

Application of Nitrate Stable Isotopes, $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$, in Bukit Merah Reservoir, Malaysia

Nur Syahirah Yacob,¹ M. I. Syakir,^{1,2} Syahidah Akmal Muhammad,^{1,3} Zarul Hazrin Hashim,⁴ Azimah Rahman,⁵ Fu-Jun Yue,^{6,7} Si-Liang Li⁸ and Widad Fadhullah^{1*}

¹Environmental Technology Section, School of Industrial Technology, Universiti Sains Malaysia, 11800 USM Pulau Pinang, Malaysia

²Centre for Global Sustainability Studies (CGSS), Universiti Sains Malaysia, 11800 USM Pulau Pinang, Malaysia

³Analytical Biochemistry Research Centre, Universiti Sains Malaysia, 11800 USM Pulau Pinang, Malaysia

⁴School of Biological Sciences, Universiti Sains Malaysia, 11800 USM Pulau Pinang, Malaysia

⁵School of Humanities, Universiti Sains Malaysia, 11800 USM Pulau Pinang, Malaysia

⁶School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, United Kingdom

⁷State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

⁸Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China

*Corresponding author: widad@usm.my

Published online: 25 October 2018

To cite this article: Yacob, N. S. et al. (2018). Application of nitrate stable isotopes, $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$, in Bukit Merah Reservoir, Malaysia. *J. Phys. Sci.*, 29(Supp. 3), 1–6, <https://doi.org/10.21315/jps2018.29.s3.1>

To link to this article: <https://doi.org/10.21315/jps2018.29.s3.1>

ABSTRACT: *Identifying nitrate sources in Bukit Merah Reservoir (BMR), Perak, Malaysia is important in order to understand the productivity of the ecosystem. For the first time, the dual stable isotopes of nitrate, $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$, were applied to assess its potential use to trace the sources of nitrate in surface water of BMR. Water samples were collected in the months of August 2016, December 2016, March 2017 and October 2017 from 10 sites within Kurau River Basin covering the upper stream, tributaries and reservoir. Water samples were analysed using the bacterial denitrification method. The variation of nitrate isotopes ranged from +0.4‰ to +14.91‰ for $\delta^{15}\text{N-NO}_3^-$ and –0.01‰ to +39.4‰ for $\delta^{18}\text{O-NO}_3^-$, respectively. Overall, based on the crossplots between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$, majority of the $\delta^{18}\text{O-NO}_3^-$ in the samples reflects atmospheric deposition*

whereas $\delta^{15}\text{N-NO}_3^-$ indicates sources from both ammonium fertiliser and soil nitrogen, and a minor contribution of sewage and manure in BMR water catchment.

Keywords: Bukit Merah Reservoir, surface water samples, dual-stable isotopes, nitrate, nitrate stable isotopes

1. INTRODUCTION

Reservoir can be influenced by external inputs of organic or inorganic pollutants into the waterbodies and nutrient loading which can deteriorate the water quality.¹ Excessive nutrient loading may cause eutrophication, which may disrupt the ecosystem functioning. Ninety lakes in Malaysia have been categorised as mesotrophic and eutrophic, respectively.^{1,2} Out of those 90 lakes, 34 lakes or 38% were evaluated to be in mesotrophic condition while another 56 lakes or 62% were in eutrophic condition including Bukit Merah Reservoir (BMR), Perak, Malaysia. Nitrate as the dominant form of nitrogen, if present excessively can trigger eutrophication, hypoxia and degradation of the water quality itself.³

Since nitrate can be derived from multiple possible sources, it is a challenge for freshwater system to trace its sources which includes atmospheric deposition, nitrogenous fertiliser, animal manure, discharge of domestic sewage and soil organic nitrogen.⁴ Traditional method of measuring nitrate concentration and evaluating the potential nitrate source faced difficulties due to multiple potential sources of nitrate including the non-point sources and complex biological processes. In contrast, stable isotopes give a specific isotopic signature which can specify potential source by using $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$.⁵ Realising the risks of the current condition in BMR, the dual stable isotopes of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ were used to see its potential application in identifying the nitrate source in BMR for better understanding of the system.

2. EXPERIMENTAL

BMR was built in 1902 and is known as the oldest man-made reservoir in Malaysia. It was built to provide irrigation water for double cropping of 24,000 ha of paddy land in the district of Kerian, Perak and to provide domestic and industrial water supply of the populace in the Kerian and Larut Matang districts.⁶ It is also used as a tool for flood and drought control. In 2015, 40.87% of land use around BMR was categorised as reserved forest by state and 28.88% as permanent reserved forest area. The land use for agricultural activities was dominated by 18.55% of palm oil

plantation, 9.37% of rubber plantation and the other 2.33% was used for farming area.

Ten sampling points were selected from the upper stream, tributary and the reservoir respectively (Figure 1). Surface water samples were collected in the months of August 2016, December 2016, March 2017 and October 2017 using pre-washed bottles and filtered in-situ with 0.2 μm of polyethersulfone syringe filter. The samples were stored under 4°C before transported to the State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences Guiyang, China. Each sample was analysed using a bacterial denitrification method by Sigman et al. and measured using a Finnigan MAT-253 isotopes ratio-mass spectrometry.⁷ For scale calibration, three references were used (USGS-32, USGS-34 and USGS-35) in the analysis. Each sample was measured in duplicates and the standard error was 0.3‰ for $\delta^{15}\text{N}-\text{NO}_3^-$ and 0.3‰ for $\delta^{18}\text{O}-\text{NO}_3^-$.

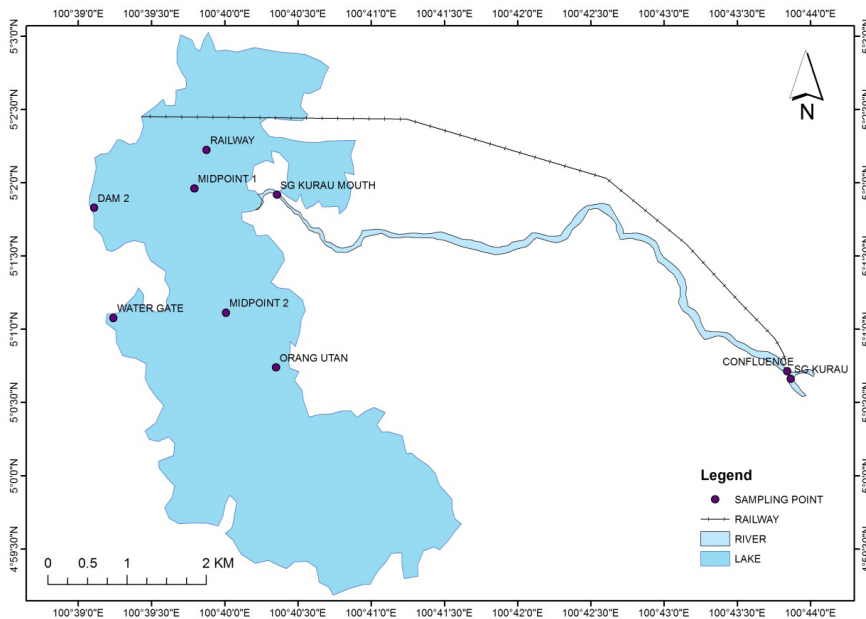


Figure 1: Map showing nine sampling points from Sungai Kurau down to the reservoir area while the other one point located at Batu Kurau is known as the upper stream of the reservoir.

3. RESULTS AND DISCUSSION

In our study, $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ varied between +0.4‰ to +14.91‰ and -0.01‰ to +39.4‰, respectively for the four selected sampling months (Figure 2). As indicated in Figure 2, nitrate from BMR was derived from four different sources: atmospheric deposition, soil nitrate, ammonium fertiliser, sewage or manure. As reported by Kendall et al., nitrate from atmospheric deposition is heavily enriched in ^{18}O up to 75‰ while lower value of ^{18}O are usually found in ammonium fertiliser, nitrate fertiliser, soil nitrogen or sewage and manure.⁸ From the figure, enriched $^{15}\text{N-NO}_3^-$ showed potential sources from sewage and manure while the lighter $^{15}\text{N-NO}_3^-$ showed soil nitrogen and ammonium fertiliser. Thus, from the result, the $\delta^{15}\text{N-NO}_3^-$ of our water samples indicated sources from both soil nitrogen and ammonium fertiliser. Sand mining activities near Sungai Kurau is one of the main sources that have contributed to the re-suspended sediment at the surrounding area suggesting soil nitrogen as the primary source for the upper stream and tributaries.⁹ As supported by previous researchers, 93% of the sediment input and nutrients in the catchment of BMR were claimed to originate from Sungai Kurau.⁶

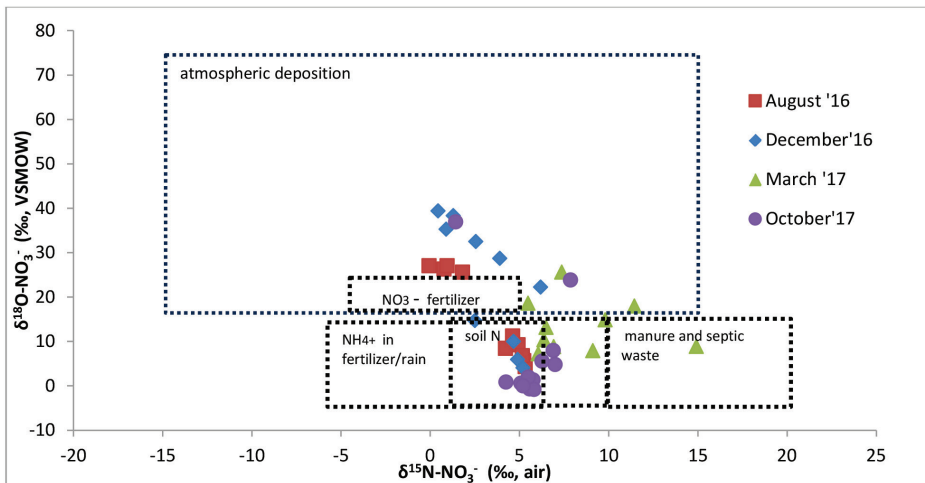


Figure 2: Cross plot between $\delta^{15}\text{N-NO}_3^-$ (‰) and $\delta^{18}\text{O-NO}_3^-$ (‰) in BMR from August 2016 to December 2016, and March 2017 to October 2017. Reported values were from Kendall et al., Kendall and Wassenaar.^{8,11,12.}

In this analysis, the $\delta^{18}\text{O-NO}_3^-$ values varied from as low as -0.01‰ in October 2017 to as high as +39.4‰ in December 2016. The nitrate derived from atmospheric deposition showed $\delta^{15}\text{N}$ values from +0.4‰ to +11.45‰ with relatively high $\delta^{18}\text{O}$ (>+14‰).^{10,11} The result of $\delta^{18}\text{O-NO}_3^-$ from all the four months indicated

that there is an atmospheric deposition influence as the major nitrate source in the catchment. Hence, based on the dual isotopic pattern, the nitrates content in the water catchment are mainly derived from both soil nitrogen and ammonium fertiliser together with atmospheric deposition.

4. CONCLUSION

Major portion of nitrate in BMR reflects atmospheric deposition and an overlap between ammonium fertilisers and soil organic nitrogen. Only a minor portion points toward sewage and manure. The results presented the potential application of nitrate stable isotopes as the tool for tracing the source of nitrate in water catchment. Further studies should incorporate analysing the potential sources of nitrate within BMR to confirm the $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ ranges.

5. ACKNOWLEDGEMENTS

This study was funded by the Malaysian Ministry of Education and Universiti Sains Malaysia's Fundamental Research Grant Scheme (FRGS) grant no. 203/PTEKIND/6711467, International Atomic Energy Agency (IAEA) grant, Coordinated Research Project (CRP) F32007 (grant no. 304/PTEKIND/650819/I111) and Opening Fund of the State Key Laboratory of Environmental Geochemistry. The authors would also like to thank Kerian District Department of Irrigation and Drainage, Perak, Malaysia for their assistance during our sampling activity and Mrs. Farah Liana Mohd Suhaimi, Data Geospatial Negara (MacGDI) for data on land use around BMR.

6. REFERENCES

1. Huang, Y. F. et al. (2015). Quality of water resources in Malaysia. In Lee, T. S. (Ed.). *Research and practice in water quality*. InTechOpen, <https://doi.org/10.5772/58969>.
2. National Hydraulic Research Institute of Malaysia. (2005). *A desk study on the status of eutrophication of lakes in Malaysia*. Seri Kembangan: National Hydraulic Research Institute of Malaysia.
3. Zheng, H. & Wu, J. (2015). Tracing the nitrate sources of the Yili River in the Taihu Lake watershed: A dual stable isotope approach. *Water*, 7(1), 188–201, <https://doi.org/10.3390/w7010188>.

4. Yue, F-J. et al. (2015). Analysis of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ to identify nitrate sources and transformations in Songhua River, Northeast China. *J. Hydrol.*, 519, 329–339, <https://doi.org/10.1016/j.jhydrol.2014.07.026>.
5. Miljevic, N. & Golobocanin, D. (2007). Potential use of environmental isotopes in pollutant migration studies. *Environ. Isot. Pollut. Stud.*, 58, 251–262, <https://doi.org/10.2478/v10004-007-0015-5>.
6. Ismail, W. R. & Najib, S. A. M. (2011). Sediment and nutrient balance of Bukit Merah Reservoir, Perak, Malaysia. *Lakes Reserv. Res. Manage.*, 16, 179–184, <https://doi.org/10.1111/j.1440-1770.2011.00453.x>.
7. Sigman, D. M. et al. (2001). A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal. Chem.*, 73, 4145–4153, <https://doi.org/10.1021/ac010088e>.
8. Kendall, C., Elliott, E. M. & Wankel, S. D. (2007). Tracing anthropogenic inputs of nitrogen to ecosystems. In Michener, R. H. & Lajtha, K (Eds.). *Stable isotopes in ecology and environmental science*, 2nd ed. London: Blackwell, 375–449, <https://doi.org/10.1002/9780470691854.ch12>.
9. Fadzilatulhusni, S. et al. (2012). Evaluation of sediment budget of Bukit Merah Reservoir and its catchment area, Perak, Malaysia. *Mal. J. Environ. Manage.*, 13(1), 69–79.
10. Xu, S., Kang, P. & Sun, Y. (2016). A stable isotope approach and its application for identifying nitrate source and transformation process in water. *Environ. Sci. Pollut. Res.*, 23, 1133–1148, <https://doi.org/10.1007/s11356-015-5309-6>.
11. Kendall, C. (1998). Tracing nitrogen sources and cycling in catchments. In Kendall, C. et al. (Eds.). *Isotope tracers in catchment hydrology*. Amsterdam: Elsevier, 517–576, <https://doi.org/10.1016/B978-0-444-81546-0.50023-9>.
12. Wassenaar, L. I. (1995). Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of ^{15}N and ^{18}O in NO_3^- . *Appl. Geochem.*, 10(4), 391–405, [https://doi.org/10.1016/0883-2927\(95\)00013-A](https://doi.org/10.1016/0883-2927(95)00013-A).