source in this study was limited, which was mainly derived from nitrate denitrification. An in-depth study to trace other potential sources of ammonium in Indonesia is yet to be investigated. Additionally, Indonesian coastal groundwater is also vulnerable to salinization [14]. At the same time, salinization itself is known to have a positive relationship with the elevated concentrations of other contaminants, including ammonium [9,15–17].

Many methods have been devised to understand the origin of ammonium-nitrogen. Among them, nitrogen isotope ($\delta^{15}\text{N}$) is one of the most reliable and widely used ammonium tracer [6,18,19]. However, some issues need to be overcome for interpreting the $\delta^{15}\text{N}$ value. For example, the different sources of ammonium may have similar $\delta^{15}\text{N}$ signatures, and fractionation may occur during ammonium transport from the subsurface to the groundwater [20]. Consequently, multi-tracer parameters are required to eliminate these problems [20]. Land-use evaluation can help to identify contamination sources. This type of evaluation has been successfully used to appraise nitrate groundwater contamination [21]. The combination of nitrogen isotope and land-use to trace ammonium source can still be enhanced by analyzing the geological setting and bacterial content in the water. Previous findings revealed that soils and sediments are related to elevated concentrations of ammonium in groundwater [6,22]. On the other hand, coliform and *E. coli* parameters are useful tracers to confirm human waste contamination which is also a potential source of ammonium contamination [4]. In this research, we trace the potential sources of ammonium in coastal alluvial groundwater using the following combined tracers; nitrogen isotope ($\delta^{15}\text{N}$), bacterial coliform analysis (total coliform and *E. coli*), land use, and geological features. In addition, the effect of saline water on ammonium was evaluated with respect to major cations contents. Finally, from the combined tracing parameters, we expect to find the anthropogenic and salinization impact on $\text{NH}_4^+ - \text{N}$ contents in groundwater.

2. Study Site

This study was conducted in the coastal alluvial aquifer of Indramayu, located in the northern part of West Java Island, Indonesia ($107^\circ 52' - 108^\circ 36'$ E and $6^\circ 15' - 6^\circ 40'$ W). Indramayu is vital as a rice- and fish-production area with increasing gross domestic regional product (GRDP) particularly in the farming and fishery sector [23]. Groundwater is essential to support livelihood activities in this region because only less than 60% of the population can access the potable water provided by the government [23]. However, comprehensive information on the groundwater quality is limited. Hence, understanding groundwater ammonium sources in this area is valuable to provide a strong scientific base for the sustainable management of groundwater.

2.1. Land Uses of Indramayu

Indramayu is a lowland area with a total area greater than 240,000 ha. The main land-use categories are agriculture, brackish-water aquaculture, and residential (Figure 1a). Agricultural land that mainly consists of paddy fields is the primary land-use category, covering over 70% of the total area. The second-largest land-use category is brackish-water aquaculture, accounting for about 13% of the land use—aquaculture is mainly adopted in the northernmost part. The last major land-use category is the settlement that covers less than 11% and is mostly located along Cimanuk River. From 2002 to 2017, the agricultural and settlement areas slightly expanded, while the area under brackish-water aquaculture decreased. Since then, there was no significant change in the three main land-use categories (Figure 1b).

Figure 1. Land-use categories (a) and land-uses change from 2002 to 2019 (b) in Indramayu, Indonesia.

During the field campaigns, we observed that agricultural areas and settlements are not strictly defined, this is explained by the fact that the agricultural area is extensive and surrounds the entire residential area. The collection of groundwater samples from agriculture and settlement areas were from houses that have dug or bore wells. Groundwater in agriculture and settlement areas were expected to have similar characteristics because of their undefined boundaries. On the other hand, the boundary between the brackish-water aquaculture and agriculture was quite clear. The groundwater samples

from brackish-water aquaculture were collected from bore wells which are used to fill the ponds. From the aforementioned land-uses, we classified them into two groups: lower coastal zone (LC) comprising brackish-water aquaculture area and the upper coastal zone (UC) consisting of agricultural and settlement areas (Figure 2).

Figure 2. Sampling points in the study site.

2.2. Geology and Aquifer System of Indramayu

The Indramayu Coast is a delta [24–26] formed by sedimentary materials supplied by the Cimanuk River [27]. Based on the Geological Map of Indramayu Quadrangle in Java [28], the study area generally consists of old to young lithologies, including tuffaceous sandstone and conglomerate (Qav), flood plain deposits (Qaf), beach ridge deposits (Qbr), coastal deposits (Qac), deltaic deposits (Qad), and young river deposits (Qa) (Figure 3a). The Indramayu region is essentially composed of quaternary rocks. The oldest Pleistocene quaternary rock units in the region are tuffaceous sandstone and conglomerate (Qav), conglomeratic sandstone, tuffaceous sandstone, and tuff. Holocene sediments are deposited on the upper part. They include flood plain deposits (Qaf) in the form of sandy-humic clay, clayey sand, and partly tuff; beach ridge deposits (Qbr) in the form of coarse to fine-grained sand and clay with abundant mollusks; coastal deposits (Qac) in the form of silt, clay, sand, and fragments of mollusks; deltaic deposits (Qad) in the form of silt, brown clay, and some mollusks; and young river deposits (Qa) in the form of sand, silt, and brown clay.

Figure 3. Geology (a) and vertical profile in the B–A cross section (b) of Indramayu, Indonesia (Completely redrawn and modified after Maria et al., 2018 [29]).

The vertical geological profile from south to north shows a large aquifer reservoir interspersed with clay and silt in the area (Figure 3b). In the north, there is the thickest clay layer derived from marine deposits. According to previous studies, the groundwater here has high chloride concentrations, ranging from 1500 to 12,000 mg/L, which is categorized as brackish-salt and salt water [30].

3. Samples Collection and Analysis

3.1. Sediment Samples

Sediment analysis was performed to evaluate the general geological conditions that possibly promote the natural attenuation of $\text{NH}_4^+\text{-N}$ in the groundwater. The sediments samples were collected at different depths from two boreholes in UC area (DH01) and LC area (DH05) (Figure 3a). We selected the depth based on the textures—clay, silt, and sand (Figure 3b). The analysis was conducted for ratio of exchangeable ammonium (NH_4^+) to total cations (NH_4^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+}), stable isotopes of nitrogen ($\delta^{15}\text{N}$), nitrogen content (%), and the cation exchange capacity (CEC). Method of analysis for each parameter is as follows: Composition of $\delta^{15}\text{N}$ (‰) was determined by Thermo Finnigan DELTAplus Advantage+FLASH2000; N content (%) was measured by high temperature combustion; exchangeable NH_4^+ was measured by soil extraction with NH_4Oac at pH 7.0 and follow by

atomic absorption spectrophotometry (AAS); and CEC value was measured by summing cations that are attracted to the negative surface charges in sediments samples.

Analysis of $\delta^{15}\text{N}$ and N content were conducted at the Chikyu Kagaku Kenkyusho (Geo-Science Laboratory, Nagoya, Japan) while ratio of exchangeable ammonium to total cations and CEC were measured at the Soil Fertility and Plant Nutrition Laboratory, University of Padjajaran, Bandung, Indonesia.

3.2. Groundwater Samples

In all, 28 groundwater samples were collected during dry season in November 2019 from LC area ($n = 10$) and UC area ($n = 18$) (Figure 2). The concentrations of $\text{NH}_4^+ - \text{N}$, nitrate-nitrogen ($\text{NO}_3^- - \text{N}$), and nitrite-nitrogen ($\text{NO}_2^- - \text{N}$) were determined using a continuous-flow automated nutrient analyzer (SwAAt, BLTEC, Tokyo, Japan) at the Biogeochemistry Laboratory, Hiroshima University, Japan. The analysis of $\text{NH}_4^+ - \text{N}$ ($\delta^{15}\text{N}_{\text{NH}_4}$) was conducted by using a continuous-flow type stable isotope ratio mass spectrometer (DELTA plus Advantage + FLASH2000; Thermo Finnigan, San Jose, CA, USA) with a precision of $\pm 0.2\text{‰}$ at the Chikyu Kagaku Kenkyusho (Geo-Science Laboratory, Dubai, UAE), Japan. Glycine, L-Alanine, and L-Histidine were used as working standards to calibrate the isotope ratio with the international standard. Sample preparation for $\delta^{15}\text{N}_{\text{NH}_4}$ analysis was performed at the Laboratory of Biogeochemistry, Hiroshima University, Japan. The $\text{NH}_4^+ - \text{N}$ in the sample was first diffused following the procedure and materials and chemicals adopted by Koba et al. (2010) [31]. However, some adjustments were made for the analysis in this study. The incubation period here was 24 h, which is sufficient for capturing all $\text{NH}_4^+ - \text{N}$ from samples to the glass filter and the maximum volume of sample was 40 mL. Besides, the laboratory analysis is limited for groundwater samples with $\text{NH}_4^+ - \text{N}$ content greater than 20 μg . First, 10 samples and 14 samples from the LC and UC groundwater, respectively, meeting the requirements for $\delta^{15}\text{N}_{\text{NH}_4}$ measurement were used. Furthermore, coliform bacteria analysis (total coliform and *E. coli*) was completed in the health department facility in Indramayu by using the most probable number method on the same day of sample collection.

Furthermore, the contents of major cations, comprising Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , were analyzed by ion chromatography with conductivity detection on an ICS-2100 (Thermo Fisher Scientific Inc., Waltham, MA, USA) with analytical precisions of $<1\%$ for Na^+ , Mg^{2+} , and Ca^{2+} , and $<2\%$ for K^+ . For dissolved organic carbon (DOC), analysis was performed using a total organic carbon analyzer (TOC-V^{CPH}, Shimadzu, Kyoto City, Japan). The analysis of major ions and DOC were carried out at the Laboratory of Geothermal Engineering, Hirosaki University, Japan.

Samples for the nitrogen isotope and chemical analysis were first filtered with 0.2 μm polytetrafluoroethylene or DISMIC-25HP (for DOC) membranes and then placed into polyethylene bottles and glass vials (for DOC). The samples bottles were pretreated before collecting the samples: they had been soaked in 10% HCl solution for 24 h, washed, and then rinsed thrice with distilled water; further, they were rinsed thrice in the field with well water before collecting the sample. For biological analysis, samples were kept in sterilized glass bottles prepared by the health department in Indramayu, Indonesia.

The statistical analysis was carried out to find the $\text{NH}_4^+ - \text{N}$ relationship with DOC and major cations. The effect of DOC and major cations on $\text{NH}_4^+ - \text{N}$ concentrations is demonstrated by coefficient determination (R^2). Furthermore, the significance of the relationship is shown by the p value with 95% confidence level.

4. Results and Discussion

4.1. Chemical Properties of Sediments

Sediments analysis results show that the ratio of exchangeable NH_4^+ to total cations (NH_4^+ and major cations) is high in both UC and LC deposits and does not vary significantly with depth (Figure 4a,b). Similarly, the $\delta^{15}\text{N}$ value does not change considerably with sediment depth and texture in either UC or LC deposits (Figure 4c,d). The $\delta^{15}\text{N}$ ratio

of UC and LC deposits varies from +3.1 to +3.9‰ and +2.9 to +3.5‰ and, respectively. According to Evans [32], the $\delta^{15}\text{N}$ value between 0 and +5‰ may indicate nitrogen conversion from organic matter to ammonium by mineralization. Furthermore, the nitrogen content in the first layer of clay and silt in UC deposits is relatively lower than that in LC deposits (Figure 4e,f). Therefore, the mineralization of soil nitrogen is more likely to occur in LC deposits. Subsequently, ammonium as a mineralization product is then mobilized by the cation exchange process and transported to sampling wells. This assumption is supported by the CEC value of LC deposits, which is relatively higher than UC deposits (Figure 4g,h). However, the properties of sediments can differ spatially. Therefore, the available sediment data only indicates the general condition of the study area.

Figure 4. Exchangeable NH_4^+ ratio (a,b), $\delta^{15}\text{N}$ (c,d), %N (e,f), and cation exchange capacity (CEC) (g,h), in the sediments of the upper and lower coastal area.

4.2. Potential Sources of Ammonium-Nitrogen in Groundwater Systems

Previous findings have shown that the concentration of NH_4^+-N in the samples is predominant compared to NO_3^--N and NO_2^--N , particularly in the LC region [30]. NH_4^+-N concentrations in LC and UC groundwater from previous studies ranged from 2.3 to 9.0 mg/L and 0.04 to 7.0 mg/L, respectively. On the other hand, the NO_3^--N concentration was mostly <0.2 mg/L, and NO_2^--N content was <0.02 mg/L. Similar to a previous study, the current study also found a high content of NH_4^+-N (Figure 5). Only two samples from UC groundwater (DH07 and DH13) had a high concentration of NO_3^--N . However, this value was still below the standard drinking water threshold [4]. The NO_2^--N content was very low (≤ 0.02 mg/L). The content of NH_4^+-N was generally higher in LC than in UC groundwater. The concentration of NH_4^+-N in LC and UC groundwater varied from 2.35 to 12.97 mg/L and 0.07 to 3.19 mg/L, respectively. Significant amounts of NH_4^+-N

compared to NO_3^- -N or NO_2^- -N may be an indicator of a reducing environment that can cause the dissolution of metals such as iron, manganese, and arsenic [22,33].

Figure 5. Concentrations of NO_3^- -N and NH_4^+ -N (mg/L) in the groundwater samples.

Nitrate may be reduced in the dissimilatory nitrate reduction to ammonium (DNRA) as a result of microbial activities facilitated by organic carbon or nitrate [33]. This process is likely to occur in the LC groundwater since DOC has a positive and significant relationship with both NO_3^- -N and NH_4^+ -N (Figure 6a,b, respectively). However, further investigation is required to confirm this origin.

Figure 6. Relationship of dissolved organic carbon (DOC) with NO_3^- -N (a) and NH_4^+ -N (b) in the groundwater samples.

The relationship of $\delta^{15}\text{N}_{\text{NH}_4}$ and NH_4^+ -N in Figure 7 shows that $\delta^{15}\text{N}_{\text{NH}_4}$ in the LC groundwater has a narrow range of values, from 1.8 to 4.8‰ (Table 1), and it is relatively stable over the wide range of NH_4^+ -N concentrations, from 2.35 to 14.6 mg/L (Table 1). Still in Figure 7, this also presents the isotopic composition of $\delta^{15}\text{N}_{\text{NH}_4}$ from several sources which have been discovered from previous studies [6,19]. By using these references, we propose that the ammonium in the LC groundwater is unlikely to be of human and animal waste origin; it probably is mainly derived from the mineralization of organic and inorganic nitrogen in sediment. Meanwhile, the groundwater at LC reveals the presence of coliform bacteria, but none of it originated from *E. coli* (Table 1). This finding indicates the absence of contamination by human and animal feces [4] which further supports the interpretation based on $\delta^{15}\text{N}_{\text{NH}_4}$. Additionally, the LC area has a thick clay layer (Figure 3b) with potentially high organic matter contents [34]. The organic matter is not only a natural source of ammonium, but is also a facilitator of microbial activities that, in turn, generate a reducing environment. This condition was confirmed earlier in several studies [6,22].

Figure 7. NH_4^+-N concentrations (mg/L) and $\delta^{15}\text{N}_{\text{NH}_4}$ values (‰) in the groundwater samples, and potential sources of NH_4^+-N based on $\delta^{15}\text{N}_{\text{NH}_4}$ values of several sources (ranges values of $\delta^{15}\text{N}_{\text{NH}_4}$ compositions for soil nitrogen, animal manure, and mineral fertilizer are adapted from Norrman et al., 2015 [6]; and for organic matter and household waste are adapted from Nikolenko et al., 2018 [19]).

On the other hand, Figure 7 also shows that the $\delta^{15}\text{N}_{\text{NH}_4}$ values in the UC groundwater are varied, from -2.9 to 16.1 ‰ (Table 1), within a relatively narrow concentration range of NH_4^+-N , from 0.42 to 3.19 mg/L (Table 1), suggesting that ammonium is derived from diverse sources. The compositions of $\delta^{15}\text{N}_{\text{NH}_4}$, >5 ‰, suggest that ammonium-nitrate are potentially derived from animal manure and household waste [6,19]. This observation is consistent with the presence of *E. coli* in the samples (Table 1). Furthermore, the source of ammonium for $\delta^{15}\text{N}_{\text{NH}_4}$ values ≤ 5 ‰ may be from the application of mineral fertilizers in paddy fields area and sewage infiltration [19]. Since most of the UC groundwater samples were collected from a shallow aquifer (≤ 8 m), the results indicate the possibility that poor wastewater treatment and utilization of pit latrine less than 2 m from the well led to the transport of leaked wastewater into the aquifer [35,36].

The comparison of NH_4^+-N concentrations and $\delta^{15}\text{N}_{\text{NH}_4}$ compositions between LC and UC groundwater showed that the LC groundwater was potentially more vulnerable to ammonium contamination. Interestingly, the relative high ammonium-nitrogen in LC groundwater was from natural source. Previous findings in more developing Indonesian coastal area suggest that anthropogenic waste is the primary source of ammonium in groundwater [13]. The presence of ammonium in both areas shows the heterogeneity of groundwater conditions in Indonesia coastal areas.

Table 1. $\text{NH}_4^+ - \text{N}$ concentrations, $\delta^{15}\text{N}_{\text{NH}_4}$ values, and coliform bacteria.

Sample	Aquifer m	Location	$\text{NH}_4^+ - \text{N}$ mg/L	$\delta^{15}\text{N}_{\text{NH}_4}$ ‰	Total Coliform (No./100 mL)	<i>E. coli</i>
DH01	25	Upper coastal aquifer	0.2	UD	NM	NM
DH02	16		3.15	9.2	1100	150
DH03	2		0.71	4.7	1100	210
DH07	3		2.48	16.1	2400	2400
DH08	4		1.87	3.7	2400	210
DH09	8		1.58	3.6	210	210
DH12	12		0.32	UD	NM	NM
DH13	16		0.18	UD	NM	NM
DH14	5		2.33	9.5	NM	NM
DH16	5		3.19	9.5	2400	1100
DH17	10		0.07	UD	NM	NM
DH18	5		0.53	UD	NM	NM
DH19	6		0.42	7.5	2400	2400
DH23	15		1.64	1.6	1100	0
DH26	5		0.77	8.7	2400	3
DH27	10		1.62	−2.9	2400	210
DH29	5		0.97	3.5	2400	1100
DH30	5		1.69	5	2400	2400
Minimum			0.42	−2.9	210	-
Maximum			3.19	16.1	2400	2400
Average			1.64	6.1	1892	866
DH05	30	Lower coastal aquifer	12.97	2.9	2400	0
DH06	20		2.35	4.0	NM	NM
DH10	20		10.88	3.8	NM	NM
DH11	100		4.21	1.8	20	0
DH15	80		2.79	1.9	7	0
DH22	20		3.19	2.4	1100	0
DH24	25		5.66	3.7	0	0
DH25	20		8.26	2.3	2400	0
DH28	20		11.81	2.2	NM	NM
DH31	5		7.95	4.8	2400	0
Minimum			2.35	1.8	0	0
Maximum			14.60	4.8	2400	0
Average			7.7	3.0	1190	0

NM = not measured; UD = under the detection limit.

4.3. Relationship between Ammonium-Nitrogen and Water Chemical Properties

The relatively high concentration of $\text{NH}_4^+ - \text{N}$ in LC groundwater is consistent with the significantly elevated concentrations of major cations, mostly Na^+ (Figure 8). High cation content is typical of high salinity water [37]. The source of high salinity is possibly associated with infiltration of brackish-water from the pond or marine clay sediment. Figure 8a–d show a strong positive and significant relationship between $\text{NH}_4^+ - \text{N}$ and cations. Hence,

exchangeable ammonium from sediments can be released into groundwater by exchanging cations, particularly Na^+ , as the dominant cation [15,16,38]. It is also important to consider that the lithology of LC site sediments is composed of thick clay (Figure 3b), which generally impedes exchangeable ammonium by the sorption process [16]. Therefore, more exchangeable ammonium can be deposited in sediments [16] and released into groundwater through the cation exchange process under high salinity conditions [15,38].

Figure 8. Relationship of NH_4^+-N and Na^+ (a), K^+ (b), Mg^{2+} (c), Ca^{2+} (d) in groundwater samples.

On the other hand, the content of major cations in UC groundwater is relatively low and has no rational relationship with NH_4^+-N (Figure 8). Moreover, the p -value for the relationship between NH_4^+-N and all cations is not considerable. This implies that the transfer of ammonium from sediments to groundwater by the cation exchange mechanism is unlikely.

Figure 9 shows the average concentrations of total major cations, NH_4^+ , and $\delta^{15}\text{N}_{\text{NH}_4}$, in three different classifications of groundwater depth: shallow (≤ 5 m), medium (≥ 5 –20 m), and deep (≥ 25 m). The total content of major cations in UC groundwater is relatively low and similar at all depths, in the range of 23 to 48 meq/L (Figure 9a). LC groundwater, on the other hand, has a very high content of major cations, which implies high salinity groundwater, especially at shallow (377 meq/L) and medium (352 meq/L) depths (Figure 9b). As a compromise, UC groundwater (Figure 9c) has significantly lower ammonium ions than

LC groundwater, respectively from 0.06 to 0.11 meq/L and 0.43 to 0.57 meq/L (Figure 9d). Moreover, the concentration of NH_4^+ in groundwater decreases as groundwater depth increases, according to the pattern of the total content of major cations relative to depth. Overall, the cations and ammonium ion contents at these two sites indicate that ammonium is likely to be mobilized because of the cation exchange at the LC site.

Figure 9. Average total major cations (a,b) (meq/L), NH_4^+ contents (meq/L) (c,d), and $\delta^{15}\text{N}_{\text{NH}_4}$ values (‰) (e,f) in three depths of groundwater in upper and lower coastal areas.

In addition, shallow UC groundwater has a relatively high value of $\delta^{15}\text{N}_{\text{NH}_4}$, $\pm 7.6\text{‰}$ on average (Figure 9e), which is typical of the $\delta^{15}\text{N}_{\text{NH}_4}$ ratio of household waste and animal manure [6,19]. This finding is consistent with previous assumptions about the leakage of wastewater and manure into shallow groundwater. Nevertheless, still in Figure 9e, UC groundwater at medium depths has a low $\delta^{15}\text{N}_{\text{NH}_4}$ value ($\pm 0.8\text{‰}$ on average) in the range of ammonium from mineral fertilizers. At the same time, the $\delta^{15}\text{N}_{\text{NH}_4}$ value was below the detection limit in deeper UC groundwater. Finally, the $\delta^{15}\text{N}_{\text{NH}_4}$ ratio in LC groundwater was more uniform ($\pm 3\text{‰}$ on average) (Figure 9f), suggesting that ammonium at all depths was potentially derived from the mineralization of nitrogen in sediments [6,19].

5. Conclusions

The combined parameters of $\delta^{15}\text{N}_{\text{NH}_4}$, coliform bacteria, land use, and geology in this research can trace well the potential sources of NH_4^+-N in the coastal alluvial groundwater in Indramayu, Indonesia. The origins of NH_4^+-N are natural and anthropogenic sources located in the lower and upper coastal areas, respectively. The mobilization of NH_4^+-

N to the groundwater differ depending on the source. From the results, the following conclusions can be drawn:

- NH_4^+ -N in the lower coastal region, occupied by brackish-water aquaculture, potentially originated from the mineralization of organic nitrogen in sediments to ammonium. In agreement with this origin, the ratios of $\delta^{15}\text{N}$ in the sediments indicate the mineralization of nitrogen. However, contamination by anthropogenic activity is possible considering the high values of total coliform bacteria. The strongly positive and significant relationship of NH_4^+ -N and Na^+ suggests that under high salinity, the exchangeable NH_4^+ is mobilized from sediments to the groundwater through cation exchange. Additionally, the high salinity of groundwater possibly arises from the brackish-water pond and marine clay.
- Further, attenuation of ammonium-nitrogen from manure, sewage, and pit latrines occurs in the groundwater in the upper coastal region, where land is used mainly for agricultural and residential purposes. Both total coliform and *E. coli* values confirm this condition. The ratios of $\delta^{15}\text{N}$ in several layers of sediments suggest the possibility of nitrogen mineralization to ammonium; nevertheless, the nitrogen contents suggest that this process is more likely in the sediments of lower coastal region. The significantly lower salinity followed by weak and not significant relationships of NH_4^+ -N and all major cations indicate less possibility of NH_4^+ -N mobilize to groundwater through cation exchange.

Author Contributions: Conceptualization, A.F.R. and S.-I.O.; formal analysis, A.F.R., M.S., M.M., F.H., K.S., and S.W.; funding acquisition, S.-I.O. and M.S.; investigation, A.F.R., S.-I.O., M.S., K.S., and S.W.; methodology, A.F.R., S.-I.O., and M.S.; project administration, S.-I.O. and M.S.; supervision, S.-I.O., M.M., and F.H.; writing—original draft, A.F.R.; writing—review and editing, A.F.R., S.-I.O., and M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This material is based on work supported by: 1. The Asia-Pacific Network for Global Change Research (APN) under Grant No. CRRP2019-09 MY-Onodera (funder ID: <http://dx.doi.org/10.13039/100005536>). 2. All opinions, findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of APN. While the information and advice in this publication are believed to be true and accurate at the date of publication, neither the editors nor APN accept any legal responsibility for any errors or omissions that may be made. APN and its member countries make no warranty, expressed or implied, with respect to the material contained herein. 3. Japanese Society for the Promotion of Sciences Grant-in-Aid for Scientific Research B (JSPS KAKENHI B) with Grant Number 17H04494. 4. Priority Research Program of Deputy of Earth Science, the Indonesian Institute of Sciences (LIPI), entitled “Degradation of Groundwater Resources and The Potential of Land Subsidence due to Climate Changes and Anthropogenic Activities in The Coastal of Cimanuk Watershed”, which was funded by LIPI in 2016–2017 fiscal year.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing not applicable.

Acknowledgments: Authors wish to thank Seiichiro Ioka from Hirosaki University and Robert M. Delinom for providing valuable discussion and highly supported analysis of some water quality parameters. Many thanks to Rizka Maria, Wahyu Purwoko, and Dady Sukmayadi from Research Center for Geotechnology Indonesian Institute of Sciences for field research support; and Kimbi Sharon Bih and Yusuke Tomozawa from Laboratory of Biogeochemistry for supporting laboratory analysis.

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