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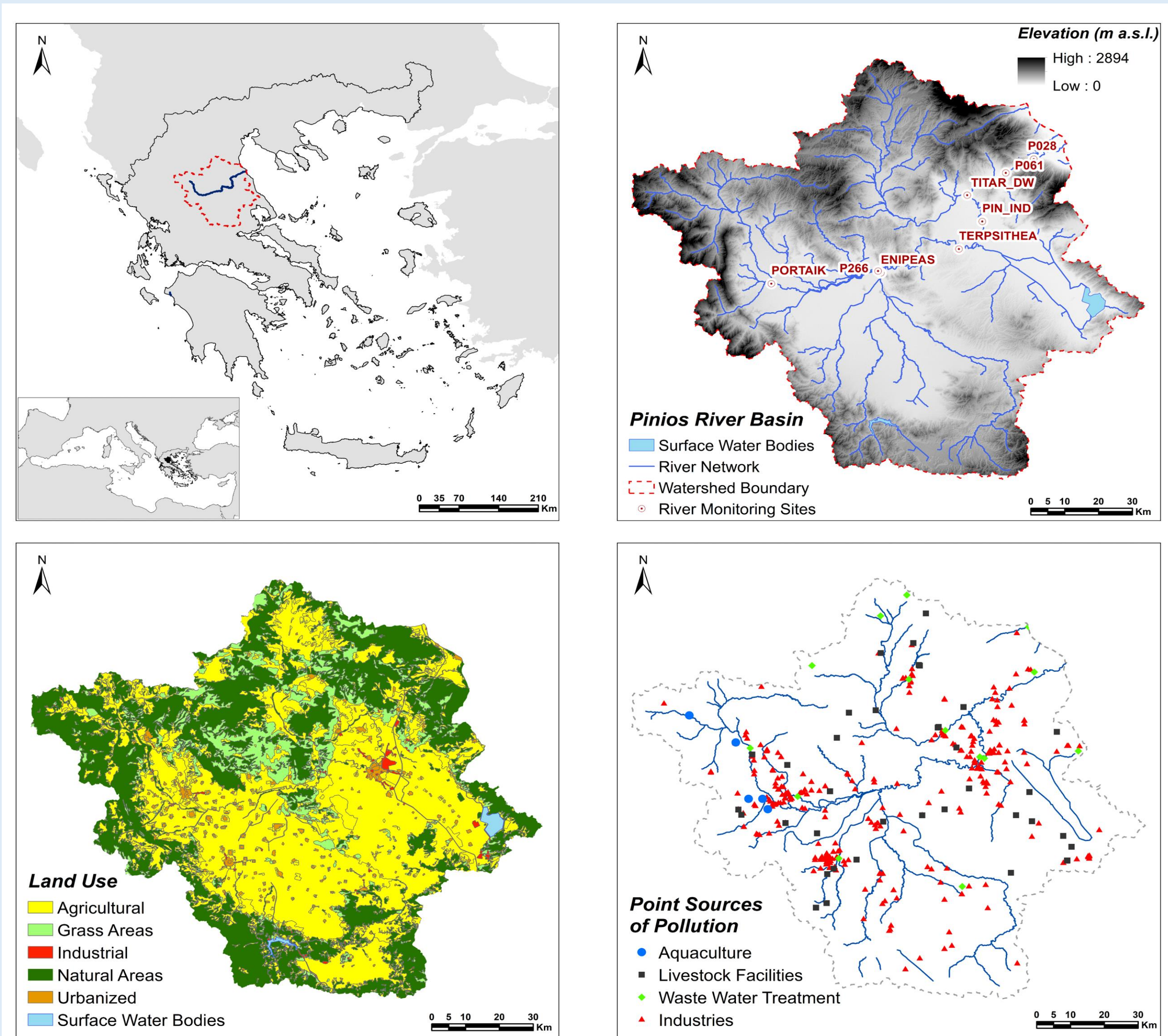
Introduction

The Pinios River Basin (PRB) is one of the most important agricultural areas of Greece suffering by water shortages, and hosts three main cities of a total population of ~400.000 citizens. The PRB also hosts 14 wastewater treatment plants and > 300 industrial units mostly related to dairies and food industries. In the PRB, there is a significant number of animal breeding facilities. The delta of the river belongs to the Natura 2000 Network (GR1420015) because it hosts important bird species and is one of the few wetlands in the area.

Here, we present the results of the first systematic monitoring (2019-2022) of nitrate isotopes and related proxies in a river basin in Greece. The objective were to:

- 1) trace the origin of nitrate pollution and its spatio-temporal evolution
- 2) study the N-cycling processes in the basin
- 3) identify linkages between nitrate isotope results, land-uses and point sources of pollution

The monitoring was done under the framework of the International Atomic Energy Agency (IAEA) Global Network of Isotopes in Rivers (GNIR).



Methods and Materials

The samples were analysed for nitrate isotope ratios (¹⁵N/¹⁴N and ¹⁸O/¹⁶O of NO₃⁻) at the ISOFYS lab of the University of Ghent (Belgium). Water isotope ratios (¹⁸O/¹⁶O of H₂O) analysis was done at the Isotope Hydrology Laboratory of the IAEA (Vienna, Austria) using a Los Gatos Research Liquid-Water Isotope Analyzer (TLWIA-912). The analytical uncertainties were: ±0.2‰ for δ¹⁵N, ±0.4‰ for δ¹⁸O of NO₃⁻ and ±0.1‰ for δ¹⁸O of H₂O.

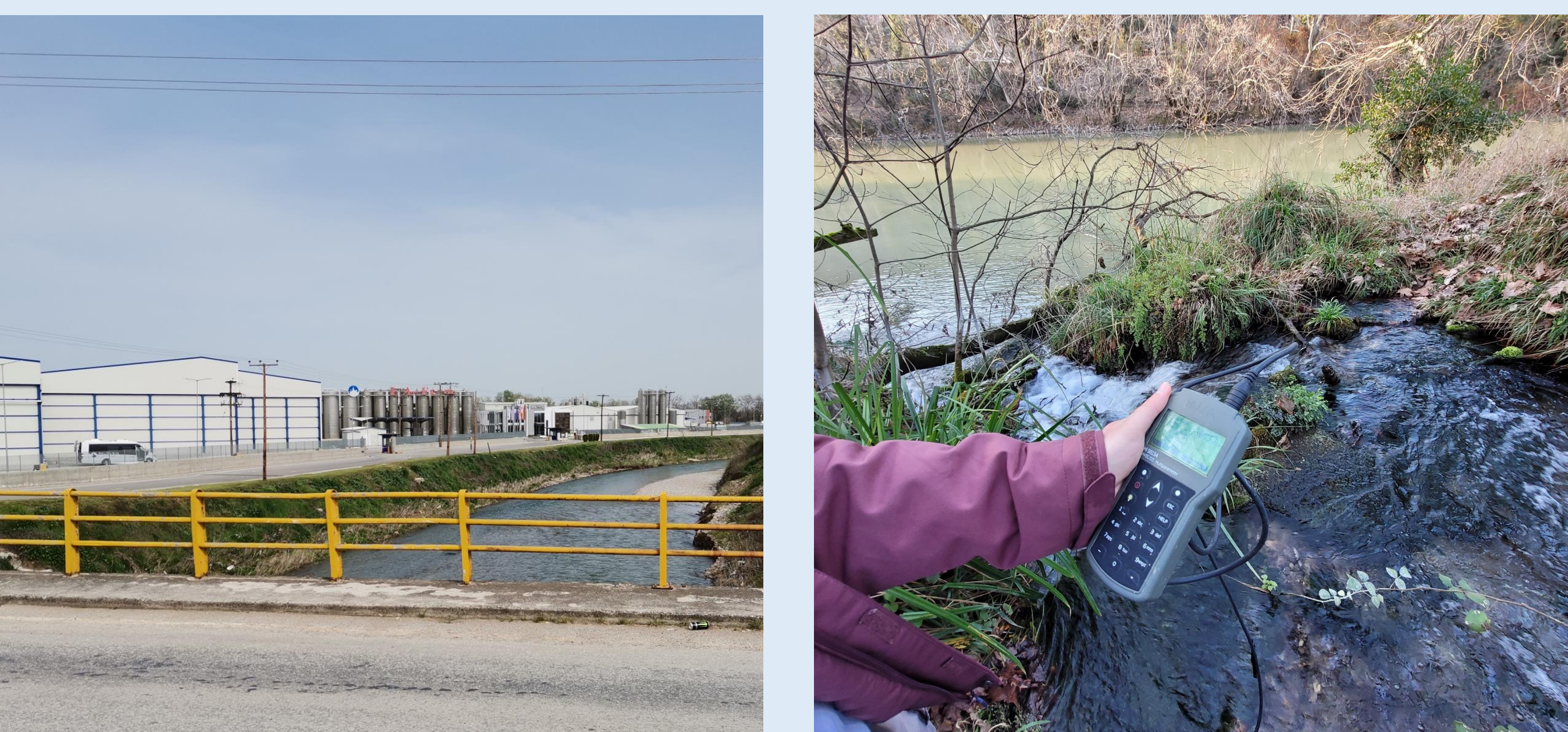
The Land Use Index (LUI) and the Point-Source pollution Index (PSI) were calculated for each sub-catchment as follows:

$$LUI = \sum(\% \text{ of Land Use} \times W)$$

$$PSI = \sum[(W_L \times A) + (W_D \times A)]$$

where W = weight of land use, W_L = the activity weight related to the potential N contamination load, W_D = is the activity weight related to distance of the point source of pollution from the river, A is the type of point source activity.

A Bayesian model (*simmr*) in R was applied for nitrate source apportionment.

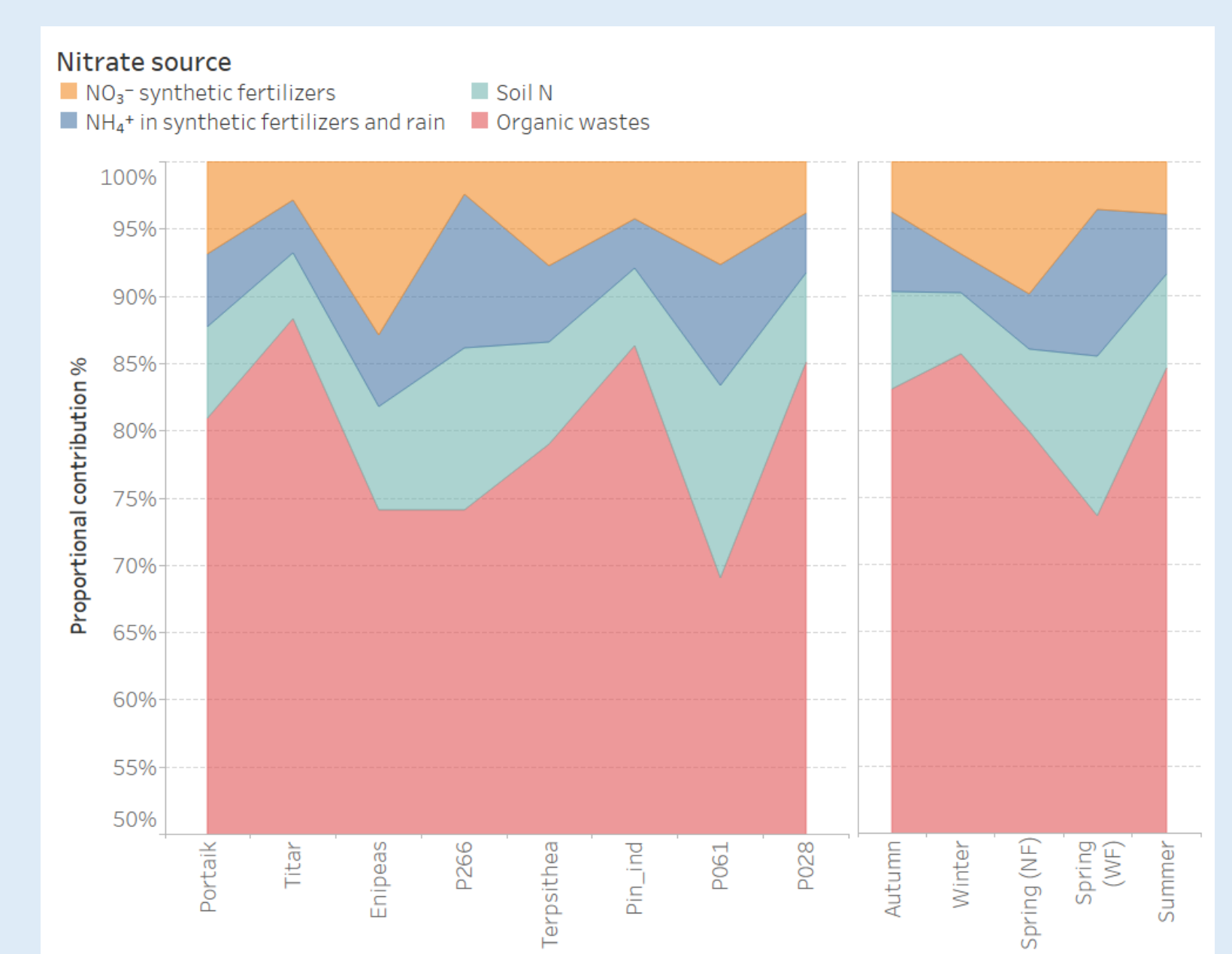
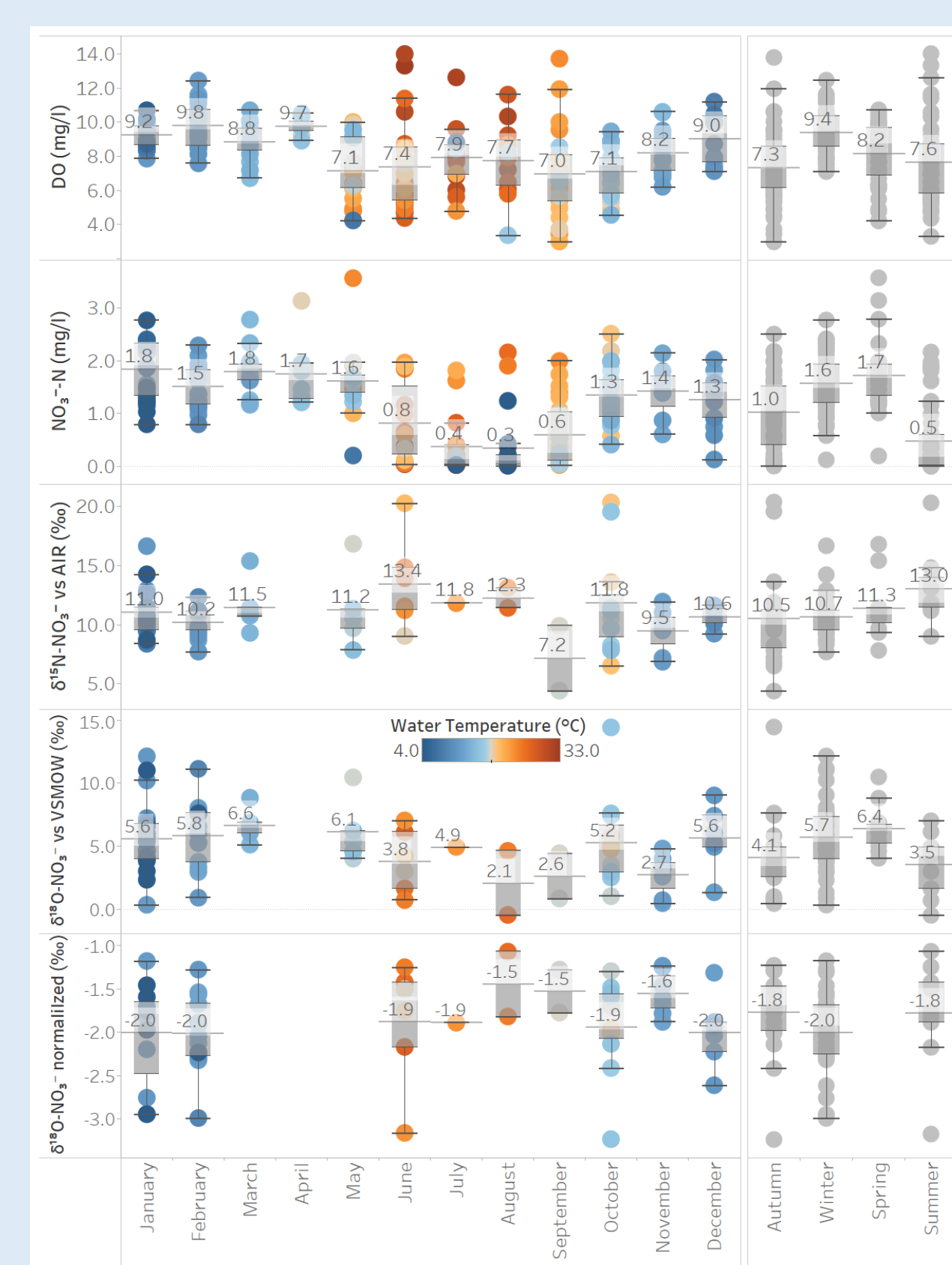
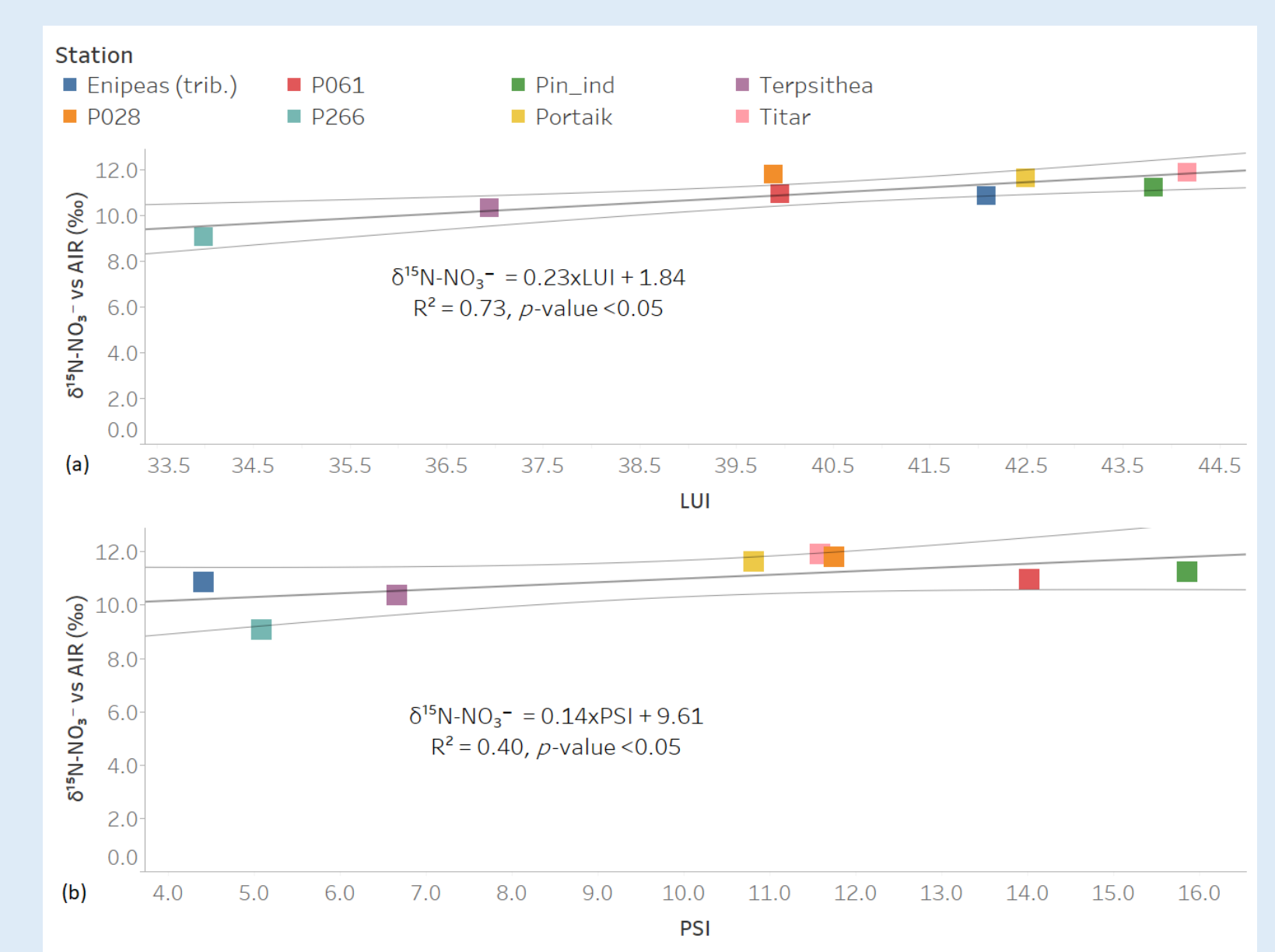
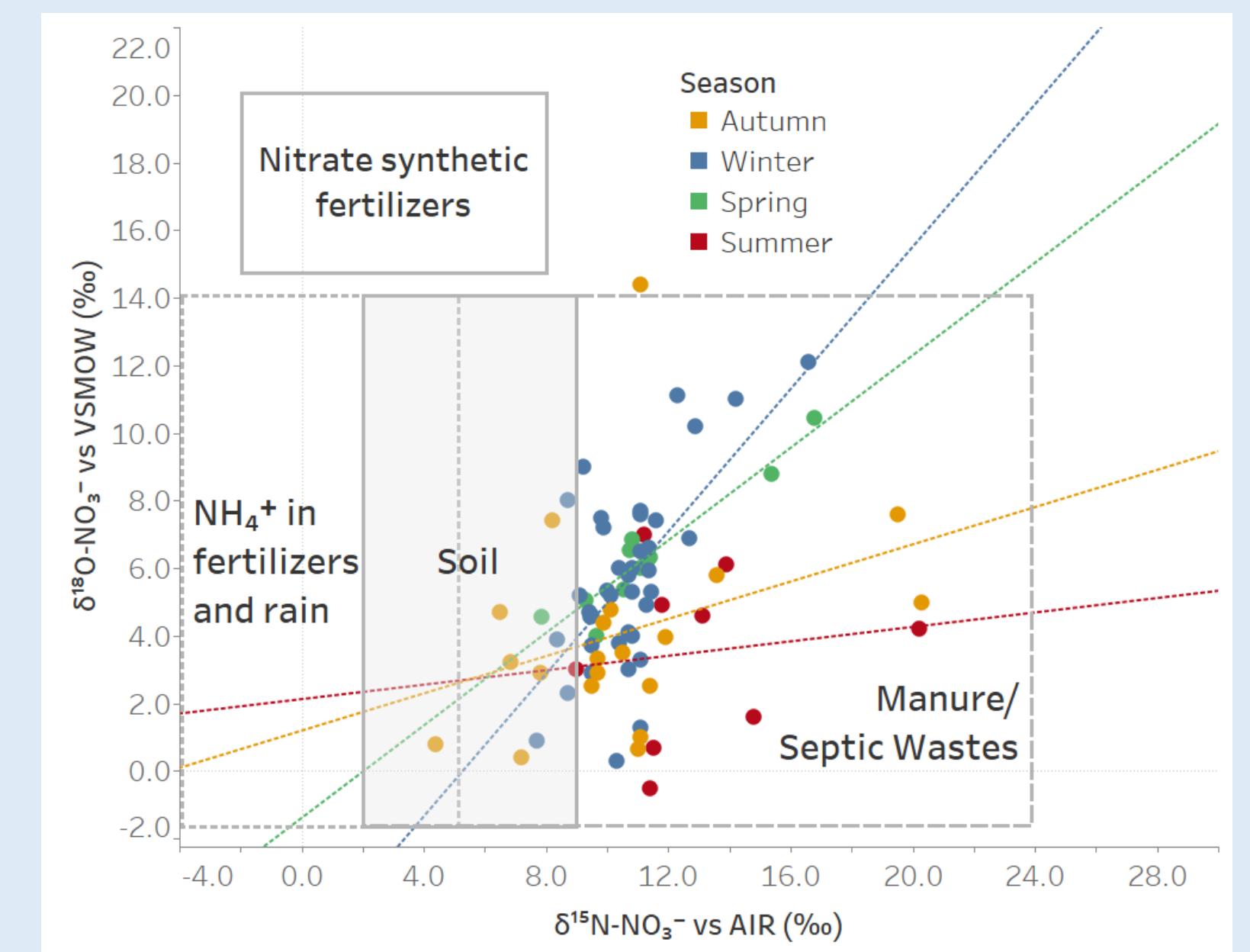
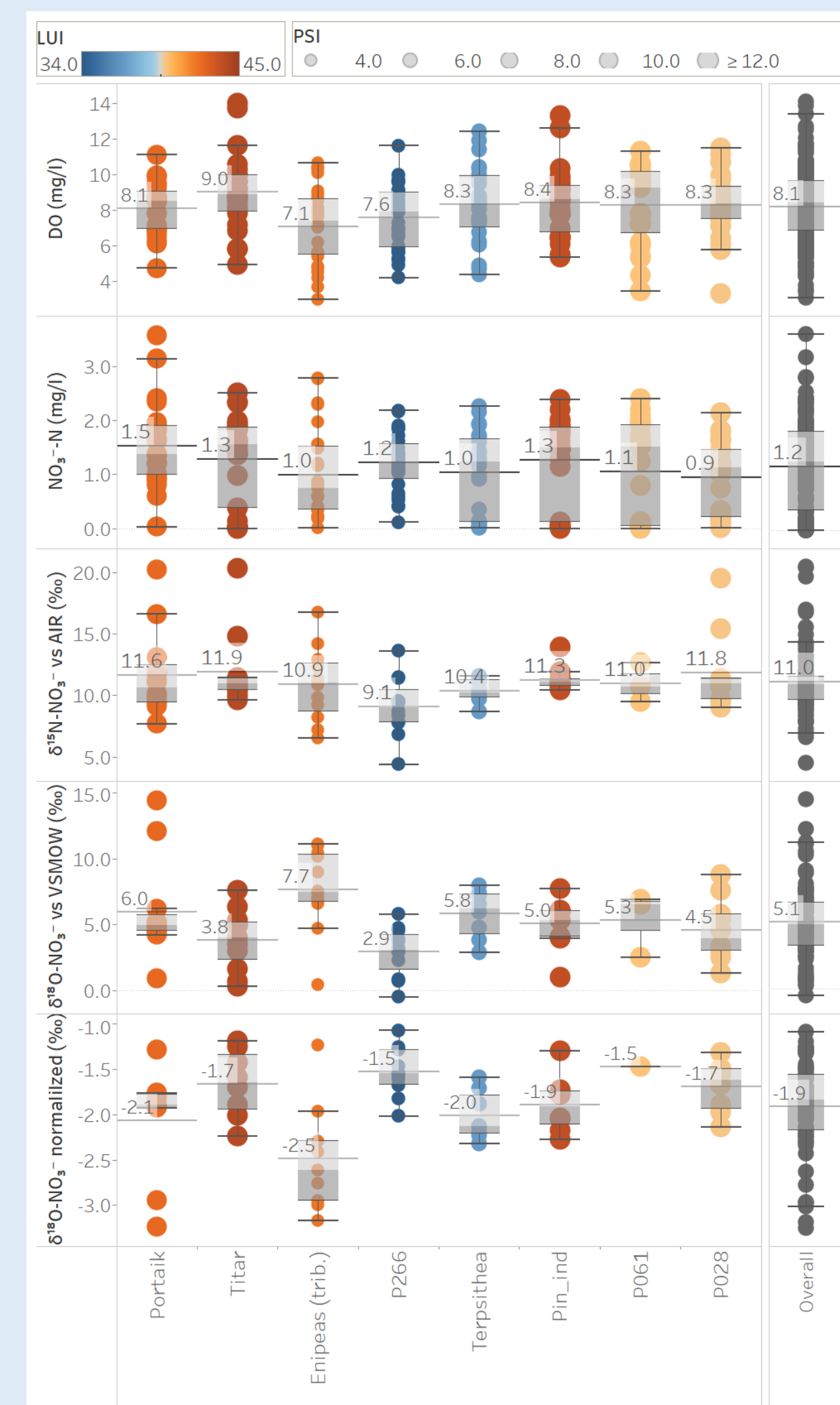


Acknowledgments

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Results & Discussion

- The NO₃⁻-N concentration ranged between <0.1 mg/l and 3.6 mg/l.
- On average, the δ¹⁵N-NO₃⁻ values were > +11 ‰ in most river sites with no correlation with the distance from the headwater source.
- The sampling sites with the lowest LUI (P266 and Terpsithea) and PSI (P266, Terpsithea and Enipeas) showed the lowest average δ¹⁵N-NO₃⁻ values.
- Increased δ¹⁵N and δ¹⁸O values of NO₃⁻ during spring were partly attributed to assimilation.
- Nitrification and washout of soils due to runoff were responsible for nitrate concentration increase in winter.



Conclusions

The isotopic composition of NO₃⁻ revealed that nitrate is the result of point and non-point sources of pollution subject to N-cycling due to biogeochemical processes. Organic wastes, particularly from food industries and animal breeding facilities, which are disposed into the river, are mainly responsible for water quality degradation. The relative contribution of organic wastes was high throughout the year (> 70 %) and masked the isotopic signal from synthetic fertilizers, which are heavily applied in the area. The study showed that in a European level the river waters suffer from nitrate pollution mostly due to nitrification of organic N, and thus action towards the protection and sustainable management of water resources should be taken.

References

1. Kendall, C., Elliott, E.M. and Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen to ecosystems. Stable isotopes in ecology and environmental science, 2(1), pp.375-449.
2. Matiatis, I., Papadopoulos, A., Panagopoulos, Y., and Dimitriou, E., 2023. Insights into the influence of morphology on the hydrological processes of river catchments using stable isotopes. Hydrological Sciences Journal (in press).
3. Matiatis, I., Lazogiannis, K., Papadopoulos, A., Skoulikidis, N., Boeckx, P., and Dimitriou, E., 2023. Stable isotopes reveal organic nitrogen pollution and cycling from point and non-point sources in a heavily cultivated (agricultural) Mediterranean river basin. Science of the Total Environment (under review).
4. Omoto, J.P.H., Martinelli, L.A., Ballester, M.V., Gessner, A., Krusche, A.V., Victoria, R.L. and Williams, M., 2000. Effects of land use on water chemistry and macroinvertebrates in two streams of the Piracicaba river basin, south-east Brazil. Freshwater Biology, 44(2), pp.327-337.
5. Parnell, A. and Parnell, M.A., 2019. Package 'simmr'. In (2016) Aquaculture big numbers. Food And Agriculture Organization Of The United Nations Rome, Italy.
6. Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M.B.J.K. and Böhlke, J.K., 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Analytical chemistry, 73(17), pp.4145-4153.
7. Stefanidis, K., Christopoulou, A., Poulos, S., Dassenakis, E. and Dimitriou, E., 2020. Nitrogen and phosphorus loads in Greek rivers: Implications for management in compliance with the Water Framework Directive. Water, 12(6), p.1531