Jurnal Sains Nuklear Malaysia, 2024, 36(No. 1): 31 – 41
ISSN: 2232-0946

SPATIAL TRENDS OF NITRATE LEVEL AND NITRATE STABLE ISOTOPES IN THE LINGGI RIVER

Munirah Abdul Zali[1,2,*], Hafizan Juahir[2], Ananthy Retnam[3], Azharruddin Abdul Aziz[3], Azrul Normi Idris[4], Anuar Sefie[4], Ismail Tawnie[4] and Masni Mohd Ali[5],

[1]Waste and Environmental Technology Division,
Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor, Malaysia
[2] East Coast Environmental Research Institute (ESERI), Gong Badak Campus,
Universiti Sultan Zainal Abidin (UNiSZA), 21300, Kuala Nerus, Terengganu, Malaysia
[3] Department of Chemistry of Malaysia, Jalan Sultan, 46661 Petaling Jaya, Selangor, Malaysia
[4]National Hydraulic Research Institute of Malaysia (NAHRIM), Lot 5377,
Jalan Putra Permai, 43300, Seri Kembangan, Selangor, Malaysia
[5]Faculty of Science and Technology, Universiti Kebangsaan Malaysia,
43600, UKM Bangi, Selangor, Malaysia
*Corresponding author: munirahzali@nm.gov.my/munirahabdulzali@gmail.com

ABSTRACT

Determining the isotopic composition of nitrate ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) in water can provide useful information to identify the sources of nitrate pollution and understand its dynamic behaviour in the aquatic ecosystem. In this study, six river water samples from the Linggi River, Malaysia were obtained to determine the nitrate level and understand possible sources of nitrate pollution using nitrate stable isotopes. The nitrate level and nitrate stable isotopes were measured using ion chromatography (IC) and Continuous Flow Elemental Analyzer Isotope Ratio Mass Spectrometer (CF-EA-IRMS) respectively. The nitrate in the river water samples ranged between 0.97± 0.01 mg L^{-1} and 36.08 ± 0.12 mg L^{-1}. The nitrate level in all river water stations was below than World Health Organization (WHO) and Malaysian Raw Drinking Water guideline level. For nitrate stable isotopes the $\delta^{15}N\text{-}NO_3^-$ values ranged from +1.4‰ to +15.6‰ and the $\delta^{18}O\text{-}NO_3^-$ values ranged from +13.8‰ to +27.4‰ in the river water samples. Based on the cross plot of nitrate stable isotopes, the Linggi River were influenced by the mixture of nitrate pollution sources process from ammonia in fertilizer, soil ammonia, sewage, manure, nitrate fertilizer and atmospheric nitrate. This study reports the signature of nitrate stable isotopes in potential nitrate pollution sources identification and these findings will help further pollution mitigation action for environmental protection.

Keywords: nitrate, nitrate stable isotopes, pollution, river water

INTRODUCTION

Worldwide, nitrates in the natural nitrogen cycle are being increasingly altered due to anthropogenic contributions, such as fossil fuel burning, sewage discharge, agricultural intensification, and intensive farming (DeVries & Zhang, 2016; Filoso, Martinelli, Howarth, & Boyer, 2006; Gutiérrez, Biagioni, Alarcón-Herrera, & Rivas-Lucero, 2018; Jiang et al., 2019; Zafirah et al., 2017; Zhang et al., 2018). In addition, since the beginning of the 20th century, the enormous impact of anthropogenic activities on the environment has altered the nitrogen cycle, doubling the amount the reactive nitrogen (Camargo and Alonso 2006; Gruber and Galloway 2008; Ver et al. 1999). Thus, precise and reliable estimation of nitrate pollution in the ecosystems is warranted.

Nitrate occurs naturally as part of the nitrogen cycle. Despite its natural occurrence, the rising concentrations of nitrate serve as ubiquitous water pollutants. The World Health Organization (WHO) and Malaysian National Raw Drinking Water Guideline have set a limit of 50 mg L^{-1} for nitrate in drinking water sources. Nitrate is a contaminant of concern because its presence is correlated to various environmental problems, such as eutrophication, and health hazards (Akinnawo 2023; Grout et al. 2023). Nitrate causes methemoglobinemia (blue baby syndrome) in children (WHO 2017). Furthermore, increased atmospheric loads of sulfuric and nitric acids from anthropogenic input lead to excess alkalinization and acidification of rivers, in addition to eutrophication (Camargo & Alonso, 2006; Gruber & Galloway, 2008; Wu, Luo, Luo, Ma, & Wang, 2018). These loads enter the river and groundwater via precipitation and may cause environmental harm.

Furthermore, the presence of nitrate in water may be considerably affected by temporal variations, precipitation, hydrogeological conditions, and land use activities (Nejatijahromi et al. 2019). Under many environmental circumstances, isotopes offer definitive source identification because different nitrate sources possess distinct nitrogen and oxygen isotopic signatures. The dual nitrogen and oxygen ratio of nitrate is a valuable fingerprinting tool to identify the predominant source of nitrate pollution in water (Kendall et al., 2007; Li et al., 2010; Michalski, Kolanowskit, & Riha, 2015; Qin, Zhang, & Wang, 2019; Venkiteswaran, Boeckx, & Gooddy, 2019; Zhang, Shi, Song, & Li, 2019). This study aims to determine nitrate levels and nitrate stable isotopes in the river water samples to understand the nitrate pollution sources in the Linggi River.

MATERIALS AND METHODOLOGY

Study Area

Linggi River is located in the Negeri Sembilan state and covers a distance of approximately 1,530 km^2. The river passes through urban areas, such as Seremban and Senawang, as well as rural areas, toward the Strait of Malacca. The Linggi catchment is dominated by residential and industrial areas in the upstream region, while major agricultural activities, small residential areas, and drinking water intake point are located from the middle stream toward the downstream areas. The coordinate points and the description of the sampling locations for this study are shown in Figure 1 and Table 1 respectively.

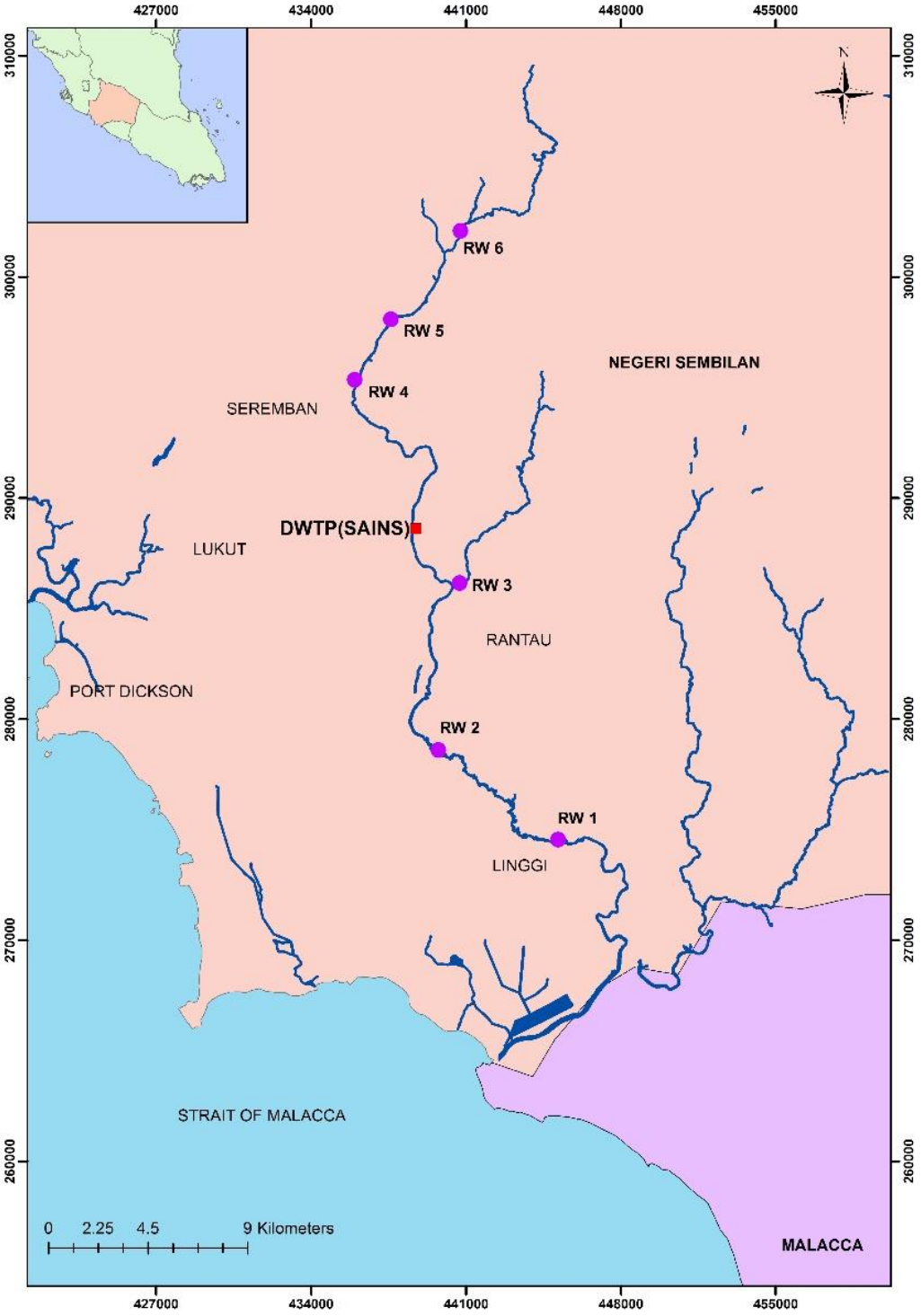

Figure 1. River water sampling location at Linggi River (DWTP= drinking water treatment plant; SAINS= *Syarikat Air Negeri Sembilan*)

Table 1: Description of sampling location

Station	Latitude	Longitude	Land Use
RW1	101.93°	2.68°	Small town, cow farm
RW2	101.91°	2.67°	Residential Areas, sewage treatment plant
RW3	101.96°	2.58°	Palm oil plantations, small towns, residential areas
RW4	101.96°	2.51°	Residential areas
RW5	102.01°	2.48°	Residential areas
RW6	101.96°	2.73°	Residential areas, animal farm

Sampling procedure

The sampling for nitrate and nitrate stable isotopes was conducted in April 2018 at Linggi, Negeri Sembilan, Malaysia. For nitrate level analysis, river water samples were collected using a clean bucket and passed through a 0.45-µm membrane filter. The samples were stored in 250-mL bottles in an icebox and kept in a refrigerator at ±4 °C in the laboratory. The water samples were analyzed within 48 hrs of collection.
For nitrate stable isotope analysis, 4 litres of river water samples were collected using a clean bucket and passed through a 0.45 µm membrane filter, followed by a 0.20 µm membrane filter. All samples for nitrate stable isotope analysis were stored in an icebox and kept in the freezer to prevent any significant chemical and biological changes till further analysis. All samples were analyzed within 48 hrs of collection.

Analysis of nitrate in the river water samples

Nitrate in the water samples was measured using ion chromatography (IC) (ICS 1000 Dionex, USA) following the American Public Health Association (APHA) 4110B standard method. Briefly, the water samples are injected into a stream of eluent in the IC system and passed through a series of ion exchangers. The target anions are separated based on their relative affinities for a low-capacity, strongly basic anion exchanger in the guard and analytical columns of the IC system. The separated anions are directed through suppressors, which continuously suppress eluent conductivity and promote analyte response which in this study in the nitrate ion. In the suppressor, the separated anions are converted to their highly conductive acid forms, while the conductivity of the eluent is greatly decreased. The separated nitrate ion in their acid forms is quantified based on their conductivity and identified based on their retention time (RT). Quantification was performed using the peak area of the ions. Five calibration points of 0.5 mg L^{-1}, 1.0 mg L^{-1}, 2.0 mg L^{-1}, 5.0 mg L^{-1} and 10.0 mg L^{-1} were established with the correlation of coefficient (R^2) of 0.997. Calibration verification (quality control standards) was done for every twenty samples that were analyzed; the values ranged between 90 and 110%. Method blanks and spiked samples were analyzed to ensure method performance with recovery between 70% and 130%. Details of the apparatus, reagent, chemicals, standards, and quality controls are described elsewhere (APHA 2017).

Analysis of nitrate stable isotopes in the river water samples

The nitrate stable isotopes ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) analyses were carried out using the ion-exchange method based on the United States Geological Survey (USGS) guideline for the determination of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ (USGS 2001) and literature (Minet et al., 2011; Silva et al., 2000; Xing & Liu, 2011). Briefly, the nitrate in the water samples was extracted using AG50-WX8 and AG1-X8 resins and eluted using 3M hydrochloric acid. After the elution, the neutralization process was performed using silver oxide salt to produce silver nitrate salt from the samples. The silver nitrate salt was freeze-dried and stored prior to analysis. The determination of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in the silver nitrate from the water samples was carried out using Continuous Flow Elemental Analyzer Isotope Ratio Mass Spectrometer (CF-EA-IRMS) (SERCON 20-22, UK).

The $\delta^{15}N$ values of samples were reported using conventional delta (δ) notations in per mil (‰) relative to the AIR standard ($\delta^{15}N$ = 0‰). Isotope signatures for $\delta^{15}N$ were calculated as $[R_{sample} - R_{standard}) / R_{standard}] \times 1000$, where R = $^{15}N/^{14}$ N. The $\delta^{18}O$ values of samples are reported using conventional delta (δ) notation in per mil (‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW) ($\delta^{18}O$ = 0‰) and calculated as $[R_{sample} - R_{standard}) / R_{standard}] \times 1000$, where R = $^{18}O/^{16}$ O.

RESULTS AND DISCUSSION

The level of nitrate in the river water samples

Figure 2 presents the values of nitrates in river water samples at RW1-RW6 from the Linggi River. The nitrate level in RW1, RW2, RW3, RW4, RW5 and RW6 were 10.28 ± 0.12 mg L^{-1}, 17.51 ± 0.15 mg L^{-1}, 36.08 ± 0.12 mg L^{-1}, 0.98 ± 0.01 mg L^{-1}, 2.42 ± 0.02 mg L^{-1}, and 2.17 ± 0.06 mg L^{-1} respectively (Figure 2). The range of nitrate concentration in the river water samples was between 0.97± 0.01 mg L^{-1} and 36.08 ± 0.12 mg L^{-1}. The highest nitrate concentration was observed at the RW3 station. This station was surrounded by residential areas and palm oil plantations. The highest nitrate level in this station may be due to the potential of nitrate sources from fertilizer and also from the discharge of sewage effluent from residential areas (Abdul Zali et al. 2021; Zainuddin et al. 2020).

The nitrate levels in samples from RW1, RW2, and RW3 exceeded the base level (5 mg L^{-1}) based on literature by Wang et al. (2017) and Panno et al. (2006) and were lower than the WHO guideline (Figure 2). Based on the literature and the author's knowledge, till recent years, the study on the base level of nitrate concentration was unavailable and/or not reported in the Malaysian region. The RW1, RW2, and RW3 stations are in the downstream part of the river, and the abundance of nitrates in samples from these stations may be attributed to input from nearby point and non-point sources as well as cumulative loading of pollutants from the upstream region (Yang et al., 2016). The anthropogenic pollution from point and non-point sources was anticipated at RW1, RW2, and RW3, however, fertilizer waste may serve as the major contributor in these regions, as they are surrounded by massive rubber and palm oil plantations (Zainuddin et al. 2020). Although the nitrate levels in samples from RW4, RW5, and RW6 were slightly lower than the base level, their concentrations should not be overlooked given the potential risk of elevated nitrate from the surrounding areas and also contribute to cumulative loading of nitrate in the downstream regions.

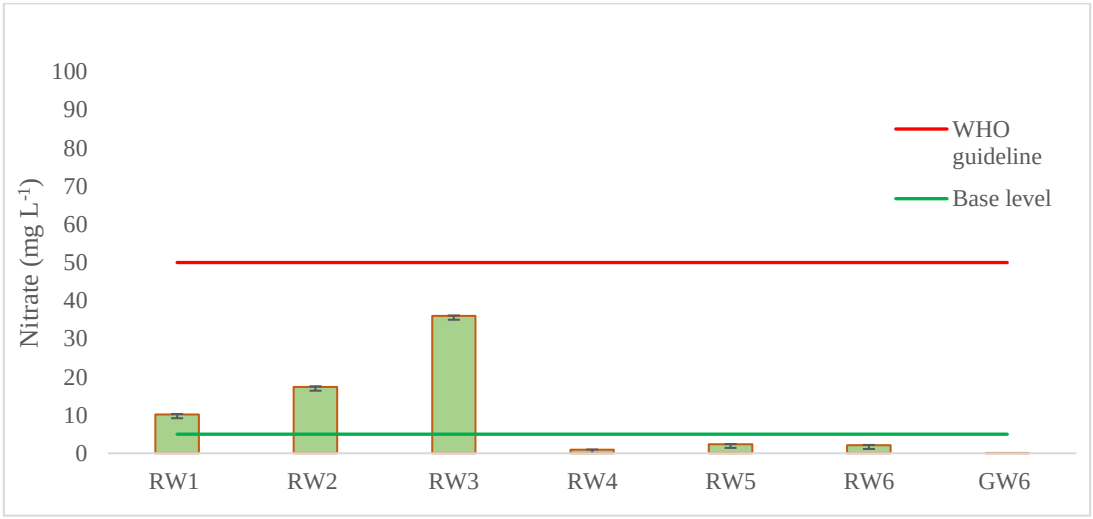

Figure 2. Nitrate concentrations in river water samples

Signature of nitrate stable isotopes in the river water samples

The determination of nitrate level in the river water samples delivers the distribution information of nitrate in the Linggi River. To understand the potential nitrate pollution sources and transformation processes of nitrates from anthropogenic activities, the $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ signatures of water samples were extracted and analyzed using CF-EA-IRMS. The $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ signatures of river water can be used for the evaluation of the potential sources of nitrate (Fenech et al. 2012; Kendall 1998). The $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ compositions of nitrate in the river water samples are plotted in Figures 3 (a) and (b) respectively. From the nitrate stable isotope analysis, the $\delta^{15}N\text{-}NO_3^-$ values ranged from +1.4‰ to +15.6‰ and the $\delta^{18}O\text{-}NO_3^-$ values ranged from +13.8‰ to +27.4‰ in the river water samples.

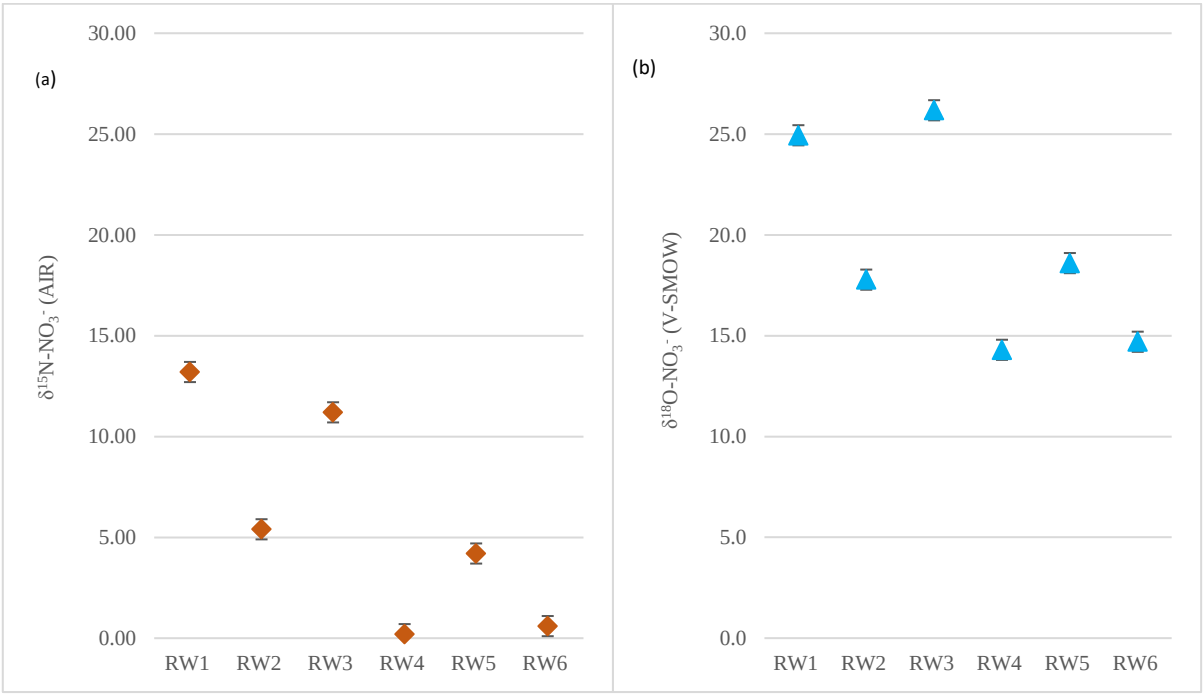

Figure 3. Spatial variations in $\delta^{15}N\text{-}NO_3^-$ (a) and $\delta^{18}O\text{-}NO_3^-$ (b) in river water samples

Sources of nitrate stable isotopes in the river water samples

In Figure 4, the measured δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values are colour coded according to spatial variations and overlaid on the estimated nitrate isotopic ranges of common sources in literature (Kendall 1998; Kendall et al. 2007; Kendall and Aravena 2000). At RW1 and RW3, the δ^{15}N-NO_3^- values were between 11.3‰ and 15.6‰ and the δ^{18}O-NO_3^- values were between 23.0‰ and 27.4‰. The high δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values at RW1 and RW3 during both seasons may be attributed to the atmospheric nitrate from fixation processes associated with the release of nitrogen oxide (NO_x) into the atmosphere from human activities (e.g., fossil fuel combustion) and natural processes (biogenic soil emission, biomass burning, and lightning) (Kendall et al., 2007; Li et al., 2020). Based on Figure 2, the high nitrate level at RW1 and RW3 stations (above base level) may due to the atmospheric nitrate sources.

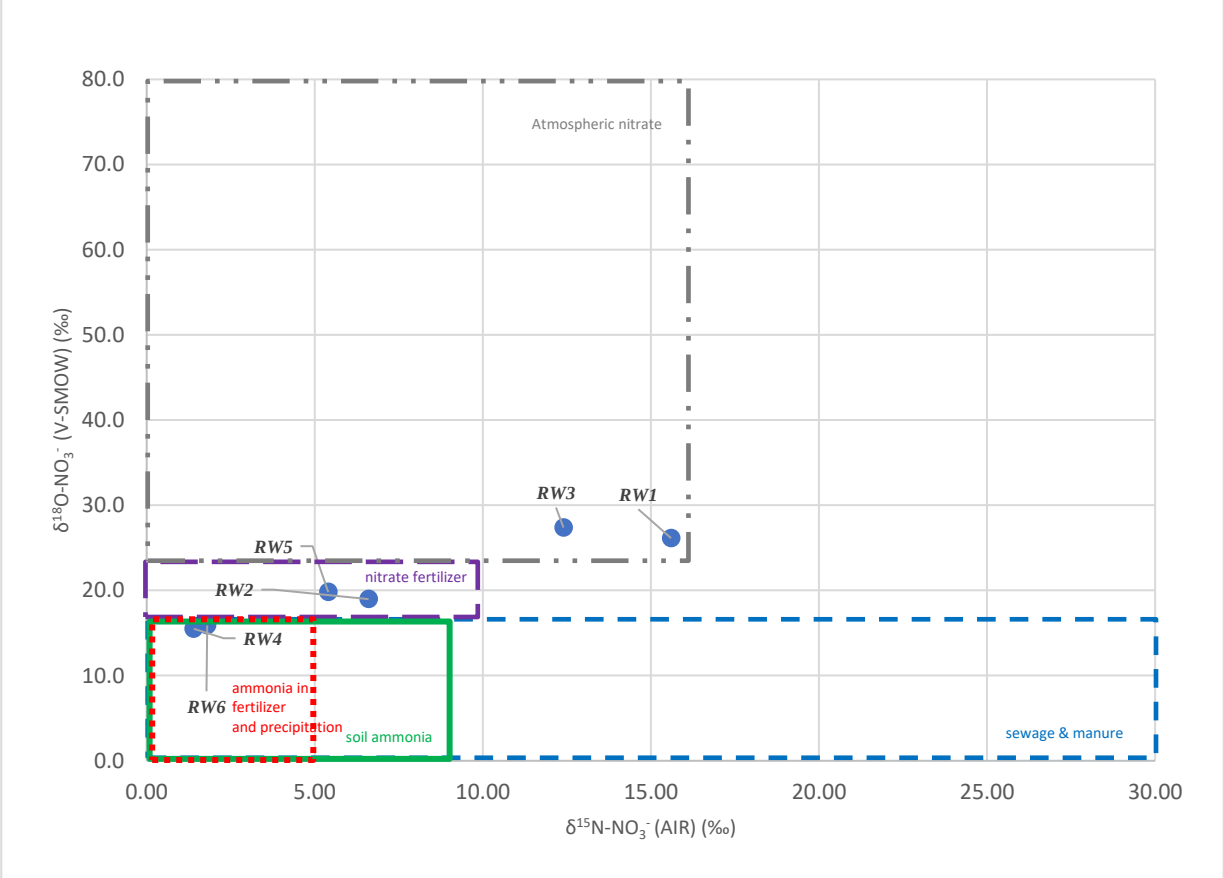

Figure 4. Cross plot of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values in river water samples. The isotopic composition of various sources in the diagram is derived from (Kendall 1998; Kendall et al. 2007)

At RW2 and RW5, nitrate-based fertilizers were the major source of nitrate, with δ^{15}N-NO_3^- values between 4.9‰ and 6.6‰ and δ^{18}O-NO_3^- values between 19.0‰ and 22.2‰. RW2 and RW5 are located near large palm oil and rubber plantations. The higher nitrate levels at RW2 (exceeding the base level) than at RW5 (below the base level) may be attributed to the larger plantation areas near RW2 (Rantau) than those near RW5 (Seremban), with a mixture of plantations and residential areas. The high and low nitrate concentration patterns from these stations were derived from similar nitrate fertilizer sources.

As shown in Figure 4, at RW4 and RW6, nitrification values were between -5‰ and 15‰ of $\delta^{18}O\text{-}NO_3^-$ values (Kendall et al. 2007). At RW4 and RW6, the $\delta^{15}N\text{-}NO_3^-$ values were between 1.4‰ and 2.3‰ and the $\delta^{18}O\text{-}NO_3^-$ values were between 13.8‰ and 15.9‰. RW4 and RW6 presented with the lowest $\delta^{15}N\text{-}NO_3^-$ values compared to other $\delta^{15}N\text{-}NO_3^-$ in other sampling stations. As shown in Figure 4, RW4 and RW6 were affected by ammonia in fertilizers, precipitation, sewage, and manure nitrate pollution sources (+0‰ to +25‰). Even though the nitrate concentration in RW4 and RW6 was below the base level, these stations were influenced by various types of potential nitrate pollution sources based on the crossplot of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$.

CONCLUSION

Nitrate concentration in river water samples exceeded the base level of nitrate and was lower than the WHO guideline. The elevated nitrate concentration at the downstream stations may be explained by the cumulative loading of nitrate from the upstream regions as well as anthropogenic activities in nearby areas as well as point sources from the nearby areas. The cross plot of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ capables to identify the potential nitrate pollution sources in the sampling locations with higher and lower nitrate concentrations compared to the nitrate base level. From the cross plot of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$, the river water samples of Linggi were affected by mixture of nitrate pollution from atmospheric nitrate, nitrate fertilizer, ammonia in fertilizers, precipitation, soil ammonia, manure, and sewage.

ACKNOWLEDGEMENT

The authors would like to thank to the Ministry of Higher Education (MOHE) of Malaysia for supporting this research under the Fundamental Research Grant Scheme (FRGS) No: FRGS/1/2017/STG01/UNISZA/02/2 and Internal UNiSZA grant: UNiSZA/2017/SRGS/18. Research funding was also provided by the Centre of Hydrogeology, National Hydraulic Research Institute of Malaysia (NAHRIM) under the project *Integrated surface and groundwater physical-based model of Linggi, Muda and Langat River Basin*

REFERENCES

Abdul Zali, M., Juahir, H., Ismail, A., Retnam, A., Idris, A. N., Sefie, A., et al. (2021). Tracing sewage contamination based on sterols and stanols markers within the mainland aquatic ecosystem: a case study of Linggi catchment, Malaysia. *Environmental Science and Pollution Research*. https://doi.org/10.1007/s11356-020-11680-5

Akinnawo, S. O. (2023). Eutrophication: Causes, consequences, physical, chemical and biological techniques for mitigation strategies. *Environmental Challenges*, *12*(May). https://doi.org/10.1016/j.envc.2023.100733

APHA. (2017). Standard Method For the Examination of Water and Wastewater. In *American Journal of Public Health and Nations Health* (23rd ed.). USA. https://doi.org/https://doi.org/10.2105/SMWW.2882.070

Camargo, J. A., & Alonso, Á. (2006). Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems : A global assessment. *Environment International*, *32*(6), 831–849. https://doi.org/10.1016/j.envint.2006.05.002

DeVries, S. L., & Zhang, P. (2016). Antibiotics and the Terrestrial Nitrogen Cycle: A Review. *Current Pollution Reports*, *2*(1), 51–67. https://doi.org/10.1007/s40726-016-0027-3

Fenech, C., Rock, L., Nolan, K., Tobin, J., & Morrissey, A. (2012). The potential for a suite of isotope and chemical markers to differentiate sources of nitrate contamination: A review. *Water Research*, *46*(7), 2023–2041. https://doi.org/10.1016/j.watres.2012.01.044

Filoso, S., Martinelli, L. A., Howarth, R. W., & Boyer, E. W. (2006). Nitrogen Cycling in the Americas: Natural and Anthropogenic Influences and Controls. *Nitrogen Cycling in the Americas: Natural and Anthropogenic Influences and Controls*, (January). https://doi.org/10.1007/978-1-4020-5517-1

Grout, L., Chambers, T., Hales, S., Prickett, M., Baker, M. G., & Wilson, N. (2023). The potential human health hazard of nitrates in drinking water: a media discourse analysis in a high-income country. *Environmental Health: A Global Access Science Source*, *22*(1), 1–11. https://doi.org/10.1186/s12940-023-00960-5

Gruber, N., & Galloway, J. N. (2008). An Earth-system perspective of the global nitrogen cycle. *Nature*, *451*(7176), 293–296. https://doi.org/10.1038/nature06592

Gutiérrez, M., Biagioni, R. N., Alarcón-Herrera, M. T., & Rivas-Lucero, B. A. (2018). An overview of nitrate sources and operating processes in arid and semiarid aquifer systems. *Science of the Total Environment*, *624*, 1513–1522. https://doi.org/10.1016/j.scitotenv.2017.12.252

Jiang, S., Müller, M., Jin, J., Wu, Y., Zhu, K., Zhang, G., et al. (2019). Dissolved inorganic nitrogen in a tropical estuary at Malaysia: transport and transformation. *Biogeosciences Discussions*, 1–27. https://doi.org/10.5194/bg-2019-7

Kendall, C. (1998). Tracing Nitrogen Sources and Cycling in Catchments. In *Isotope Tracers in Catchment Hydrology* (pp. 519–576).

Kendall, C., & Aravena, R. (2000). Nitrate isotopes in groundwater system. In P. Cook & A. ;. Herczeg (Eds.), *Environmental tracers in subsurface hydrology* (pp. 261–297). CSIRO Land and Water, Glen Osmond, Australia: Springer Science+ Business Media LLC. https://doi.org/10.1007/978-1-4615-4557-6

Kendall, C., Elliott, E. M., & Wankel, S. D. (2007). Tracing anthropogenic inputs of nitrogen to ecosystems. In R. Michener & K. Lajtha (Eds.), *Stable Isotopes in Ecology and Environmental Science* (pp. 375–445). Blackwell Publishing.

Li, C., Li, S. L., Yue, F. J., He, S. N., Shi, Z. B., Di, C. L., & Liu, C. Q. (2020). Nitrate sources and formation of rainwater constrained by dual isotopes in Southeast Asia: Example from Singapore. *Chemosphere*, *241*. https://doi.org/10.1016/j.chemosphere.2019.125024

Li, S.-L., Liu, C.-Q., Li, J., Liu, X., Chetelat, B., Wang, B., & Wang, F. (2010). Assessment of the sources of nitrate in the Changjiang River, China using a nitrogen and oxygen isotopic approach. *Environmental science & technology*, *44*(5), 1573–1578. https://doi.org/10.1021/es902670n

Michalski, G., Kolanowski, M., & Riha, K. M. (2015). Oxygen and nitrogen isotopic composition of nitrate in commercial fertilizers, nitric acid, and reagent salts. *Isotopes in environmental and health studies*, (July 2015), 1–10. https://doi.org/10.1080/10256016.2015.1054821

Minet, E., Goodhue, R., Coxon, C. E., Kalin, R. M., & Meier-Augenstein, W. (2011). Simplifying and improving the extraction of nitrate from freshwater for stable isotope analyses. *Journal of environmental monitoring : JEM*, *13*(7), 2062–6. https://doi.org/10.1039/c1em10289c

Nejatijahromi, Z., Nassery, H. R., Hosono, T., Nakhaei, M., Alijani, F., & Okumura, A. (2019). Groundwater nitrate contamination in an area using urban wastewaters for agricultural irrigation under arid climate condition, southeast of Tehran, Iran. *Agricultural Water Management*, *221*(April), 397–414. https://doi.org/10.1016/j.agwat.2019.04.015

Panno, S. V., Kelly, W. R., Martinsek, A. T., & Hackley, K. C. (2006). Estimating Background and Threshold Nitrate Concentrations Using Probability Graphs. *Ground Water*, *44*(5), 697–709. https://doi.org/10.1111/j.1745-6584.2006.00240.x

Qin, Y., Zhang, D., & Wang, F. (2019). Using nitrogen and oxygen isotopes to access sources and transformations of nitrogen in the Qinhe Basin, North China. *Environmental Science and Pollution Research*, *26*(1), 738–748. https://doi.org/10.1007/s11356-018-3660-0

Silva, S. R., Kendall, C., Wilkison, D. H., Ziegler, A. C., Chang, C. C. Y., & Avanzino, R. J. (2000). A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. *Journal of Hydrology*, *228*(1–2), 22–36. https://doi.org/10.1016/S0022-1694(99)00205-X

USGS. (2001). Instruction for Collection and Recovery of Nitrate for d15N and d18O Analysis. https://wwwrcamnl.wr.usgs.gov/isoig/guidelines/nitrate/index.html. Accessed 1 December 2016

Venkiteswaran, J. J., Boeckx, P., & Gooddy, D. C. (2019). Towards a global interpretation of dual nitrate isotopes in surface waters. *Journal of Hydrology X*. https://doi.org/10.1016/j.hydroa.2019.100037

Ver, L. M. B., Mackenzie, F. T., & Lerman, A. (1999). Carbon cycle in the coastal zone: Effects of global perturbations and change in the past three centuries. *Chemical Geology*, *159*(1–4), 283–304. https://doi.org/10.1016/S0009-2541(99)00042-X

Wang, S., Zheng, W., Curerell, M., Yang, Y., Zhao, H., & Lv, M. (2017). Relationship between land-use and sources and fate of nitrate in groundwater in a typical recharge area of the North China Plain. *Science of the Total Environment*, *609*, 607–620. https://doi.org/10.1016/j.scitotenv.2017.07.176

WHO. (2017). Guidelines for drinking-water quality, 4th edition, incorporating the 1st addendum.

Wu, Y., Luo, Z., Luo, W., Ma, T., & Wang, Y. (2018). Multiple isotope geochemistry and hydrochemical monitoring of karst water in a rapidly urbanized region. *Journal of Contaminant Hydrology*, *218*(March), 44–58. https://doi.org/10.1016/j.jconhyd.2018.10.009

Xing, M., & Liu, W. (2011). An improved method of ion exchange for nitrogen isotope analysis of water nitrate. *Analytica Chimica Acta*, *686*(1–2), 107–114. https://doi.org/10.1016/j.aca.2010.11.051

Yang, X., Liu, Q., Fu, G., He, Y., Luo, X., & Zheng, Z. (2016). Spatiotemporal patterns and source attribution of nitrogen load in a river basin with complex pollution sources. *Water Research*, *94*, 187–199. https://doi.org/10.1016/j.watres.2016.02.040

Zafirah, N., Ilham, J. I. J., R., M., A., M. S., Shaiful, Y., & Syakir, M. I. (2017). Isotopic (13C and 15N) Variation in Tropical RIver Sediments of Kelantan, Malaysia: A Reconnaissance Study of Land Use Impact to the Watershed. *Applied ecology and Environmental Research*, *15*(4), 1101–1119. https://doi.org/10.15666/aeer/1504

Zainuddin, A. H., Wee, S. Y., & Aris, A. Z. (2020). Occurrence and potential risk of organophosphorus pesticides in urbanised Linggi River, Negeri Sembilan, Malaysia. *Environmental Geochemistry and Health*, *42*(11), 3703–3715. https://doi.org/10.1007/s10653-020-00604-4

Zhang, Y., Shi, P., Li, F., Wei, A., Song, J., & Ma, J. (2018). Quantification of nitrate sources and fates in rivers in an irrigated agricultural area using environmental isotopes and a Bayesian isotope mixing model. *Chemosphere*, *208*, 493–501. https://doi.org/10.1016/j.chemosphere.2018.05.164

Zhang, Y., Shi, P., Song, J., & Li, Q. (2019). Application of nitrogen and oxygen isotopes for source and fate identification of nitrate pollution in surfacewater: A review. *Applied Sciences (Switzerland)*, *9*(1). https://doi.org/10.3390/app9010018