Short thesis for the degree of doctor of philosophy (Ph.D.)

Modelling of heavy metal accumulation in aquatic ecological system, development of selective sorbents for metal ion sorption

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List of abbreviations

ANOVA	analysis of variance
BCF	bioconcentration factor
EDTA	ethylenediaminetetraacetic acid
ICP-OES	inductively coupled plasma optical emission spectrometry
IUPAC	International Union of Pure and Applied Chemistry
LDLS	laser diffraction light scattering
MP-AES	microwave plasma atomic emission spectrometry
RDA	redundancy analysis
SD	standard deviation
SE	standard error
SEM	scanning electron microscopy
TTF	trophic transfer factor

I. Introduction

As a result of industrial activity, a large number of different pollutants contaminate surface waters. Heavy metals have particularly high health risk. Physical and chemical methods with a wide variety of indicator functions are available to test the water quality. However, these tests provide limited information on the actual state of the aqueous environment. Using bioindicator organisms gives the opportunity to investigate the complex effect of pollutants present in water on living organisms. By involving more species, building each other in the trophic chain the accumulation of the pollutants along the food chain can also be examined. Only limited data is available on the effect of iron and manganese on aquatic organisms and on the accumulation of these elements along the aquatic food chain compared to typical toxic heavy metals. For this reason, these two metal ions were in the focus of our research.

The removal and the analysis of heavy metal compounds present in surface waters are a complex task. Beside the target component, many other organic and inorganic compounds are present in high concentration. In the environmental industry, different technologies are used to remove heavy metals from aquatic media. Sorption technologies are cost-efficient due to their simplicity and versatility. The most promising sorbents are porous solid materials with high specific surface area. Their performance and selectivity can be increased by an extremely large extent by incorporating functional groups. Mesoporous aerogels are biocompatible and can be functionalized in many ways, thus they are very promising sorbents for environmental remediation. For these reasons, we have developed aerogel-based sorbents for the removal of heavy metal compounds from aqueous media.

II. Aims

In my research work, we set the following goals:

- Investigation of the accumulation of iron and manganese compounds along the aquatic food chain (from zooplankton organisms to fish).
- Investigation of the contribution of exposure routes (uptake from water; uptake through food) to the heavy metal concentrations in aquatic organisms.
- Development of selective sorbents for removing heavy metal compounds from aquatic media.
- Quantitative description of the metal ion sorption, finding optimal conditions for sorption.
- Developing a simple toxicological model system containing aquatic organisms that can provide information about the effectiveness of the sorbents for environmental remediation.

III. Methods

During our research work, we developed a **multi-species laboratory model system** for rearing and treating zooplankton organisms and fish under laboratory circumstances that represents the natural conditions. To find the appropriate analytical methods for the sample preparation and the elemental analysis of the biological indicator organisms, a standard reference material was used prepared from fish muscle (*Pollachius virens*, **ERM®-BB42).** Based on the analysis of this sample **atmospheric wet digestion** in open vessel combined with **microwave plasma atomic emission spectrometry** was chosen for the analysis of the organisms. Five treatments were applied to investigate the accumulation of iron- and manganese compounds along the aquatic food chain. Different concentrations of iron(III) and manganese(II) were combined in the treatments (Table 1).

Table 1: Treatments applied for the enrichment of *Daphnia pulex*

Number	Code	Fe(III) supplementation (mg L^{-1})	Mn(II) supplementation (mg L^{-1})
1.	**Fe(–)/Mn(–)**	5,70	2,90
2.	**Fe(–)/Mn(+)**	5,70	6,25
3.	**Fe(+)/Mn(–)**	15,0	2,90
4.	**Fe(+)/Mn(+)**	15,0	6,25
5.	**K (control)**	–	–

First, the accumulation of the compounds was investigated in zooplankton organisms. *Daphnia pulex* organisms were kept in iron and manganese supplemented aquatic media for 24 hours. In multi-species tests zebrafish (*Danio rerio*) were fed daily with the treated *Daphnia* organisms for 14 days. Multi-species tests were carried out by carps (*Cyprinus caprio*) too, applying the same conditions as in the case of zebrafish. Because of their bigger body size these fish can be dissected into organs. Thus the accumulation of the elements can be analyzed by organs.

The statistical evaluation of the experimental data was carried out by software package **SpSS® Statistics v.22.0**. The significance level of the deviation of the applied treatments was calculated by ANOVA. The homogeneity of variance was verified by Levene's test, the significant differences in the data were determined by Tukey test. Redundance analysis was carried out for studying the interactions between the species and the environmental media by Canoco for Windows 4.5.

Aerogel based sorbents were synthetized by **sol-gel method** and applying supercritical CO_2 drying. Different methods were used to characterize the wet and dry aerogel. **Scanning electron microscopy** (SEM) was used to study the size and shape of the primer globules of the aerogel. The specific surface area, pore size distribution and the pore volume of the aerogel was examined by **N_2 sorption porosimetry** applying the IUPAC recommendation. The particle size distribution of the suspended aerogels was studied by **optical microscopy** and **laser diffraction light scattering** (LDLS). The zeta potential of wet ground aerogels was measured on a **MALVERN Zetasizer Nano ZS** instrument.

The affinity of the aerogels towards different heavy metal ions was tested in conventional **batch sorption experiments** at constant pH. These experiments were carried out by mixing the aerogel suspension with a metal ion solution by following a standardized protocol. The heterogeneous samples were agitated with a magnetic stirrer typically for 2 h to reach the equilibrium. Then the samples were centrifuged (VWR MEGASTAR 1.6R) and the supernatant was quantitatively separated from the aerogel pellets. The metal ion contents of both phases were measured by **inductively coupled plasma optical emission spectrometry**. The sorption of different metal ions was studied both individually and in the simultaneous presence of multiple metal ions. Curve shape analysis was performed on the measured isotherms. The sorption capacity was estimated using the simplest equilibrium isotherm model, the Langmuir model. Time-resolved experiments were performed to study the rate at which the sorption equilibrium is reached on the aerogel sorbents. The reversibility of the sorption of metal ions was tested by washing the previously equilibrated aerogel pellets with different solutions (distilled water, 0.50 M NaCl solution, 0.25 and 2.5 mM EDTA solution). In independent batch sorption experiments the sorbents were tested under realistic aquatic conditions (natural pond water, low metal ion concentration).

An aquatic toxicological model system was developed to test the remediation efficacy of the aerogels containing living bioindicator cultures (*Paramecium caudatum*). The motility of paramecia proportional to their viability was monitored by **time-lapse video microscopy** (zenCell Owl incubator microscope). The viability of paramecia was quantified by analyzing the pixel differences of the sequential images by Image J software. The survival time of paramecia was estimated by fitting a linear trendline on the data points.

IV. New scientific results

1. We have developed a multi-species ecological model system suitable to investigate heavy metal accumulation along the aquatic food chain. Sample preparation and elemental analytical methods were optimized for the analysis of the biological samples.

1.1) A model system was developed for rearing and treating zooplankton organisms and fish representing the natural conditions optimal for living organisms. The model system gives information about the complex effect of different pollutants in aquatic organisms. By involving two or more organisms building on each other in the aquatic trophic chain the accumulation of the pollutants along the food chain can also be monitored.
1.2) It was stated by analyzing ERM®-BB422 reference material, that the more cost-effective MP-AES technique is suitable for the representative determination of elemental content of biological samples combined with conventional atmospheric wet digestion in open vessels.

2. Zebrafish fed by iron and manganese enriched zooplankton organisms significantly accumulate these elements. The iron and manganese levels measured in zebrafish are in a statistically significant relationship with the concentration of these elements in the live food.

2.1) First the accumulation of iron and manganese compound was investigated in zooplankton organisms (*Daphnia pulex*). Our results show that the manganese concentration of *Daphnia* organisms increased in proportion to dissolved manganese concentration in the rearing media (Figure 1). The accumulation of iron was an order of magnitude larger compared to manganese. The accumulation of the iron in the zooplankton organisms was not proportional to the applied treatments.

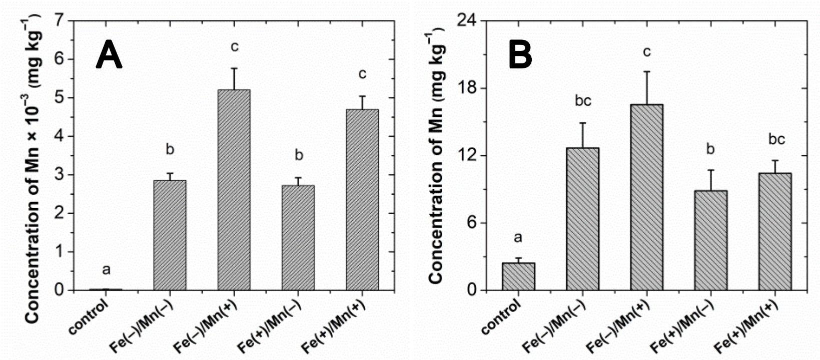

Figure 1. The Mn concentration of *Daphnia pulex* (A) and zebrafish (B) after the 24 hours of enrichment period (mean ± SE dry weight, N = 3). Letters above the column indicate the significant difference.

2.2) In general, the accumulation tendency of iron and manganese measured in *Daphnia* organisms as a result of the applied treatments, are largely preserved in the case of zebrafish.

2.3) The result of the redundancy analysis, the bioconcentration factors (*BCF*) and trophic transfer factors (*TTF*) have proved the correlation between the iron and manganese concentration of *Daphnia* organisms and zebrafish. Thus, we have confirmed that in the case of an iron and manganese pollution affecting an aquatic ecosystem, it is absolutely necessary to take into account the enrichment of these elements through the food chain (not only via water).

2.4) The values of trophic transfer factor are 5-6 orders of magnitude lower compared to bioconcentration factors. Based on these, biomagnification was not observed along the water to *Daphnia pulex* to zebrafish trophic route.

2.5) It was proved that feeding with iron and manganese enriched *Daphnia pulex* has a small but statistically significant negative influence on zebrafish growth.

3. The accumulation of iron and manganese compounds via live food varies significantly among the metal compounds and organs in the case of the significantly larger *Cyprinus caprio*. The highest accumulation extent for manganese was measured in liver.

3.1) There was no significant difference in either organ between the iron concentration of the control and the treated groups.
3.2) In contrast, feeding with manganese enriched *Daphnia* resulted in significantly higher manganese level in different organs of carps compared to control. The highest manganese concentrations were measured in the liver of the fish. The second highest accumulation was measured in the gills of the fish. In the case of the eye, the concentration of manganese is significantly higher in most of the treated groups compered to control, but the accumulation is lower compared to the previous two organs. The applied treatments did not cause significantly higher manganese concentrations in the brain and the muscles.
3.3) In the case of common carp feeding with iron and manganese enriched *Daphnia* resulted no reduced growth performance. This is a difference compared to the smaller zebrafish species.

4. We proved by detailed equilibrium and kinetic experiments that silica-gelatin hybrid aerogels are selective sorbents of dissolved Hg(II).

4.1) The sorption of metal ions was studied individually and also in the simultaneous presence of multiple metal ions. All of the batch sorption experiments consistently show that silica−gelatin hybrid aerogels have unprecedentedly high selectivity for binding Hg(II). The only ion which binds to the hybrid aerogels besides Hg(II) is Ag(I), but competitive sorption tests confirmed the superior selectivity of the sorbents toward Hg(II) (Figure 2).

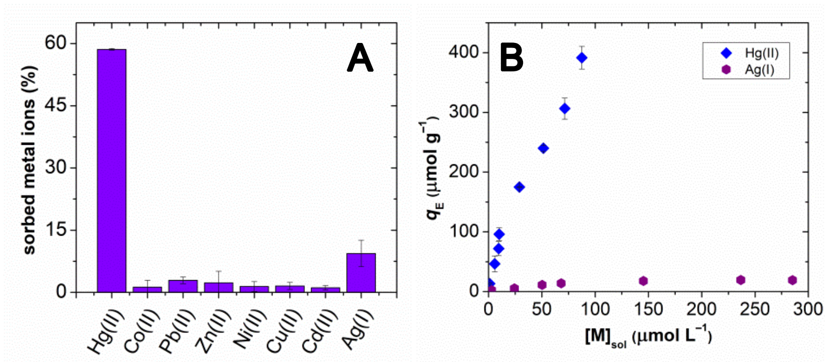

Figure 2. (A) Amounts of metal ions taken up at equilibrium by the 24 wt % hybrid aerogel at pH = 6.0, c_M = 10 mg L^{-1} metal ion, and 0.32 mg mL^{-1} aerogel (measured in the simultaneous presence of competing metal ions). (B) Symbols: experimental isotherms describing the simultaneous sorption of Hg(II) and Ag(I) on the 24 wt % hybrid aerogel at pH = 6.0, 0.32 mg mL^{-1} aerogel.

5. The optimal conditions were established for the sorption process, and a model is proposed to describe the binding of Hg(II).

The effects of pH, gelatin content and initial Hg(II) concentration were tested in independent batch sorption experiments.

5.1) The best sorption capacity was measured at the highest applicable pH value, at pH = 6.0 (Figure 3).

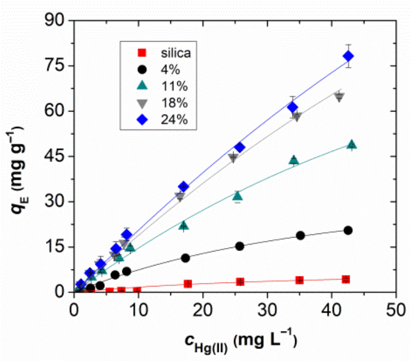

Figure 3. Sorption isotherms of Hg(II) on silica and silica-gelatin hybrid aerogels at pH = 6.0 and 0.32 mg mL^{-1} aerogel concentration. Markers: experimental points. Lines: Non-linear fits with the "Langmuir" isotherm model.

5.2) The sorption capacity of the hybrid aerogels markedly increases with increasing gelatin content, indicating that the biopolymer constituent is the main binder of Hg(II). The lower affinity of Hg(II) toward pure silica is also confirmed by the batch sorption experiment performed with the parent silica aerogel. The sorption capacity was estimated using the simplest equilibrium isotherm model, the "Langmuir model". A maximum sorption capacity of 209 ± 60 mg g^{-1} can be extrapolated for the 24 wt % gelatin hybrid by using the "Langmuir model", complemented with an equilibrium constant of K_L = 0.032 ± 0.013 L mg^{-1}.

5.3) The sorption equilibrium is already established after 5 min of agitation (and 10 min of centrifugation). The rate of the binding of Hg(II) is practically independent of the initial Hg(II) concentration and the gelatin content of the aerogel.

5.4) Aerogel pellets equilibrated with Hg(II) in batch sorption experiments were washed with different solutions (distilled water, 0.50 M NaCl solution, 0.25 and 2.5 mM EDTA solution) to examine the reversibility of the binding of Hg(II). Complete recovery (95−102%) was achieved by washing the pellet with 2.5 mM EDTA solution (33 times EDTA excess). The regenerated silica−gelatin aerogel of 24 wt % gelatin content shows only a minor decrease (maximum 9% compared to the first cycle) in sorption capacity even after five cycles of sorption and regeneration.

5.5) The proposed binding scheme, which takes into account the speciation of dissolved Hg(II) as well as the protonation of the functional groups of the aerogel, is shown in Figure 4. This approach is classified in the literature as “surface complexation modeling”. (At pH = 6, the $Hg(OH)_2$ species is dominant. Its solubility is higher (3.2×10^{-4} M) than the highest applied concentration in our experiment). The isoelectric point of the 24 wt.% hybrid is approximately pH = 4, therefore, in the pH range useful for practical applications (pH = 4–6) the surface of the hybrid aerogel is negatively charged.)

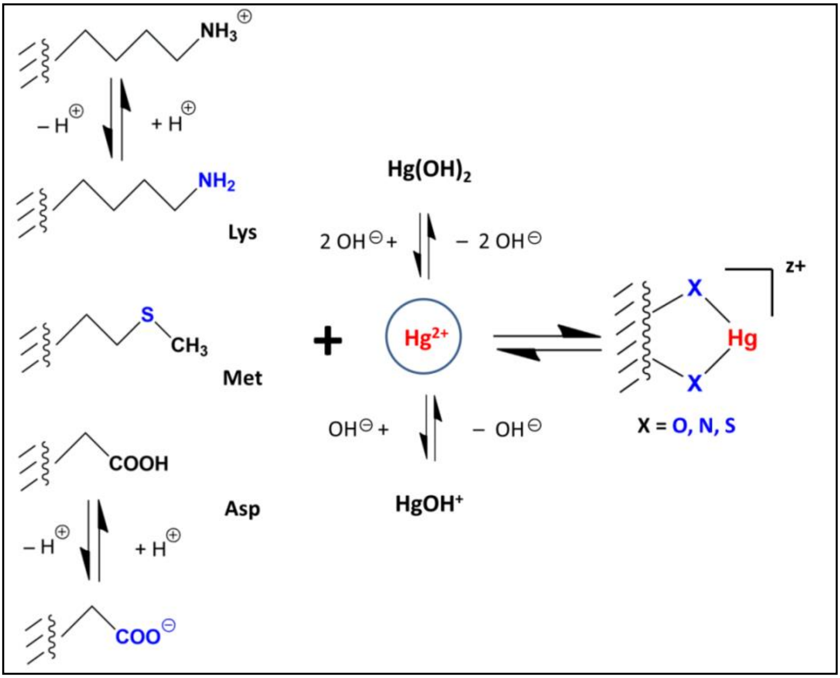

Figure 4. The proposed binding scheme of Hg(II) and the determining equilibrium processes.

6. We have developed an ecotoxicological model system involving bioindicator organisms (*Pramecium caudatum*). Using this model system we established a dose-response relationship for Hg(II) toxicity. We showed that survival of paramecia increases significantly in the presence of the aerogel sorbent.

6.1) We proved that Hg(II) removal efficiency of the hybrid aerogel is not compromised under realistic conditions (in natural water sample, low initial Hg(II) concentration range).

6.2) We have developed a toxicological model system involving bioindicator organisms (*Paramecium caudatum*) to test the remediation efficiency of the silica-gelatin hybrid aerogel. By using this model system the motility of the cells can be monitored in real time. The viability of the cells as a function of time can be quantified by analyzing the sequential images.

6.3) *Paramecium* cultures exposed to increasing concentrations of aqueous Hg(II) show a clear dose-response relationship regarding Hg(II) toxicity. The survival time steeply decreases in an approximately linear manner with the increase of the Hg(II) concentration from 125 μg L^{-1}. The estimated LC50 values for the toxicity of aqueous Hg(II) to *Paramecium caudatum* is in agreement with results of the toxicity experiments reported in the literature.

6.4) We have proved the biocompatibility of the aerogel sorbent by using the developed model system. None of the applied aerogel concentrations caused the decrease of the survival time of the paramecia during the observation period.

6.5) We showed that the survival of paramecia increases significantly when 0.1 mg mL^{-1} aerogel sorbent is present in the Hg(II) exposed cultures. In the present of the aerogel sorbent the viability of the cells decreases only at Hg(II) concentrations higher than 500 μg L^{-1} (Figure 5).

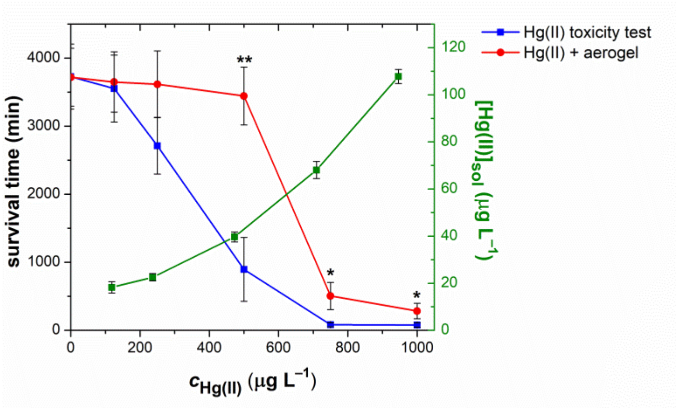

Figure 5. The survival time of paramecia as function of aqueous Hg(II) concentration. The BLUE markers correspond to the Hg(II) toxicity experiments carried out in the absence of the aerogel sorbent, and the RED markers correspond to the remediation experiments carried out in the presence of 0.1 mg mL^{-1} aerogel sorbent under otherwise identical conditions. The GREEN markers show the equilibrium aqueous Hg(II) concentration as a function of the initial Hg(II) concentration established in the presence of 0.1 mg mL^{-1} aerogel sorbent in the cell free culture medium.

V. Possible utilization of the results

During our research, we investigated the accumulation of iron and manganese compounds in aquatic organisms. Our results show the that iron(III) and manganese(II) accumulate to different extents in the case of a contamination in aquatic organisms. The distribution of the metal ions depends on which levels of the trophic chain the organisms are from, and in higher level organisms the distributions of the metal ions show organ specificity. The developed multispecies model system is suitable for the investigation of the transfer of contaminants along the aquatic food chain under laboratory conditions.

We proved that silica-gelatin hybrid aerogel selectively binds Hg(II). We established the optimal conditions for sorption of Hg(II). Based on our results, the aerogel shows advantageous properties for practical applications: high sorption capacity, high sorption rate, it can be regenerated. Thus, it can even serve as a prototype for industrial development.

We have developed a model system containing bioindicator organisms, monitored by time lapse video microscopy. By using this model system we have confirmed the remediation efficacy and the biocompatibility of an aerogel sorbent. Using the developed model system, we can obtain information on the toxicity of various substances and the applicability of sorbents in the environment in an automated way. We managed to observe a significantly larger number of individuals compared to the published, manual individual counting methods.

Articles related to the dissertation

Foreign language scientific articles in international journals

1. P. Herman, A. Kiss, I. Fábián, J. Kalmár, G. Nagy:
In situ remediation of the model aquatic culture of unicellular *Paramecium caudatum* exposed to Hg(II) using advanced aerogel adsorbent.
Chemosphere 275, 1-8 (**2021**)
DOI: 10.1016/j.chemosphere.2021.130019
IF (2020): 7,086; D1

2. P. Herman; M. Fehér; Á. Molnár; S. Harangi; L. Stündl; I. Fábián; E. Baranyai:
Iron and manganese retention of juvenile zebrafish (Danio rerio) exposed to contaminated dietary zooplankton (Daphnia Pulex) – a Model Experiment.
Biological Trace Element Research 199 (2), 732-743 (**2020**)
DOI: 10.1007/s12011-020-02190-z
IF (2020): 3,738; Q2

3. P. Herman, I. Fábián, J. Kalmár:
Mesoporous Silica‒Gelatin Aerogels for the Selective Adsorption of Aqueous Hg(II).
ACS Applied Nano Materials 3 (1), 195-206 (**2020)**
DOI: 10.1021/acsanm.9b01903
IF (2020): 5,097; Q1

4. P. Herman, S. Harangi, M. Fehér, E. Baranyai:
The development of analytical methods for the elemental determination of biotic indicators present in aquatic ecosystems.
Studia Universitatis Babes-Bolyai Chemia 62 (2), 213-222 (**2017**)
DOI:10.24193/subbchem.2017.2.16
IF (2017): 0,305; Q4

Articles not detailed in the dissertation

Foreign language scientific articles in international journals

1. L. Juhász; K. Moldován; P. Herman; Z. Erdélyi; I. Fábián; J. Kalmár; Cs. Cserháti: Synthesis and Stabilization of Support-Free Mesoporous Gold Nanoparticles.
Nanomaterials 10 (6), 1-11 (**2020**)
DOI: 10.3390/nano10061107
IF (2020): 5,076; Q1

2. Zs. Szabó; B. Buró; J. Szabó; Cs. A. Tóth; E. Baranyai; P. Herman; J. Prokisch; T. Tomor; Sz. Szabó: Geomorphology as a Driver of Heavy Metal Accumulation Patterns in a Floodplain.
Water 12 (2), 1-16 (**2020**)
DOI: 10.3390/w12020563
IF (2020): 3,103; Q1

3. Zs. Sajtos; P. Herman; S. Harangi; E. Baranyai:
Elemental analysis of Hungarian honey samples and bee products by MP-AES method. *Microchemical Journal* 149, 1-8 (**2019**)
DOI:10.1016/j.microc.2019.103968
IF (2019): 3,594; Q2

4. A. Forgács; K. Moldován; P. Herman; E. Baranyai; I. Fábián; G. Lente; J. Kalmár:
Kinetic Model for Hydrolytic Nucleation and Growth of TiO2 Nanoparticles.
Journal of Physical Chemistry C 122 (33), 19161-19170 (**2018**)
DOI 10.1021/acs.jpcc.8b04227
IF (2018): 4,309; D1

5. S. Harangi, E. Baranyai, M. Fehér, Cs. N. Tóth, P. Herman, L. Stündl, I. Fábián, B. Tóthmérész, E. Simon:
Accumulation of metals in juvenile carp (Cyprinus carpio) exposed to sublethal levels of iron and manganese: survival, body weight and tissue.
Biological Trace Element Research 177 (1), 187-195 (**2017**)
DOI 10.1007/s12011-016-0854-5
IF (2017): 2,399; Q2

Hungarian language scientific articles in national journals

1. Herman P.: Zooplankton szervezetek vas és mangán terhelésének vizsgálata atomspektroszkópiai módszerekkel.
Hidrológiai Közlöny 96/különszám 40-43. (**2016**)

2. Herman P., Harangi S., Simon E., Baranyai E.:
Zooplankton szervezetek nehézfém terhelésének vizsgálata atomspektroszkópiai módszerekkel.
Economica 8 128–136. (**2015**)

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Subject:	PhD Publication List

Candidate: Petra Herman
Doctoral School: Doctoral School of Chemistry
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List of publications related to the dissertation

Foreign language scientific articles in international journals (4)

1. **Herman, P.**, Kiss, A., Fábián, I., Kalmár, J., Szemán-Nagy, G.: In situ Remediation Efficacy of Hybrid Aerogel Adsorbent in Model Aquatic Culture of Paramecium caudatum Exposed to Hg(II).
   Chemosphere. 275, 1-8, 2021. ISSN: 0045-6535.
   DOI: http://dx.doi.org/10.1016/j.chemosphere.2021.130019
   IF: 7.086 (2020)
2. **Herman, P.**, Fehér, M., Molnár, Á., Harangi, S., Sajtos, Z., Stündl, L., Fábián, I., Baranyai, E.: Iron and Manganese Retention of Juvenile Zebrafish (Danio rerio) Exposed to Contaminated Dietary Zooplankton (Daphnia pulex)-a Model Experiment.
   Biol. Trace Elem. Res. 199 (2), 732-743, 2021. ISSN: 0163-4984.
   DOI: http://dx.doi.org/10.1007/s12011-020-02190-z
   IF: 3.738 (2020)
3. **Herman, P.**, Fábián, I., Kalmár, J.: Mesoporous Silica-Gelatin Aerogels for the Selective Adsorption of Aqueous Hg(II).
   ACS Appl. Nano Mater. 3 (1), 195-206, 2020. ISSN: 2574-0970.
   DOI: http://dx.doi.org/10.1021/acsanm.9b01903
   IF: 5.097
4. **Herman, P.**, Harangi, S., Fehér, M., Fábián, I., Baranyai, E.: The Development of Analytical Methods for the Elemental Determination of Biotic Indicators Present in Aquatic Ecosystems.
   Stud. Univ. Babes-Bolyai Chem. 62 (2), 213-222, 2017. ISSN: 1224-7154.
   DOI: http://dx.doi.org/10.24193/subbchem.2017.2.16
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List of other publications

Hungarian scientific articles in Hungarian journals (2)

5. **Herman, P.**: Zooplankton szervezetek vas és mangán terhelésének vizsgálata atomspektroszkópiai módszerekkel.
   Hidrol. Közlöny. 96 (Klsz.), 40-43, 2016. ISSN: 0018-1323.

6. **Herman, P.**, Harangi, S., Simon, E., Baranyai, E.: Zooplankton szervezetek nehézfém terhelésének vizsgálata atomspektroszkópiai módszerekkel.
   Economica. 8 (3), 128-136, 2015. ISSN: 1585-6216.

Foreign language scientific articles in international journals (5)

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   Water. 12 (2), 1-16, 2020. EISSN: 2073-4441.
   DOI: http://dx.doi.org/10.3390/w12020563
   IF: 3.103

8. Juhász, L., Moldován, K., **Herman, P.**, Erdélyi, Z., Fábián, I., Kalmár, J., Cserháti, C.: Synthesis and Stabilization of Support-Free Mesoporous Gold Nanoparticles.
   Nanomaterials. 10 (6), 1-11, 2020. EISSN: 2079-4991.
   DOI: http://dx.doi.org/10.3390/nano10061107
   IF: 5.076

9. Sajtos, Z., **Herman, P.**, Harangi, S., Baranyai, E.: Elemental analysis of Hungarian honey samples and bee products by MP-AES method.
   Microchem J. 149, 1-8, 2019. ISSN: 0026-265X.
   DOI: http://dx.doi.org/10.1016/j.microc.2019.103968
   IF: 3.594

10. Forgács, A., Moldován, K., **Herman, P.**, Baranyai, E., Fábián, I., Lente, G., Kalmár, J.: Kinetic Model for Hydrolytic Nucleation and Growth of TiO2 Nanoparticles.
    J. Phys. Chem. C. 122 (33), 19161-19170, 2018. ISSN: 1932-7447.
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11. Harangi, S., Baranyai, E., Fehér, M., Tóth, C. N., **Herman, P.**, Stündl, L., Fábián, I., Tóthmérész, B., Simon, E.: Accumulation of Metals in Juvenile Carp (Cyprinus carpio) Exposed to Sublethal Levels of Iron and Manganese: Survival, Body Weight and Tissue. *Biol. Trace Elem. Res. 177* (1), 187-195, 2016. ISSN: 0163-4984.
DOI: http://dx.doi.org/10.1007/s12011-016-0854-5
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