



PHOSPHORUS CONTENT OF MINERALS IN LAKE SEDIMENTS

DOCTORAL (PHD) THESIS

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Introduction

The aim of my research was to study the sediment of Lake Balaton and suspended particles in the water, in order to determine the various forms of mineral-bound phosphorus, an element that plays an important role in the eutrophication of lakes.

Eutrophication – excessive plant growth resulting from nutrient enrichment – has several consequences, one of which is the development of algal blooms. In calcareous lakes, the primary limitation for algal growth is the availability of dissolved phosphorus. Lake Balaton is an excellent model for shallow, calcareous lakes. As a result of lake management measures introduced in the 1980's, the external phosphorus load of the lake decreased, thereby reducing the extent and frequency of eutrophication. However, in the summer of 2019 an unexpected and large-scale algal bloom occurred in the western part of Lake Balaton, followed by several smaller blooms in subsequent years. Prior to the 2019 algal bloom, no significant change in the external phosphorus load to Lake Balaton was detected; therefore, internal processes must have triggered the event. It is assumed that anoxic conditions led to the reduction of sediment minerals, leading to the release of phosphorus.

Phosphorus speciation in lake sediments is generally assessed using sequential extraction methods. These methods separate the phosphorus content of the sediment into fractions based on their solubility and quantitatively evaluate each fraction. In the sediments of calcareous lakes such as Lake Balaton, phosphorus is considered to be bound to carbonates, iron oxides or, less frequently, to silicates, or stored in phosphate minerals, such as apatite. According to the classical eutrophication model, algal blooms associated with sediment reduction are attributed to the release of phosphorus adsorbed to iron oxides. Previous sequential extraction studies suggest that phosphorus in the sediment of Lake Balaton is primarily bound to carbonate minerals and, to a lesser extent, to iron oxides, while phosphate minerals such as apatite have not been detected. However, no recent and direct (non-dissolution-based) data are currently available on the mineralogical speciation of phosphorus.

In order to characterize the mineralogical properties of phosphorus-containing particles, I used transmission electron microscopy (TEM) to identify and characterize the phases in which the presence of phosphorus can be detected using the X-ray spectrometer connected to the microscope. TEM provides more direct information about P-rich particles than the dissolution-based methods; however, it has a relatively high detection limit for phosphorus (≈ 0.2 wt%). The examined samples included: i) sediment samples collected from Lake Balaton, ii) suspended matter collected from the lake during algal blooms, iii) sediment

samples from Kis-Balaton reservoir, and iv) products of laboratory precipitation and adsorption experiments. The aim of the laboratory experiments was to model specific processes occurring in the lake, primarily the fixation of phosphorus by iron oxides.

Objectives and hypotheses

1.) Role of iron-oxide-bound phosphorus in the phosphorus cycle of Lake Balaton.

We assumed that the 2019 algal bloom was triggered by sediment reduction, which led to the release of phosphorus bound to iron oxides. The objective of this study was to characterize the phosphorus associated with iron minerals in the sediment of Lake Balaton.

2.) Characterization of phosphorus bound to carbonate minerals

Carbonate minerals constitute the largest portion of the sediment of Lake Balaton. However, the amount and the type of phosphorus association with carbonates – whether through surface adsorption or structural incorporation – are not yet fully understood. The aim of this work was to characterize carbonate-bound phosphorus using TEM methods.

3.) Characterization of phosphorus-rich particulates

In addition to carbonate and iron oxide minerals, the presence of other phosphorus-rich phases (e.g., calcium phosphates) cannot be excluded on the basis of literature. An additional objective of my study was therefore to identify all phosphorus-containing constituents in the sediment of Lake Balaton.

4.) Role of other minerals in the phosphorus cycle

In addition to the adsorption of phosphorus, sediment minerals may also participate in the phosphorus cycle through other mechanisms, such as catalysis or hydrolysis. Part of my doctoral research focused on the characterization of sediment minerals involved in the phosphorus cycle of Lake Balaton.

Novel scientific results

1. In a lake environment phosphate adsorption onto iron oxides can lead to calcium phosphate precipitation.

I investigated the homogeneity of phosphate adsorbed onto iron oxides. Literature models predict heterogeneous surface adsorption; however, using TEM methods, I did not observe such heterogeneity in the case of goethite or lepidocrocite crystals. In contrast, adsorption on ferrihydrite was inhomogeneous. At sites with high phosphorus density, surface precipitation was observed, resulting in the formation of amorphous calcium phosphate.

2. Phosphorus bound to iron oxides is negligible in the case of Lake Balaton.

My results challenge long-standing views – and my own initial hypothesis – regarding the importance of iron oxides in the phosphorus cycle of Lake Balaton. Phosphorus bound to iron oxide minerals has traditionally been considered a significant fraction of sedimentary phosphorus and a major contributor to the 2019 algal bloom. However, my research shows that there is no significant iron oxide in the sediment of Lake Balaton, and the amount of phosphorus adsorbed on iron oxides is negligible.

3. Calcium phosphates play a significant role in the phosphorus cycle of Lake Balaton.

My results once again contradict an existing paradigm, this time regarding the presence of authigenic apatite and other calcium phosphate phases in the sediment of Lake Balaton. I detected and characterized nanoscale Ca-phosphate phases in the sediment, including apatite.

4. Microbial polyphosphate is an important component of the phosphorus cycle in lakes.

The role of polyphosphate in lake ecosystems has been recognized previously; however, my work is the first to i) measure and compare the composition of polyphosphate particles inside blooming algae and in their extracellular environment, and ii) demonstrate a correlation between the polyphosphate inclusions, extracellular phosphorus-rich particles, and phosphorus-rich particles in the sediment.

5. Smectite promotes the transformation of calcium phosphate nanoparticles.

I have shown that, in the sediment, both calcium phosphate and iron oxide phases are associated with clay minerals, primarily smectite. Smectite likely promotes the formation of the most stable calcium phosphate phase, apatite, thereby removing a portion of the phosphorus from the lake cycle.

Publication list

- Rácz, K.**, Nyirő-Kósa, I., Kövér, R., Molnár, Zs., Somogyi, B., Kovács, A. W., Istvánovics, V., Pósfai, M. (2026). Biogenic origin and clay-assisted sink of 'visible phosphorus' in a shallow, calcareous lake. *Biogeochemistry*, (accepted)
- Pósfai, M., Molnár, Z., Nyirő-Kósa, I., **Rácz, K.**, Pekker, P., & Istvánovics, V. (2024). Carbonate mineral formation in the vicinity of blooming algae in a shallow lake. In *Geomicrobiology: Natural and Anthropogenic Settings* (pp. 261–280). Springer Nature Switzerland. (könyvfejezet) https://doi.org/10.1007/978-3-031-54306-7_13
- Rostási, Á., **Rácz, K.**, Fodor, M., Topa, B., Molnár, Z., Weiszbürg, T., & Pósfai, M. (2022). Pathways of carbonate sediment accumulation in a large, shallow lake. *Frontiers in Earth Science*, 10. <https://doi.org/10.3389/feart.2022.1067105>
- Mukhtar, S.; Szabó-Bárdos, E.; Óze, C.; Juzsakova, T.; **Rácz, K.**; Németh, M.; Horváth, O. (2025) g-C₃N₄ Modified with metal sulfides for visible-light-driven photocatalytic degradation of organic pollutants. *Molecules*, 30, 253, <https://doi.org/10.3390/molecules30020253>
- Hidalgo, J. S., Mukhtar, S., Horváth, O., Kovacs, N., Hidalgo, L., Vilasó-Cadre, J. E., Reyes-Domínguez, I. A., **Rácz, K.**, Uddin, I., Galambos, I., Fort, C. I., & Turdean, G. L. (2025). Nanocomposite matrix based on gerhardtite-type copper (II) hydroxy nitrate and ZnO/CeO₂ nanoparticles - a sensitive platform for aminomethylphosphonic acid detection. *Electrochimica Acta*, 540, 147255. <https://doi.org/10.1016/j.electacta.2025.147255>
- Hidalgo, J. S., Vilasó-Cadre, J. E., Tamás, K., Galambos, I., Reyes-Domínguez, I. A., Kovács, N., Hidalgo, L., Cuadrado, C., **Rácz, K.**, Boros, A., Machado-García, R., & Arada-Pérez, M. de los A. (2026). An ultrasensitive electrode modified with a molecularly imprinted PEDOT-TiO₂ nanocomposite for voltammetric atrazine detection in environmental samples. *Talanta*, 297, 128780. <https://doi.org/10.1016/j.talanta.2025.128780>

Conference presentations and posters

- Rácz, K.**, Nyirő-Kósa, I., Pósfai, M. (2025). Pathways of phosphorus cycling and phosphate mineral precipitation in lake sediments, *12th Granada-Münster Discussion Meeting*, Münster, 2025.11. 26-28., presentation
- Rácz, K.**, Nyirő-Kósa, I., Kövér, R., Pekker, P., Pósfai, M. (2025) Foszforgazdag nanorészecskék a Balaton üledékében, *Magyarhoni Földtani Társulat Közép- és Észak-dunántúli Területi Szervezet, Szombathely, 2025.05.16-17. előadóülés*, presentation in hungarian
- Rácz, K.**, Nyirő-Kósa, I., Kövér, R., Molnár, Z., Pekker, P., Pósfai M. (2025) Foszforgazdag részecskék a Balaton vizében és üledékében, *Balaton tudományos műhelynap 2025*, Veszprém, 2025.05.13., presentation in hungarian
- Rácz, K.**, Molnár, Zs., Nyirő-Kósa, I., Istvánovics, V., Pósfai, M. (2023). 'Visible phosphorus' in shallow, calcareous Lake Balaton (Hungary), *Goldschmidt 2023*, Lyon, 2023.07.09-14., presentation
- Rácz, K.**, Molnár, Zs., Pósfai, M. (2022) Distribution and composition of phosphorus-bearing particles in lake sediments, *9th Granada-Münster Discussion Meeting*, Granada, 2022.11.30-12.02, poster

Contributions to conference presentations and posters

- Nyirő-Kósa, I., Molnár, Zs., **Rácz, K.**, Pósfai, M. (2025). Carbonate phase transitions affected by clay minerals and environmental factors: results from a mesocosm experiment, *12th Granada-Münster Discussion Meeting*, Münster, 2025.11. 26-28. presentation
- Staicu, L. C., Cosmidis, J., **Rácz, K.**, Stolz, J., Pósfai, P. (2025). Insight into biogenic arsenic sulfides: the case of extracellular respiration, *GMBN 2025*, London, 2025.10.07-08., presentation
- Nyirő-Kósa, I., **Rácz, K.**, Molnár, Zs., Pósfai, M. (2025). Mesocosm experiment on carbonate formation in algal blooms, *Goldschmidt 2025*, Prága, 2025.07.06-11., poster
- Proroková, E., **Rácz, K.**, Falteisek, L., Mikuš, T. (2025). Nanocrystalline features of birnessite, a layered Mn oxide, with high Ca and Zn content, *Goldschmidt 2025*, Prága, 2025.07.06-11., poster
- Pósfai, M., Nyirő-Kósa, I., Molnár, Zs., **Rácz, K.**, Pekker, P. (2025) Algavirágzások és a karbonátásványok képződésének összefüggései a Balatonban, *Magyarhoni Földtani Társulat Közép- és Észak-dunántúli Területi Szervezet, Szombathely, 2025.05.16-17. előadóülés*, presentation in hungarian
- Pósfai, M., **Rácz, K.**, Molnár, Z., Nyirő-Kósa, I., Kövér, R., Pekker, P., Istvánovics, V. (2024). Carbonate formation, particulate phosphorus and algal blooms: Sediment minerals affect life in a shallow lake, *Joint 6th Central European Mineralogical Conference and 9th Mineral Sciences in the Carpathians Conference*, Visegrád, 2024.09.02-04., presentation
- Nyirő-Kósa, I., Molnár, Z., **Rácz, K.**, Pósfai, M. (2024). Modeling carbonate formation in Lake Balaton on a mesocosm scale. *Joint 6th Central-European Mineralogical Conference and 9th Mineral Sciences in the Carpathians Conference*, Visegrád, 2024.09.02-04., presentation

- Nyirő-Kósa I., Molnár Z., **Rácz K.**, Pósfai M. (2024). Balatoni karbonátkiválás mezokozmosz léptékű modellezése. Magyar Mikroszkópos Társaság Konferenciája, Siófok, 2024.05.15-17., presentation in hungarian
- Pósfai M., **Rácz K.**, Molnár Z., Nyirő-Kósa I., Kövér R. (2024). Foszforgazdag nanorészecskék a Balaton vizében és üledékében. 19. Téli Ásványtudományi Iskola, Veszprém, 2024.01.18-19., presentation in hungarian
- Nyirő-Kósa, I., Molnár, Z., **Rácz, K.**, Pósfai, M. (2024). Modeling of carbonate formation in Lake Balaton at a mesocosm scale. 19. Téli Ásványtudományi Iskola, Veszprém, 2024.01.18-19., presentation in hungarian
- Pósfai, M., **Rácz, K.**, Molnár, Z., Nyirő-Kósa, I., Kövér, R., Somogyi, B, Kovács, A., Pekker, P., Istvánovics, V. (2023). Formation of carbonate minerals and phosphorus-rich nanoparticles in association with algal blooms in Lake Balaton. 19th World Lake Conference, Balatonfüred, 2023.11.07-10., presentation
- Pósfai, M., Molnár, Zs., **Rácz, K.**, Pekker, P. (2022). Carbonate precipitation and transformation in a shallow lake during algal blooms and in the sediment. Granada - Münster Discussion Meeting #9, Granada, 2022.11.30-12.02., presentation
- Pósfai, M., Molnár, Zs., **Rácz, K.**, Pekker, P., Istvánovics V. (2022). Precipitation and transformation of carbonate minerals in Lake Balaton, *Geochemistry and Mineralogy of Carbonate Minerals Workshop*, Veszprém, 2022.07.04-05., presentation
- Pekker, P., Molnár, Zs., Kristály, F., Dódony, I., **Rácz, K.**, Pálfi, I., Magyar, E., Pósfai, M., (2022). STEM study of Ca-Mg ordering on atomic scale in protodolomite (experimental aspects and results), *Geochemistry and Mineralogy of Carbonate Minerals Workshop*, Veszprém, 2022.07.04-05., presentation
- Molnár, Zs., **Rácz, K.**, Pekker, P., Dódony, I., Istvánovics, V., Pósfai, M. (2022). Relationships between minerals and microorganisms in Lake Balaton. Annual Meeting of the Hungarian Microscopy Society, Siófok, 2022.05.05-07, presentation in hungarian
- Molnár Zs., Pekker P., **Rácz K.**, Dódony I., Istvánovics V., Pósfai M. (2021). Karbonátásványok képződése a Balatonban és lehetséges szerepük a tó foszfor körforgalmában. LXII. Hidrobiológus Napok, Tihany, 2021.10.06-08., presentation in hungarian
- Pósfai, M., Molnár, Zs., Pekker, P., **Rácz, K.**, Dódony, I., Pálfi, I., Kristály, F., Meister, P., Frisia, S., Magyar, E. (2021). Protodolomite: structure and formation in lakes. Goldschmidt2021, online, 2021.07.04-09. presentation.