

Application of Dual Isotopes ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$) to Determine Nitrate Contamination Sources in Cr(VI)-impacted Groundwater of Central Greece Aquifers

E. Kelepertzis¹, K. Pyrgaki¹, A. Argyraki¹, F. Botsou², P. Boeckx³, I. Megremi¹, S. Karavoltzos², M. Dassenakis²

(1) Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Greece,

kelepert@geol.uoa.gr

(2) Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

(3) Isotope Bioscience Laboratory-ISOFYS, Ghent University, Gent, Belgium

High nitrate (NO_3^-) concentrations in groundwater occur in many areas around the world, largely as a result of excessive application of fertilisers, animal manure and inappropriate sewage management. A series of recent publications have established that naturally-occurring Cr(VI) is prevalent in groundwater associated with ultramafic aquifers in Greece (*e.g.*, Kaprara *et al.*, 2015). There is some evidence that increased NO_3^- in alluvial aquifers of agricultural areas may exacerbate the mobilisation of Cr(VI) via intensive groundwater recharge through the vadose zone and associated increased contact with Cr-containing minerals or nitrification of ammonium in fertilisers (Mills *et al.*, 2011). Coupled nitrogen and oxygen isotopes of NO_3^- have proven useful in providing detailed information regarding the NO_3^- sources and transformations in groundwater systems. Here, we applied the combined use of the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO_3^- in groundwater systems in Greece, previously identified to contain elevated Cr(VI) concentrations (*e.g.*, Pyrgaki *et al.*, 2016), with the aim to determine the NO_3^- sources and examine the possible linkage of N cycling to Cr(VI) mobilisation. The porous aquifers from Schinos, Central Evia and Thiva regions have served as prime examples where both anthropogenic NO_3^- contamination and ultramafic-derived Cr(VI) affect groundwater chemistry.

A total of 28 groundwater samples from productive wells and bores were collected from the three study areas during November 2017 (dry period): 9 samples from Schinos (borehole depth ranging from 4 to 55 m), 13 samples from Evia (depth ranging from 4 to 250 m) and 6 samples from Thiva (depth ranging from 150 to 250 m). Concentrations of dissolved NO_3^- and Cr(VI) were determined after well-established international protocols for water sampling, handling, preservation and analysis. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- were analysed using the bacterial denitrification method. Hexavalent Cr concentrations for this specific data set ranged from 10 to 112 $\mu\text{g/l}$ in Thiva, 12 to 121 $\mu\text{g/l}$ in Schinos and 11 to 189 $\mu\text{g/l}$ in Evia. Nitrate concentrations showed a different distribution, with the highest concentrations determined in Evia (median 120 mg/l, range from 18 to 334 mg/l), followed by those in Thiva (median 66 mg/l, range from 21 to 151 mg/l) and Schinos (median 46 mg/l, range from 9 to 70 mg/l). The isotopic composition of NO_3^- for the whole data set ranged from 2.4 ‰ to 21 ‰ for $\delta^{15}\text{N}$, and from -0.73 ‰ to 15.3 ‰ for $\delta^{18}\text{O}$. Potential sources of NO_3^- in the studied aquifers include the application of synthetic fertilisers and manure in the agricultural fields of Evia and Thiva regions, and the existence of residential waste cesspools in Schinos and Evia areas. The NO_3^- isotope ratios in most studied water samples fall in the compositional range of NH_4^+ in fertiliser, soil N and manure/septic waste (Fig. 1). The soil N cannot be considered to be the main origin of NO_3^- because NO_3^- concentrations were much higher than expected concentrations produced by the mineralisation of soil organic N. A cluster of samples from Schinos and Evia exhibited $\delta^{15}\text{N}$ values close to or higher than 8‰, falling in the field of animal and/or human waste; especially for Schinos, and given the absence of intensive agricultural practices in this area, it is deduced that domestic sewage is the main source of NO_3^- in groundwater. On the other hand, isotope data indicated that nitrification of NH_4^+ -based fertilisers is responsible for the high NO_3^- concentrations measured in groundwater from Thiva, and partially from Evia. The high $[\text{NO}_3^-]/[\text{Cl}^-]$ ratios identified in these water samples signified that chemical fertilisers are the principal source of dissolved NO_3^- .

No clear relationship could be established between Cr(VI) and NO_3^- in this study, when the entire data set was taken into account; several samples with elevated Cr(VI) concentrations exhibited low NO_3^- concentrations and vice versa. Nonetheless, we found a significantly positive correlation between these solutes in the case of Schinos groundwater system ($r=0.83$, $p=0.005$) which might indicate an enhanced Cr(VI) generation when sewage wastes interfere with Cr-containing ultramafic source material. For Evia and Thiva groundwater samples, the nitrification of NH_4^+ in fertilisers, as evidenced by the isotope data of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO_3^- , could be responsible for the production of environmentally relevant amounts of Cr(VI) because the increased concentrations of H^+ may increase the mobility of Cr(III) and its subsequent oxidation on Mn oxides (Mills *et al.*, 2011). Although, it is difficult to support a direct link between the isotope data and Cr(VI) concentrations (Fig. 1), it appears that the process of nitrification, either from human/animal waste or synthetic fertilisers, trigger the geochemical occurrence of geogenic Cr(VI) in groundwater. Both NO_3^- and Cr(VI) occur primarily in oxic groundwater, deduced by the high Eh and dissolved oxygen (DO) values measured in the samples, providing a deciding geochemical environment that promotes the persistence of these constituents in solution. Locally in the aquifer, decreasing DO concentrations along flowpaths favour the process of denitrification. This is evident in one groundwater sample from Schinos ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of 21.5 ‰ and 15.3 ‰, respectively) that exhibited the lowest Cr(VI) concentration (8 $\mu\text{g/l}$) determined in the data set. The results of this study assist in the clear identification of NO_3^- contamination origin and provide science-based information to the general public and municipal key stakeholders for a more effective water management planning.

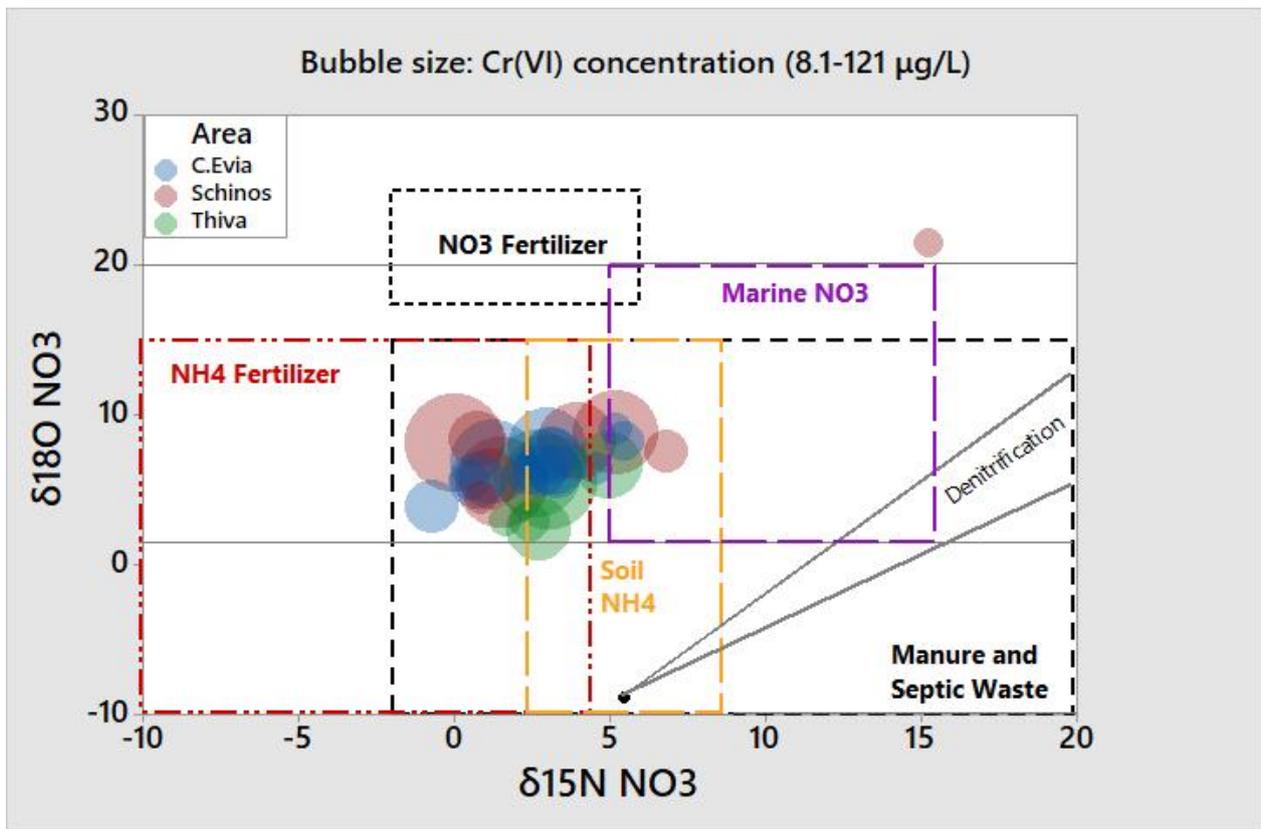


Figure 1. Isotopic values of NO_3^- for the studied groundwaters along with graduated symbol plot of Cr(VI) concentrations. Typical ranges of $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values for different nitrate sources were taken from Kendall and Aravena, (2000).

Acknowledgements

The present work was co-funded by the European Union (ERDF) and Greek national funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation", under the ERANETMED 1st Joint Call on Water Resources (project acronym: CRITERIA/ project code: T3EPA-00004).

References

- Kaprara, E., Kazakis, N., Simeonidis, K., Coles, S., Zouboulis, A.I., Samaras, P., Mitrakas, M., 2015. Occurrence of Cr(VI) in drinking water of Greece and relation to the geological background. *Journal of Hazardous Materials* 281, 2-11.
- Kendall, C., Aravena, R., 2000. Nitrate isotopes in groundwater systems, in: Cook, P.G., Herzeg, A. (Eds.), *Environmental tracers in Subsurface Hydrology*. Kluwer Academic Publishers, Boston, 261-297.
- Mills, C.T., Morrison, J.M., Goldhaber, M.B., Ellefsen, K.J., 2011. Chromium(VI) generation in vadose zone soils and alluvial sediments of the southwestern Sacramento Valley, California: A potential source of geogenic Cr(VI) to groundwater. *Applied Geochemistry* 26, 1488-1501.
- Pyrgaki, K., Argyraki, A., Kelepertzis, E., Paraskevopoulou, V., Botsou, F., Dassenakis, E., Skourtsos, E. 2016. Occurrence of hexavalent chromium in the ophiolite related aquifers of Loutraki and Schinos areas. *Bulletin of the Geological Society of Greece* 50, 2261-2270.