DOMAIN-RESTRICTED NONLINEAR MODELS FOR GROUNDWATER SYSTEMS: INSIGHTS FROM POLYMER KINETICS, COOPERATIVE PHENOMENA, AND DISTRIBUTION FUNCTIONS

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INTRODUCTION

Groundwater quality is increasingly affected by anthropogenic pressures, particularly agricultural activities that contribute to nitrate contamination. [1] In addition to pollution sources, groundwater abstraction can significantly influence contaminant transport and concentration, emphasizing the need for reliable predictive models.

This study investigates the application of sigmoidal growth functions for modeling nitrate concentrations in groundwater. Unlike previously used models [2,3,4] defined over the entire real number domain, the proposed functions are restricted to positive values, reflecting the physical reality that variables such as pumping rate and distance from a pollution source cannot be negative. The results show that these constrained models provide a better fit to experimental data and offer a more realistic representation of groundwater contamination processes.

The proposed approach represents a useful tool for groundwater quality assessment and sustainable water resource management.

METHODOLOGY

The study was conducted at the Varaždin and Bartolovec (Figure 1) wellfields in northern Croatia, located within the same alluvial aquifer system. Groundwater quality in the area is generally satisfactory, except for elevated nitrate concentrations at the Varaždin wellfield, where values exceeded the regulatory limit of 50 mg/L NO_3^-, leading to its shutdown in 2004.

To ensure water supply and reduce nitrate levels, pumping rates were adjusted among regional wellfields. The aquifer consists of two permeable gravel–sand layers separated by a semi-permeable aquitard.

This study focuses on groundwater samples collected from the upper aquifer layer, where nitrate concentrations are highest.

Figure 1. Locations of the Varaždin and Bartolovec wellfields.

RESULTS AND DISCUSSION

Increasing monotonic models were fitted to groundwater quality data from the Bartolovec wellfield. All models showed good agreement with the experimental data, with coefficients of determination (R^2) exceeding 0.8. Model performance was further evaluated using the corrected Akaike Information Criterion (AICc), where lower values indicate a better fit. The Rosin–Rammler 1 model provided the best fit (AICc = 14.10), while the Richards model showed the poorest performance (AICc = 20.18). Overall, sigmoidal functions defined on the domain $[0, +\infty)$ performed better than those defined on $(-\infty, +\infty)$, supporting the study hypothesis.

Statistical analysis showed that all models had t-values exceeding the critical tα value, indicating overall reliability. However, parameter significance testing revealed that parameters B and C of the Michaelis–Menten model were not statistically significant ($p > 0.05$), suggesting that this model cannot be considered fully reliable (Figure 2).

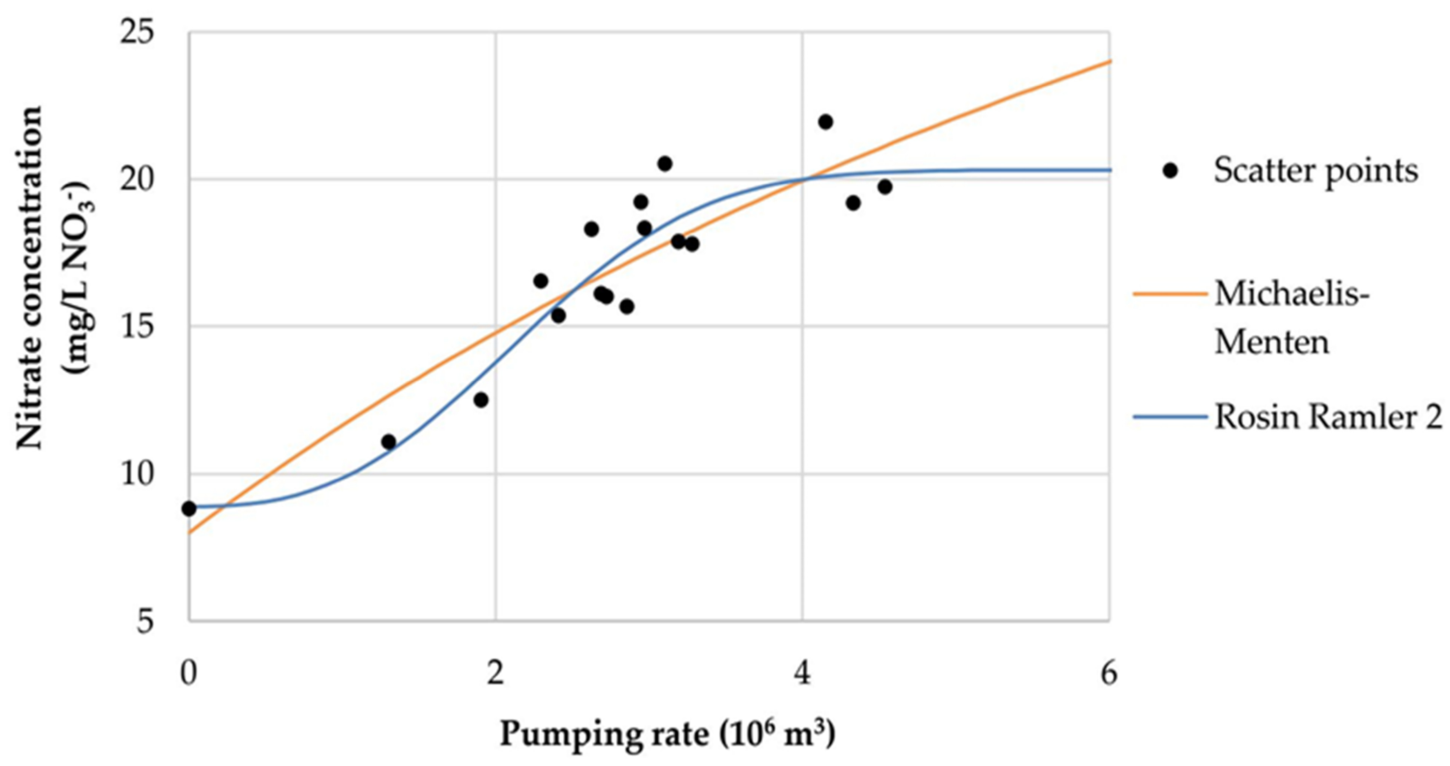

Figure 2. Scatter diagram: Nitrate concentration vs. Pumping rate and fitted Michaelis-Menten and Rosin Ramler 2 increasing models.

Decreasing monotonic models were applied to nitrate concentration data from the Varaždin wellfield. All models showed strong agreement with the experimental data, with coefficients of determination (R^2) exceeding 0.96. Model comparison using the corrected Akaike Information Criterion (AICc) identified the Hill 1 function as the best-performing model (AICc = 11.59), while the Richards function showed the poorest fit (AICc = 20.44). As in the previous analysis, models defined on the domain $[0, +\infty)$ provided a better fit than those defined on $(-\infty, +\infty)$, supporting the proposed hypothesis.Statistical testing showed that all models had t-values above the critical threshold, indicating general reliability. However, parameter significance (t and p values) confirmed full reliability only for the Hill 1 and Rosin–Rammler 1 functions (Figure 3).

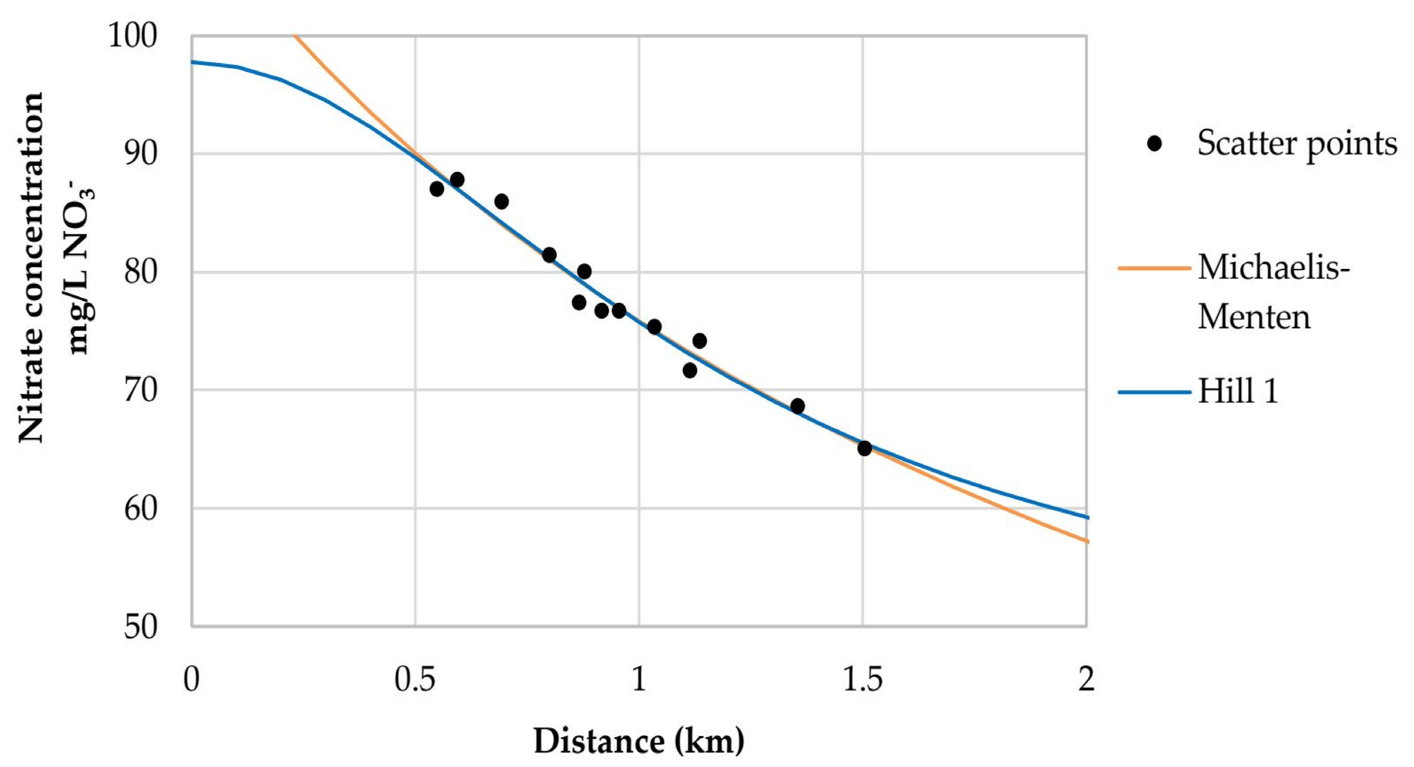

Figure 3. Dispersion diagram: Nitrate concentration vs. Distance from the landfill and fitted Michaelis-Menten and Hill 2 decreasing models.

CONCLUSIONS

This study evaluates the use of sigmoidal groundwater quality models restricted to the positive domain $[0, +\infty)$, compared with traditional functions defined over the entire real line. Two cases were analysed: nitrate dependence on pumping rate and on distance from the pollution source. In both cases, positively constrained models provided a better fit to experimental data.

The best performance was achieved by the Hill 1 and Rosin–Rammler 1 models, supported by the lowest AICc values and statistically significant parameter estimates. Although all models were generally reliable, only these two satisfied full parameter significance criteria. Results indicate that nitrate levels may remain below the MAC under increased pumping at the Bartolovec wellfield, but continuous monitoring is still required. In the Varaždin case, models effectively described spatial nitrate distribution and pollution influence.

Overall, the results support the use of positively constrained sigmoidal models in groundwater quality assessment, although broader validation is needed before generalization.

LITERATURE

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