SZENT ISTVÁN EGYETEM

Szent István University
Ph.D. School of Environmental Sciences

The effect of wastewater on plant development, element uptake and gas emissions (CO_2, N_2O, NO)

Thesis of Ph.D. dissertation

Szaniszló Albert

GÖDÖLLŐ
2020

Ph.D. Scool: Ph.D. Scool of Enviromental Sciences

Discipline: Enviromental Sciences

Head of School: Dr. Erika Csáki-Michéli, Corresponding member of the ITAS
Professor
Szent István University
Faculty of Agricultural and Environmental Sciences
Institute of Environmental Sciences
Department of Soil Science and Agrochemistry

Scientific supervisor: Dr. habil. Ágnes Mészáros - Bálint
Associate Professor
Obuda University,
Faculty Rejtő Sándor and
Environmental Engineering
Environmental Engineering and Natural
Science Institute

....
Approval of Head of School **Approval of Scientific supervisor**

1. BACKGROUND OF THE WORK, OBJECTIVES

1.1 Introduction

An important area of global change in the future is climate change and, indirectly, the reduction of greenhouse gas emissions (GHG - CO_2, CH_4, N_2O, CFC, NO). Agriculture and transport account for one of the largest emissions of these gases, but increasing the efficiency of industrial technologies can play a major role in reducing their emissions.

Based on the emission reduction scenarios, it identifies two main sectoral areas (Industry and Energy) with a sectoral breakdown of CO_2 emissions. In the medium term, the fastest and cheapest results can be achieved in the field of energy efficiency of buildings. In the long run, however, more efficient, energy-saving and renewable energy technologies should be used as widely as possible in industry and energy production.

Reducing deforestation and afforestation alone is no longer enough to expand carbon sinks. In addition to society, there is also a need for a significant change in attitudes and changes in consumer and industrial habits among industrial actors.

In agriculture and industry, energy producers and users are responsible for the current critical situation of the global ground and air pollution. This sector is characterized by high material, and intensive energy use. The use of energy-wasting technologies on the production and consumption side is very common. During these processes, most of the input sources are released into the environment as useless waste (heat, dust, liquid or solid, etc.).

We need to reduce harmful emissions from the burning of fossil fuels used and emitted during human activities. At present, we need to keep one and a half times the land holding capacity at the utilization level. To do this, we need to reduce emissions to the optimal case. One of the key points of these problems is energy consumption. Nowadays, the topic has come to the fore and the search for alternatives to the fossil fuels currently in use has olso begun. Therefore, it is important to improve the applicability of alternatives.

1.2 **Objectives**

My goal is to examine these alternatives with possible solutions in the process of wastewater treatment. The industry is developing more natural technology, how greenhouse gas emissions occur in the process of wastewater treatment. The main research goal is the integration of plants that can be used in biological treatment, the examination of plant development, the analysis and evaluation of the changes in their element uptake and gas emissions.

Based on the above mentioned requirements, the objectives of this research are the following:

- Study of the process of cascade wastewater treatment.
- I prepared the possibility of developing the living machine wastewater treatment process, based on the concept of wetlands.
- I studied the insertability of different flora elements (efficiency of the applicability of propagating materials, optimization of the amount of biomass).
- I compared the role of the plant element that proved to be the best in the treatment process (biofilm surface and amount, dissolved oxygen content, organic and inorganic element components) and the changes in important parameters measured in wastewater treatment.
- I studied the growth factors of plant biomass and the proportion of elements mobilized from wastewater in plant parts.
- I determined the effects of the wetland created by energy reeds in the FCR wastewater treatment system, and have proven the advantages of the ecological system.

2. MATERIALS AND METHODS

2.1 Description of the sampling area

Cultivation and sampling took place in the Telki Ecotechnology Development Center operated by Organica Zrt. The work was done on an experimental biological wastewater treatment system operating at this site. The method used a combination of traditional technology and living organisms. The experimental system used the municipal wastewater of Telki municipality. The technology combined activated sludge, biofilm and root zone cleaning processes. The system was implemented in sequentially connected reactors. The biofilm formed on the artificial supports placed in the biofilm reactors is used for the decomposition of organic matter and the treatment of wastewater. The reactors were covered with plant supports. Swamps, tropical and ornamental plants have been planted in the holders. Plants sealed the surface of the sewage. This would create an artificial green surface. Function of odor mitigation. The plant had no role in removing nutrients. The decomposition of organic matter is performed by microorganisms living on the support surface.

2.2 Presentation of the sampling process

2.2.1 Gas sampling

The injected samples were transported in a 12 cm^3 glass jar (Fiola: Labco Exetainer®, 0RK8W), which were cleaned and evacuated prior to sampling. The Enkamat® nets served as the frame and support for the growing module. To collect the gas, I used 2 gas traps per reactor, which were formed from 250 ml ground glass jars with a plastic lid with a 4 mm septum. Preliminary sampling was performed at three 10-minute, one 20-minute, and one 30-minute intervals. The purpose of the measurements was to explore the emissions and gas components of the wastewater treatment reactors and to observe the differences between the reactors. Based on the results obtained in the preliminary survey, the duration of the detailed sampling was further divided into 0, 10, 20, 30, 60, 70 minute periods, while the sampling method did not change (syringe, sampling site).

2.2.2 Gas sample analysis

The gas chromatographic system was characterized by the complete separation of the various gas components (CO_2 and N_2O). My measurements were performed using an HP 5890 Series II gas chromatograph, which was described by Simarmata et al. (1993) and worked as described by Kovács (1996) and Kriszt (1996). The only difference was that the ECD was operated at 250 ° C. The 250 ml gas samples were injected into the HP 5890 Series II GC by Hamilton syringe manual sampling. The integration was done with the HP 3390 Series II integrator as well as the HP ChemStation software.

2.3 **Element analysis**

Element analysis of heavy metals in reeds in the case of destructive preparation:

ICP-AES *(Inductive-Coupled Plasma Atomic-Emission Spectrometer)*

The study focused mainly on the detection of heavy metal components after destructive preparation. For the determination, I used the HORIBA Jobin Yvon ACTIVA-M ICP-OES spectrometer, which is able to capture the entire spectral range of UV-VIS with full scanning CCD detection (Odile Hirsch 2007; Frankowski et al. 2011). Plant samples were measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES Jobin-Yvon 24; Ricardo et al. 2020).

Element analysis of heavy metals in reeds in the case of non-destructive preparation:

a.) The Neutron Activation Analisis (NAA)

Neutron Activation Analysis (NAA) studies were performed in the laboratory of the Department of Neutron Physics of the Joint Institute for Nuclear Research (JINR) in Dubna, Russia. The IBR-2, fast-pulsed reactor provided fission neutrons withenergy values ranging from ultra-cold (10^{-7} eV) and fast (20 MeV). Epithermal and fast neutrons were applied in three different irradiation time intervals: 3 min, 0.5 h, and 1 h, which gave adequate neutron fluxes for the activation process of different nuclei (Frontasyeva and Pavlov 2000; Pavlov et al. 2016; Frontasyeva et al. 2019).

For the determination of short-lived isotopes such as Al, V, Mn and I, samples weighing 0,5 g were packed in polyethylene bags and placed in an irradiation channel for 3 min with irradiation at $1{,}3 \cdot 10^{12}$ n cm^{-2} s^{-1} with neutron current density. The gamma spectrum of the induced activity was measured twice for 3 min, 5-7 min and 12-15 min after degradation.

Long-living isotopes, such as Sc, Fe, Co, Ni, Zn, As, Br, Rb, Sr, Ag, Sb, Cs, Ba, Th and U, in a cadmium filter channel using epithermal neutrons, $1{,}6 \cdot 10^{12}$ n cm^{-2} s^{-1} flux density. During the longer irradiation method, the samples were irradiated for 90 hours, repackaged, and then weighed twice. First, after 4–5 days of decay, the radiated spectrum was recorded for a period of 45 min, and then after 20 days of decay, the test was performed for a period of 2.5–3 h.

b.) Determination of the Carbon and Nitrogen amount

Huang et al. (2004) found a correlation between N_2O and CO_2 emissions between soluble organic carbon content and plant. The C and N contents of the samples were determined using the NA 1500 NC type Carbon-Nitrogen Analyzer (Carlo Erba). The samples were prepared in aluminum packaging in the amount of 2-10 g of sample. The measurements were performed with the analysis program in the EAGER200 software package, the CN analyzer software.

c.) Determination of gas samples by gas chromatography and nitrogen monoxide (NO) emission

In the semi-operational experimental system of Telki Organica, I have investigated the gas above the reactors participating in different purification processes. From this, the content of nitrous oxide (N_2O) and carbon dioxide (CO_2) was measured by gas chromatography (GC). Furthermore, the amount of nitrogen-monoxide (NO) was determined by manual injection using a NO analyzer. Using external standards and an accurate linear calibration.

2.4 **Investigation of Chinese reed growth**

The bud activity and regeneration dynamics tests were performed weekly in the Telki Development Center between March and May 2013. I started examining the rhizomes 6 days after planting (in the growing module) and divided them into 10 cycles. Each test cycle lasted 22 days, within which I performed several measurements of the activity of the buds (appearance of side buds). This was followed by the determination of the length of the axial shoots (in-cycle shoot/stem length).

2.4.1 Planters and insertion tools

The solution to the surface of the wastewater is difficult to solve. It depended on the type, variety, specific needs, water tolerance and tolerance of the above parameters used. In the preliminary tests, I divided the plants into two groups. Conventional arable (rooted) plants and floating aquatic (root-haired) plants have been botle included. The incorporation into reactors similarly required the need for two different methods. Depending on the selected plant types, a tool system (wetland) was created in the reactor to freely follow the water level fluctuations and placed on fixed plant supports.

3. RESULTS AND DISCUSSION

3.1 Developments in crop yield

Growth study of the energy reed (Chinese reed)

From the growth test results, I present yield increase activity and shoot activity. The energy reed shows the optimal environment for the given environment with the appearance of the shoots after the placement. The shoots were examined at four points in the multi-stage experimental biological wastewater treatment system. The reason for this was that I could deduce from the results obtained in this way the specificity of the wastewater treatment stages, which location is tolerated by the Miscanthus and which section is optimal for their cultivation.

The results of the plants placed in the **second reactor** clearly lagged behind the control in the initial and subsequent treatment stages. It may follow from the low number of shoots that a medium with a composition similar to that of raw effluent is not fully suitable for rhizomes. This was probably also influenced by the low temperature of the water. In addition, there was a failure in the reactor (water level fluctuations and occasional foaming), which could have occurred as an undesirable stress effect.

The plants installed into **fourth reactor** have already shown better results. In the initial period, the number of shoots fell short of control. The plants later produced more shoot numbers than the control. Here, higher ammonia and lower COD have already had a positive effect on growth.

Propagating materials installed in the **sixth reactor** outperformed the control plants already in the initial period. At this stage of the biodegradation of organic matter, the oxygen demand decreases and the proportion of non-microbiologically non-biodegradable organic matter increases. This had a positive effect on bud activity.

Rhizomes started to grow best in the **eighth reactor**. The initial high shoot number reached full sprout for the third sampling. All implanted rhizomes produced at least one shoot. The number of shoots performed 25% better in the initial period compared to the control. This fact proves that the conditions developed for the propulsion of the energy plant in this reactor were the most optimal. As a result, has also showed a significant (positive) difference in the number of shoots compared to the control.

The growth of shoots did not depend on the number of shoots. The shoots showed approximately the reactor-specific growth rate. The trends observed in reactors in the previous drive ratio study were also shown in this method. In the more favorable reactors, the buds achieved a higher growth rate. With the exception of the second reactor, all other reactors exceeded the shoot length of the control plants at the first two sampling times. In the third sampling, the shoots of the second reactor already surpassed the control plants.

The best growth was shown by the reed shoots of reactors six (reactor 6) and eighth (reactor 8). It is true for all of the samples that the initial rapid growth fell back to the third sampling. There may be several reasons for this, but mainly rainy weather (which can have a diluting effect on wastewater concentration), a decrease in the amount of usable sunlight, or a combined effect. In control plants, I experienced bud activity in March and early September. This did not apply in the growing module. The activity was not significant or was caused by a sudden, short-term increase with decreasing ambient temperature.

3.2 Analytical studies

3.2.1 Inductively coupled plasma (ICP) analysis

The **ICP-AES** element analysis tool. The device is capable of determining 23 elements, including lead (Pb). Elements that are usually present in higher concentrations in wastewater are heavy metals. Therefore, I investigated the possibility of their accumulation in plant samples. Of the detected heavy metals, the concentration of aluminum (Al) in reactor 2 is significantly higher than in the control sample, in the other reactors (from reactor 4 to 8) it is lower than in the control sample. The iron (Fe) concentration of the control sample is also lower than that measured in reactor 2. The element concentration towards reactor 8 (along the purification process) is continuously decreasing. The manganese (Mn) concentration is the highest in the control and, like Fe, decreases continuously towards reactor 8.

Unlike the previous elements, the zinc (Zn) concentration increases continuously compared to reactor 2 until reactor 6. However, it lags significantly behind in the last reactor. The highest Zn concentration was detected in the control sample.

3.2.2 Neutron Activation Analysis (NAA)

The non-destructive sample preparation technique. Due to the lower and minimum detectable concentration (MDC), the NAA gave accurate results in 45 of the 46 elements examined. According to Wood (1974), chemical elements can be classified into four classes according to their toxicity and availability.

Group of non-critical elements:

Based on the NAA results of non-critical elements in the plant samples, it can be concluded that the K, Cl, Br, and Rb contents of the control plants were higher than the concentrations of these elements in the reference CW plants. For the various reactors, we usually measured the highest element concentration in the plants from cascade element 2, which contained untreated water almost identical to the inflowing (raw) wastewater. These high concentrations generally decrease gradually at the end of the wastewater treatment reactor line, although a slight increase is observed in reactor 8. On the contrary, the concentration of K increased continuously in the cascade reactor system, reaching the maximum value of the plants in reactor 8. The S and Fe content varied in an opposite trend, and the mobility of the elements continuously decreased, resulting in a minimal concentration of the plants living in reactor 8.

Group of very toxic and relatively rarely elements:

The NAA results for the highly toxic and relatively accessible elements of the plant samples revealed, that the Ag, Co, and Se contents of the control plants were higher than in the CW reactors. In plants, two trends can be observed in the change in concentration of the elements depending on which reactor they were placed in.

The concentration of one type of element (e.g. As and Cs) decreases from reactor 2 to reactor 8. These elements bind strongly to plants and are therefore highly concentrated in the initial reactors. Strong binding to plants reduces the concentration of these elements in wastewater. The concentration of these elements in the wastewater will be low during the process, so the adsorbed amount of these elements will also decrease in the in-line reactor system. The binding properties of some elements (e.g. Cd and Se) are similar to Co, but their concentrations were unexpectedly high in reactor 8. I did not find an explanation for the unexpected increase of the concentration of such elements in reactor 8.

Another trend was that concentrations of elements (e.g. Hg and Co) increased from reactor 2 to reactor 4. After reactor 4, the concentrations decrease along the process. These elements were less absorbed than members of the previous group. In reactor 2, most of the receptors (binding sites) were occupied by strongly absorbing elements, so there were not enough free receptors for less strongly binding elements. Concentrations of strongly binding elements are lower in reactor 4 than in reactor 2. Therefore, in reactor 4, less binding sites remain for less strongly binding elements than in reactor 2.

Toxic but very insoluble or very rare elements:

Considering the NAA results of toxic but very insoluble or very rare elements, it can be concluded that the content of Ba, Nb and La in the control plant samples was higher than the concentration of these elements in the wastewater treatment reactors. It can also be stated that I generally detected higher concentrations from the plants of reactor 2 than from the plants living in reactors 4 and 6. There was an increase in concentration in reactor 8 at the end of the water purification process. A similar trend can be observed for Ba, Nb and Ce, although the increase started at the 4th or 6th rector. In terms of the concentrations of U and Sm, their concentrations decreased continuously throughout the water treatment line.

Items that do not fall into the Wood classification or fall into more than one category:

Examining the NAA results of these elements, it was observed that the concentrations of Cs, Cr and Mo in the control plants were similar to the concentrations of the elements measured in the plants of the CW system. Generally, it measured a high element content from the plants of Reactor 2, which gradually decreased in successive reactors. In addition, V- and Sc-concentrations in reactor 8 were reduced to a minimum. In the case of I, in the series of continuous decrease, the plants in reactor 6 accumulated more elements than the plants in reactors 4 and 8, where the value of the local maximum concentration was shown.

Measurements show, that wastewater treatment (FCR system) supplemented with wetland planted with Chinese reeds (Miscanthus sinensis) can effectively reduce the nutrient load of the wastewater. Reactors installed with Chinese reeds also reduce the heavy metal content of the wastewater. For most of the elements (e.g. Zn, Cu, Cd, Na, Cl), the concentrations of heavy metals in the plants decrease from reactor 1 to reactor 6 at different stages of the cascade treatment. Differences at specific sites in the adsorption capacity of plants - by the convergence of the free receptor surfaces - causes.

3.2.3 Gas Chromatographic (GC) analysis

3.2.3.1 Preliminary assessment of greenhouse gas components (N_2O, CO_2)

The purpose of the preliminary survey is to determine the amount and dynamics of gas emissions from the cascade system. For the measurements, I captured the gas components in the different reactors along the cascade rows using a glass gas trap over an 80-min time interval.

Based on the evaluation of the results, the stages of the purification process are followed by reactor emissions. These were created by microbiological processes aimed at converting nitrogen forms by reducing the water load. The difference in emissions between the plant habitat and the water surface test points demonstrates that the processes in the wastewater treatment plants are facilitated by the wetlands. They result in higher gas emissions at the cleaning process.

In both cases, there was a significant correlation between CO_2 and N_2O emissions during the study period. This is due to complex microbiological procedures. Thus, any change in the system (such as dilution) results in a different degree of water pollution instability, which must be taken into account in the discharge. These influencing effects are more stably buffered by the presence of plants (using wetlands - CW).

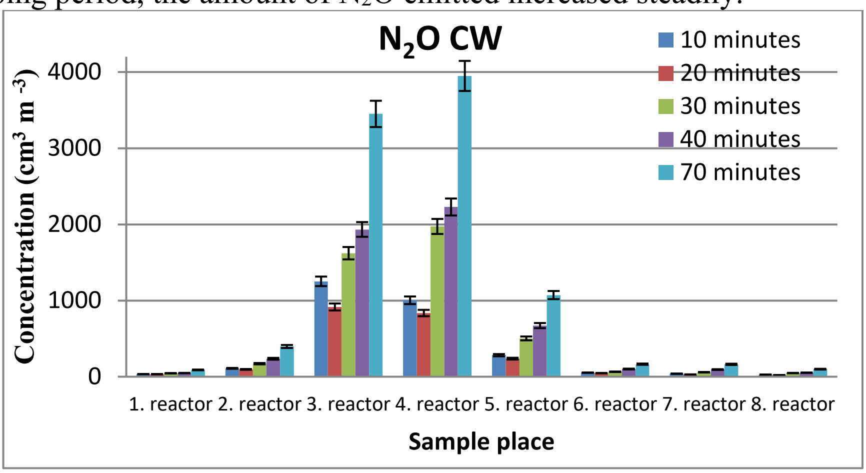
An increase of the N_2O usually includes an increase of the CO_2. The difference in N_2O concentration between the two sampling points was 61%

on average. The difference in CO_2 concentration was 71% on average, but the initial, initial concentration was about the same. The flux value of the initial coverage of the gas trap is not the same as the ambient gas emission, which is of a higher concentration.

3.2.4 Evaluation of N_2O formation (determined by detailed investigation)

At the detailed studies, I have evaluated the time difference of the emissions and their relative ratio. For N_2O, for the mass of gas collected in 10 min, the sample taken in the wetland was approximately 40% higher than the surface water emission measured during the same period. A different trend was characteristic for the longest measurement period. The 20-, 30- and 40-minutes emissions were of the same order of magnitude for the entire purification process. Overall, the shortest 10-min and longest 70-min sampling periods had the largest difference in total N_2O at the two sampling sites.

Based on the results of the gas samples taken at the surface of the wastewater, it because clear that the selection of GHGs from different sampling periods and reactors shows a different trend and emission rate. From the emission values it can be stated that the formation of N_2O components measured on the surface of the wastewater can hardly be detected in the case of the initial, raw wastewater, which is also typical at the end of the treatment process starting from the reactor 6. It can be seen that the microbial degradation begins in the reactor 2 and ends in reactor 5. The highest gas emissions were observed in reactors 3 and 4. Depending on the trapping period, the amount of N_2O emitted increased steadily.



3.2.1. figure – Results of the detailed study N_2O in the established wetland (CW)

The samples taken in reactor 3 were characterized by a small deviation of the emission values during the 10 and 20 minute measurements and during the

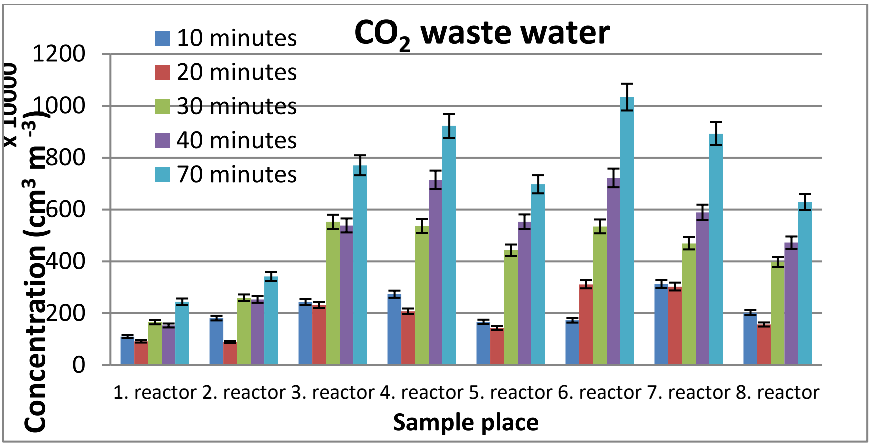
30 and 40 minute periods, which may be due to the balanced decomposition processes and the presence of the large amounts of the organic matter.

The wetland (CW) was much more dynamic compared to the wastewater surface and had higher discharges. The decomposition processes took place similarly in reactor spaces 3 and 5. At the emissions measured in the reactors, it was observed that the highest emissions in their proportions occurred at the shortest period of 10 minutes. This is due to the microbial variability of the wetland and the temporary (temporal) decline in intensive release. This phenomenon characterized N_2O emissions for all reactors and regardless of the length of the gas trap. It can be stated that the N_2O emission of the wetland was characterized by a one-third higher emission compared to the wastewater, regardless on the measurement location and length. Furthermore, none of the additional parameters affect N_2O emissions.

3.2.5 Extent of CO_2 generation (determined by detailed investigation)

In the detailed studies, I have also evaluated the time difference of the emissions and their relative proportions. Unlike N_2O, for CO_2 emissions at full flux, samples from wastewater were approximately 30% higher for wetland (growing module) formation measured during the same period. This trend characterized the longest measurement period. Trapping at 20-minutes intervals it had the largest rate of deviation, at 43%. Regarding the whole treatment process, the formation of CO_2 components was higher in the samples taken from the wastewater surface. Overall, in the shortest sampling period of 20 minutes, the largest difference was in the CO_2 emissions of the two sampling sites. The highest CO_2 concentration occurred in the longest period - 70 minutes.

Gas samples taken at the surface of the wastewater and in the wetland showed that emissions from different sampling periods and reactors show a similar trend and proportion. From the emission values, the CO_2 emissions measured on the surface of the wastewater are the lowest in the case of the initial raw wastewater. At the end of the purification process, it is typical to start from reactor 7 with a drop in CO_2 emissions in all measurement periods. The emission intensification process begins in reactor 2 and decreases in reactor 6. The highest levels of gas emissions are in reactors 3 and 4. Depending on the trapping period, the concentration of the emitted CO_2 increased steadily. The samples were generally characterized by a slight decrease in emission values between the 10 and 20 min measurement periods. The reason is the presence of the high levels of organic matter.



3.2.2. figure – The detailed study of CO_2 results in water surface

Wastewater surface samples had a similar trend to wetland and higher discharges. Decomposition processes took place from reactor 2 to the last reactor. At the emissions measured in the reactors, it was observed that the samples taken in the wetlands were lower compared to the surface emissions from the wastewater. In terms of proportions, the highest flux occurred in the medium-term period of 30 minutes. The 10-minute emission showed higher concentrations in most reactors than in the 20-minute measurement (with the exception of reactors 6 and 7). It can be stated, that the CO_2 formation of the wetland is lower in proportion to the wastewater. This means higher emissions for all reactors, regardless of measurement location and length. The reason that the wetland reduced CO_2 emissions as a CO_2 scavenger for this gas component.

3.2.6 The occurrence of NO release

In the detailed NO-studies, I evaluated the time difference of the component formations and the relative ratio of the emissions separately. For NO-emissions, unlike the concentrations measured in 10 minute, the sample taken in the wetland was approximately 70% higher than the values measured on the surface of the wastewater during the same period. In contrast, in the longest measurement period, this value was approximately 2%, in which case the deviation was the smallest. For emissions measured over a 30-minute period, a sample taken from the surface of the wastewater had a higher emission compared to the wetland (CW). Regarding the purification process, NO-emissions in the wetland samples were higher only in the 40-minute sampling interval. Overall, in the shortest 10-minute sampling period, the difference in NO-emissions was highest for the two sampling sites. The highest NO-concentration occurred in the longest period - 70 minutes.

In the gas samples taken at the surface of the wastewater, the emissions of different sampling periods and reactors show different tendencies and proportions. It is clear from the emission values, that the NO-flux measured on the surface of the wastewater can hardly be detected in the case of the initial, raw service. It can be seen, that the gas emission activity starts in reactor 2 and intensifies in approximately the same proportion in reactor line, with the exception of reactor 5. The highest gas emissions were observed in reactors 5 and 6. Depending on the trapping period, the amount of NO formed increased continuously. High concentrations of NO-other than in the reactor line were observed only in reactor 5. The samples taken in reactor 5 were characterized by a small difference between the 10- and 20 minute measurements and the 30- and 40 minute periods, which may be due to a decrease in the reactors pH value of water and an increase in the dissolved oxygen content of the wastewater.

The sampling point of the wetland results in NO-emissions with different dynamics compared to the samples taken on the surface of the wastewater. Wetland (CW) sampling points showed higher releases than water surface releases, with the exception of 30-minute samples from reactor 5. In contrast to the water surface, samples taken in the wetland show that NO-production starts and continues in the former purification process because it has already taken place in reactor spaces 4, 5 and 6. At the concentrations measured in the reactors, it was observed, that the highest flux in their proportions occurred at the shorter period of 10- and 20 minutes. The reason for this is the degradation due to the more complex, species-rich fauna (worms, insects, microbes) of the wetland. The results show that the formation of the NO-component in the wetland was characterized by one-third higher emissions in proportion to the wastewater, regardless of the measurement location and length.

3.2.7 C and N content in plant samples

CN analysis of plant samples taken from the plants of a wetland (growing module) in a semi-industrial wastewater treatment plant can find out the change in the ratio of carbon and nitrogen in the plant. From the different ratios we can deduce the use of test plants C and N in different reactors. These can influence the processes in the reactors (gas flux, C content of reactors). From the rate of accumulation, we can deduce the amount of nutrients available to the plants and determine the rate of utilization in the plants. From this, we can deduce in which purification process the presence of dissolved C and N (CO_2 and N_2O gas emission influencing factor) is more optimal.

During the study, I examined plant samples taken from reactors 4, 6, and 8 because these are the phased elements of the purification steps. The initial

stage (reactors 1 and 2) could not be patterned because there was not enough patterned plant biomass due to a technological error.
The measurements show that the traditional field-grown (control) plant had a higher C and N contant in the reeds. Regarding Chinese reeds, it can be said that in the case of reed samples, the proportion of C in adult (second generation) plants is higher than in the initial (first generation) samples and continuously decreases from the 4th reactor. In contrast to it, the proportion of N in reactor 4 in the initial reed sample is 44% higher than in the more advanced one. This is only 22% in reactor 6. In reactor 8, the N content of the mature plant in the initial plant samples is already 24% higher. It follows from the accumulation of the C and N content how the C and N saturation of the reactors changes. The C and N content directly influences the rate of N_2O and CO_2 dissolution at a constant dissolved oxygen content. Compared to the control sample, the ratio of C to N decreases in both samples. As the plant develops, the N ratio increases. The N ratio of the plant in reactor 6 shows a maximum. This means the highest N_2O and CO_2 emission intensification in the cleaning process according to the C and N content influence.

3.2.8 A Wetland and grassland association gas emission dynamics

N_2O is the third most important greenhouse gas component in the sectors and is released from the soil through nitrification processes (Velthof and Oenema, 1997). Soil N_2O release depends on abiotic factors (soil temperature, groundwater content, pH), biotic factors (substrate availability, soil carbon content, soil bacteria) and treatment types (Horváth et al., 2010; Soussana et al., 2010). Soil N_2O emissions increase in relatively oxygen-free, moderately moist soils where substrates (organic matter residues) are available (Horváth et al., 2008).
Describing and assessing the temporal variability of spatial patterns of CO_2 and N_2O fluxes in habitats is a difficult task. Changes in fluxes can be attributed to different indicators and such a modifying effect can be attributed to different management systems, for example, in the case of grasslands, the effects of grazing and mowing, and the existence of an ecosystem system for wastewater treatment.

The flux pattern

Due to the uniform surface on the surface of the investigated wastewater and reactors, a flux with a non-fluctuating distribution can be assumed. However, different flow conditions within the reactor body or in the artificial habitat, organic matter accumulating in different depressions, and associated biologically active surfaces may result in different flux patterns. The effect of these factors may regulate wetland respiration and N_2O flux. This is expected to be larger in such depressions. The reason is that the studied ecosystem has a constant moisture content, a substrate and a typically constant temperature environment. The correlation of the N_2O pattern proved to be positive in the wetland and due to different reactors. I did not find robust spatial correlations for wastewater. Therefore, it is justified to compare the differences in the duration of the wetland and to explore its pattern.

Flux variability over time was measured at 10, 20, 30, 40 minute in different measurement periods. CO_2 and N_2O were characterized by outliers. Outstanding deviations from the mean value caused variability in sampling points, suggesting a different pattern of wetland flux. At measurments of the gas emission components, I compared the average emission with the deviation from the average. The reason is the verification of the flux pattern in different reactors. For the components, outliers occur only in the wetland and in the middle of the cleaning process, within the process at reactors 2 and 5. This is because biological activity and the breakdown of organic matter typically take place at this stage. Therefore, I also examined the possibility of spatial variation here. At 20- and 40 minute samplings, I measured different variability and high concentration for both components in reactors 3 and 5.

At measuring the N_2O emission durations, the average deviation ratios represented a different pattern per reactor, which monitored the biological foci of the formed ecosystem and the biofilm activity accumulated in the pits. In the case of the N_2O component, the deviation of the third measurement from the average of the gas traps in the reactor 2 at intervals of 10- and 20 minutes showed heterogeneous, unexpectedly induced higher emissions. In the longer interval, the deviation from the mean was below 5% in all cases. In reactor 3, I found a higher deviation from the average for the second and third measurements only in the case of gas trapping at 20-minute intervals, which was approximately the same. This discrepancy showed a discrepancy in time activity within the sample, resulting in higher emissions than the measurement mean. In the longer interval, the deviation from the mean was below 5% in all cases.

In the N_2O component in Reactor 4, the deviation of the very first measurement from the mean for gas trapping at 10-minute intervals was remarkably high. Similarly, at intervals of 20- and 30 minutes, at least one ratio was significantly different from the mean value. In the 5-minute interval gas trapping in reactor 5, I found a higher deviation from the average for the third and fourth measurements. This was approximately the same. In the case of gas trapping at 20-minute intervals, I found similar effects in the second and third measurements. This discrepancy showed the significance of time activity within the sample, which results in higher emissions than the measurement average. At longer intervals (30-, 40- and 70 minute), the rate of deviation from the mean was less than 5% in all cases. Based on these results it can be stated that the spatial variation or pattern of N_2O flux can be

characterized by temporal variability, which must be taken into account both in the calculation of net emissions and in the characterization of purification processes.
In the study of CO_2 emission durations, the average deviation rates were similar to the N_2O component. The pattern was also expected for this gas component, as the (significant) relationship between the two gas components had already been proven in advance. In the case of this component, the deviation of the third measurement from the average in the gas traps at intervals of 10- and 20 minutes in reactor 2 showed induced higher emissions. At the 30-minute interval, the rate of deviation from the mean was less than 5% in all cases. At the 40-min interval, the first and third samples showed a significant difference. In reactor 3, I found a higher deviation from the mean value only in the 40-minute interval gas trapping and in the third measurement, the previous samples were characterized approximately by the same amount of flux. This discrepancy showed the phenomenon, appearance and equal proportion by approximatley of temporal activity within the pattern. This results in higher emissions than the measurement average. At intervals differendt than 40 minute of sampling, the rate of deviation from the mean was less than 5% in all cases. In reactor 4, the deviation from the very first measurement average for the 10-minute interval gas trap showed a remarkably high difference (similar to the N_2O component). Similarly, at intervals of 20-, 30- and 40 minute, at least one ratio of outliers differed from the mean value, with different temporal variability. In the 5-minute interval gas trapping in reactor 5, I found a higher deviation from the average for the third and fourth measurement results, which occurred at approximately the same rate. For gas trapping at 20 and 30 minute intervals, the deviation rate was below 5%. This discrepancy showed the occurrence of temporal activity within the pattern. At the 40-minute interval, the flux was continuously increasing for the three measurements. This was the highest deviation rate for the third measurement. Based on the above, the CO_2 flux pattern may be characterized by temporal variability, which should be taken into account when we characterize the purification processes. The spatial variability of the CO_2 and N_2O components is the same for each reactor, with a similar relationship. Where the spatial pattern of CO_2 shows intensification, there is typically an opposite rate of spatial variation in the N_2O pattern. There is a demonstrable relationship between the temporal and spatial patterns of gas components that differ from reactor to reactor. Typically, 3 types of spatial patterns can be distinguished from the measurements: one-off, well above average, parallel to the same extent, and a pattern of continuous intensity increase. Persistence could not be detected in the spatial patterns. I could not

detect general co-samples and their durability in two measurements at different times and at different components.

3.2.9 Cascading wastewater treatment (FCR System) development

Establishment of a wetland (CW) with a growing module

Similar to the example of animal husbandry, alternatives to treatments within wastewater treatment technologies can significantly reduce the contribution to climate change gases. Similar to animal husbandry, the use of different habitats (grasslands) in specific pedoclimatic and breeding systems can reduce emission factors from proven applications (Narayan K. et al. 2018; Renáta S. et al. 2018).

Application of fixed plant supports

Based on the experience of laboratory tests, I fixed the fixed plant supports 50 mm lower than the average water level of the given reactor. I indicated the existing supports with a black “Enkamat” mesh, which I filled with expanded clay. Chinese reed rhizomes were placed over the wettable expanded clay layer (20–30 mm), which was covered with an additional 140–150 mm expanded clay.

Based on the experience of laboratory tests, fixed anchors were also well suited for the installation of aquatic plants, however, the semi-industrial system encountered problems due to the stronger aeration system and flow, as well as higher water temperature and intermittent foaming. The selected aquatic plants constantly floated out of place and were easily damaged, so I designed a cushioned plant holder (module) taking into account the needs of the aquatic plants and the technology. With the help of the development, the problems experienced earlier could be eliminated, and the second (later) installation could be completed successfully.

Application of the cushioned plant support (module)

3.2.3. figure – Expanded clay cushion developed for FCR reactor aquatic plants

Figure 3.2.3. shows a cushion designed to secure aquatic plants, which I produced by sewing two 920 x 470 mm “Enkamat” nets and filling with expanded clay. I made a 20 x 40 mm opening corresponding to the size of the leaf surface of the plants. After placing the plant, I performed additional expanded clay filling at the stems and under the leaves. By installing with this method, the problem of flow, foaming and buoyancy could be eliminated.

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

Based on the described measurements, we concluded that the wastewater treatment (FCR) based on Chinese reeds (Miscanthus sinensis) can have significant benefits. Non-destructive neutron activation analysis (NAA) is a suitable method for measuring the concentration of heavy metals. It can be stated that it has an extremely low limit of determination and a high selectivity for metals.

A wastewater treatment process supplemented with wetlands (CW) can effectively reduce the nutrient load on wastewater, as evidenced by results, and using the system developed, it can provide renewable energy biomass for energy cane production, thus it is not occupying conventional production area (arable land). The incorporation of the Chinese reed into cascade wastewater treatment makes the treatment processes more efficient and it also reduces the heavy metal content of the wastewater (Cr, Zr, Zn, Hg, As, Fe, As, Al). The heavy metal (e.g. Zn, Cu, Cd) concentrations in the plants decrease at different stages of the cascade treatment. On the other hand, the concentration of other elements increases along the cascade in the plant (e.g. K, S, Fe). Concentrations of some elements (e.g. Co, Ni, Ag, and Hg) in the reactor 4 plants show maximum concentrations. In most of the samples, the concentration of elements was higher (e.g. Eu, Hf, Sm, U, Cd, Hg, Cr, Mo, Cs, Sc) than in the control plant. This difference indicates the efficiency of the system. It can be seen that the strongly adsorbed elements block most of the receptor sites in the first reactors, so the elements capable of weak surface binding cannot be adsorbed at these sites. Elements with poor binding properties can be adsorbed if the concentration of elements with strong surface binding decreases and sufficient free active receptor space remains for their adsorption. In these cases, the concentration of the weakly adsorbent element increases in the plants along the cascade sequence.

From all there results it can be concluded that in the case of the examined gas components (CO_2, NO, N_2O) more intensive emissions can be achieved by using CWs. Gas emissions increased by about a third in the cascade system, as confirmed by preliminary studies.

The location of the N_2O flux did not change compared to the conventional cascade system, because the emission took place at reactors 2 and 5 in both cases. Emissions increased significantly with the use of CW, with emissions concentrated in reactors 3 and 4. Emissions were highest between the 10- and 20 minute periods.

The location of CO_2 emissions did not change compared to the conventional cascade system, because the gas component formation took place in the entire reactor line in both cases (reactors 1-8). Emission levels increased significantly with the use of conventional FCR plant holders as expected (literature experience, C/N ratio), however, in the case of the supplemented growing module (wetland), it was formed at a lower concentration than the wastewater emission (on average 21%). In the case of wastewater, the discharge is typically of value 3-6, was higher in the reactor, however, in the wetland, the 3-8. reactors, which had the highest proportion in the 10-minute measurement interval.

The value of NO-emission did not change compared to the conventional cascade system, the formation of the gas component took place in both cases in the entire reactor line (reactors 1-8). The level of NO-concentration increased with the use of CW, the discharge in wastewater was typically higher in reactors 5 and 6, but in the wetland it occurred earlier (up to reactors 1-6). The NO-flux ratio was highest between 10- and 40 minute.

In addition to the examination of the gas emission of the wastewater, I explored the CO_2 gas absorption function of the wetland formed by the growing module. Based on the flux measurements, I experienced emission pattern per reactor. The emission pattern, spatial and temporal variability of the gas component determines the flux dynamics of the wetland (CW). The phenomenon is similar to the spatial emission pattern of grassland associations. The dynamics of the release is of great importance in the formation of the spatial pattern of the studied CW, where the biological activity is frequent or biofilm accumulation is formed. Ecosystems can create different levels of heterogeneity or homogeneity, the regulatory effect of which on spatial patterns has only been seen in wetlands (CW). The temporal persistence of spatial patterns was also a dynamic phenomenon.

4.2 **Suggestions**

Based on these results, further studies are proposed on the binding of heavy metal to the plant (Chinese reed) as well as on gas emissions. It would be important to know the reason for the increased accumulation of heavy metal concentrations in the final reactor. In the case of gaseous emissions, it is recommended to investigate additional gas components such as methane (CH_4) and the use of larger volume gas traps. In any case, pattern analysis of flux per reactor and exploration of persistence relationships are essential. In the case of the 8-element cascade FCR equipment, the number of reactors in terms of treatment parameters corresponds to the tested wastewater treatment process. However, it is suggested that reviewing their numbers and supplementing them with additional plants may increase water treatment efficiency.

5. SUMMARY

In order to optimize the studies, analyzes and optimization of the semi-operational biological reactor system for the development of FCR wastewater treatment technology, I consider the impact of **wastewater included in my objectives on plant development, element uptake and gas emissions (CO_2, N_2O, NO) as** a new scientific result:

1. I determined the effect of wastewater on the development of an energy plant (Chinese reed) and explored the effect of the cultivation module (wetland) integrated into the ecosystem on the wastewater treatment process, which causes an increase in N_2O and CO_2 emissions. Using analytical methods, I demonstrated the effect of the plant integrated into the semi-industrial FCR wastewater treatment system on the battery uptake and gas emissions.

2. In an 8-element cascade system I determined the concentration points of the different element groups - 45 elements, 5 element groups (according to Wood - 1974) - in the plant, its reasons, and the element concentration in the cascade row, in which reactor, which element is concentrated. Accumulation of batteries in plants also means removal from wastewater. There are three types of cleaning process: single descending, 4-6. reactor-specific accumulation in the last (reactor 8) cascade.

3. I found out how and in which reactor the wetland formed by Chinese reeds installed in the cultivation module influences the CO_2, N_2O and NO gas emissions, and that the wastewater in the wetland created in the wastewater treatment plant has no negative effect on the control compared to the control - during the vegetation period in all cascade elements exceeds - and an increase in biological activity in the reactor line could be detected.

4. The wetland (growing module) created in the FCR system enhances the cleaning efficiency and the test plant intensifies the cleaning process. Cultivation conditions result in similar biomass production in the wastewater CW as a conventional field cultivation.

5. From the emissions of different gas components we could deduce the microbial activity of the cascade reactor systems, which is proved by the results of the CO_2 gas component. During the formation of the plant and the wetland, microbes that bind direct CO_2 have also appeared, thus reducing CO_2 emissions. The wetland could be used to increase biological activity (cleaning surface, biofilm augmentation, insects, worms), which can intensify the degradation processes - N_2O formation was on average 70,4% higher than CW - thus removing organic matter from wastewater. and cleaning efficiency. I determined the CO_2 uptake function of the wetland (CW) in biological wastewater treatment, which has been proven to reduce GHG emissions in the wastewater sector. On average, emissions are 21,4% lower, which should be higher in proportion, based on the C / N ratio, similar to N_2O gas component emissions.

6. I revealed a correlation in the flux pattern of grassland and wetland (CW). Similar to the grassland association, I showed a periodic, intensity difference based on the values of emission concentrations. My overall results showed that patterns of spatial differences, depressions, and maxima are of primary importance in shaping the spatial patterns of the habitats studied. At the same time, I also found that the expected spatial relationships have changed over time, and different treatment systems may have an important impact on them, characterizing the spatial and temporal variability of the gas components of wetlands applicable to wastewater.

6. Related publications

1. Peer-reviewed research articles

With impact factor (according to WEB OF SCIENCE), in English:

Péter Koncz, Krisztina Pintér, János Balogh, Marianna Papp, Dóra Hidy, Zsolt Csintalan, Erik Molnár, **Albert Szaniszló**, Györgyi Kampfl, László Horváth, Zoltán Nagy (2017). Extensive grazing in contrast to mowing is climate-friendly based on the farm-scale greenhouse gas balance, Agriculture, Ecosystems and Environment 240 (2017) 121–134. DOI: https://doi.org/10.1016/j.agee.2017.02.022

Szilvia Fóti, János Balogh, Marianna Papp, Péter Koncz, Dóra Hidy, Zsolt Csintalan, Péter Kertész, Sándor Bartha, Zita Zimmermann, Marianna Biró, László Hováth, Erik Molnár, **Albert Szaniszló,** Krisztina Kristóf, Györgyi Kampfl, and Zoltán Nagy (2017). Temporal Variability of CO_2 and N_2O Flux Spatial Patterns at a Mowed and a Grazed Grassland, Ecosystems, Springer Science+Business Media New York, DOI: https://doi.org/10.1007/s10021-017-0138-8

Without impact factor, in English:

Albert Szaniszló, H E A F Bayoumi Hamuda, Ágnes Bálint (2015) Ecological Opportunities to Develop Biological Process for Wastewater Treatment. Óbuda University e-Bulletin 5 (1) : 187-196.

Lóránt Szabó, **Albert Szaniszló,** (2017): Solar power plant station in Fishland., Int. Rev. Appl. Sci. Eng., 8(1), 37–43. Akadémia kiadó, Budapest, DOI: https://doi.org/10.1556/1848.2017.8.1.6

Albert Szaniszló; Krisztina Demény (2018): Evolution of the absorption of heavy metals in function of nutrients, Columella: Journal of Agricultural And Environmental Sciences, 5(1), pp. 37-44., 8 p. DOI: https://doi.org/10.18380/SZIE.COLUM.2018.5.1.37

Without impact factor, in Hungarian:

Szaniszló Albert, H E A F Bayoumi, Bálint Ágnes (2015). Alternatív termőhely, mint új lehetőségek alkalmazása a biológiai szennyvíztisztításban. (In English: Alternative production site as application of new possibilities in biological wastewater treatment.) ECONOMICA(SZOLNOK) VIII. :(3) pp. 294-300.

Szaniszló Albert (2014) Az energianád (*Miscanthus spp.)* alkalmazási lehetősége alternatív termőhelyeken. (In English: Possibility of using energy cane (*Miscanthus spp.*) in alternative production areas.) AGROFÓRUM 25:(12) pp. 44-49.

In newspaper, without impact factor, full Conference papers in English:

Albert Szaniszló, Rita Pecze, Ágnes Bálint (2016) Examination the heavy metal contamination of municipal waste incinerator and M3 motorway in Budapest Proceedings of Ecopole, 10: (2), pp. 523-532. Zakopane, Lengyelország: 2016.10.05-2016.10.08.

DOI: https://doi.org/10.2429/proc.2016.10(1)056

Bálint Ágnes; Kiss Rita; **Szaniszló Albert**; Bayoumi Hamuda H.E.A.F. (2018): The effect of heavy metals to be found in the environment on the human body. Proceedings of Ecopole, 12(1), pp. 11-20., DOI: https://doi.org/10.2429/proc.2018.12(1)001

Albert Szaniszló, Ágnes Bálint, Viktória Szmolka, Bernadett Gyarmati, Györgyi Kampfl (2013): Examination of biofilm gas emission in foog chain reactor system. Növénytermelés, 62(Supplement), pp. 397-400.

G Bernvalner, **A Szaniszló**, B Gyarmati, M Horváth, Á Bálint (2012): The effect of acid rain and heavy metal on garden cress (Lepidium sativum), Növénytermelés, 61(Supplement), pp. 93-96.

Bernadett Gyarmati, **Albert Szaniszló**, Balázs Törő, Ágnes Bálint (2010): Application of the garden cress (Lepidium sativum) as possible biological indicator of a heavy metal accumulation. Növénytermelés, 59(Supplement), pp. 333-336.

2. Conference proceedings with ISBN, full papers in English:

Bayoumi Hamuda Hosam, **Szaniszló Albert**, Paukó Andrea, Bálint Ágnes (2015) Impact of Engineered Metal Oxide Nanoparticles on Plant-Growth Promoting Substances Produced by Symbiotoc N_2-Fixing Rhizobium In: Páy Gábor, Sikolya László, Ungureanu Nicolae (szerk.) International Multidisciplinary Conference: 11th Edition. 182, p. Conferencia place, date: Nyíregyháza, Hungary, 2015.05.20-2015.05.22. Nyíregyháza: Bessenyei Publishing House, 2015. pp. 29-34. (ISBN:978-615-5545-51-1)

Szaniszló Albert, Bayoumi Hamuda Hosam, Bálint Ágnes (2015) Application of Garden Cress (Lepidium sativum) as Biological Indicator in Case of Heavy Metal Contamination, In: Páy Gábor, Sikolya László, Ungureanu Nicolae (szerk.) International Multidisciplinary Conference: 11th Edition. 182 p. 157-160. Conferencia place, date: Nyíregyháza, Hungary, 2015.05.20-2015.05.22. Nyíregyháza: Bessenyei Publishing House, 2015. pp. 157-160. (ISBN:978-615-5545-51-1)

Albert Szaniszló, Györgyi Kampfl, Ágnes Bálint (2014). Investigation of gas emission in food chain reactor system, 5th ICEEE-2014 International Conference: Global Environmental Change and Population Health: Progress and Challenges. Konferencia helye, ideje: Budapest, Magyarország, 2014.11.19-2014.11.21. Budapest, pp. 88-94. (ISBN:978-615-5460-26-5)

7. REFERENCES

FRANKOWSKI MARCIN, U., ANETTA ZIOŁA-FRANKOWSKA, IWONA KURZYCA, KAREL NOVOTNÝ, TOMAS VACULOVIČ, VIKTOR KANICKÝ, MARCIN SIEPAK and JERZY SIEPAK (2011): Determination of aluminium in groundwater samples by GF-AAS, ICP-AES, ICP-MS and modelling of inorganic aluminium complexes. Environmental Monitoring and Assessment,182, pp.71–84.

HORVÁTH L, GROSZ B, MACHON A, TUBA Z, NAGY Z, CZÓBEL SZ, BALOGH J, PÉLI E, FÓTI SZ, WEIDINGER T. 27 (2010): Estimation of nitrous oxide emission from Hungarian semi-arid sandy and loess grasslands; effect of soil parameters, grazing, irrigation and use of fertilizer. Agriculture, 29 Ecosystems & Environment, 139, pp. 255–63.

HORVÁTH, L., GROSZ, B., CZÓBEL, Sz., NAGY, Z., PÉLI, E., SZERDAHELYI, T., SZIRMAI, O., TUBA, Z. (2008): Measurement of methane and nitrous oxide fluxes in 10.14751/SZIE.2016.02499 Bodrogköz, Hungary; preliminary results. In: Acta Biologica Szegediensis, 52(1), 119–122. p. http://www2.sci.u-szeged.hu/ABS/2008/tart08a.html

HUANG Y., ZOU J., ZHENG X., WANG Y., XU X. (2004): Nitrous oxide emissions as influenced by amendment of plant residues with different C: N ratios. Soil Biology and Biochemistry 36. 973-981. p.

KOVÁCS K. (1996): Mikroszervezetek denitrifikációs tevékenységének nyomonkövetése gázkromatográfiás módszerrel. Gödöllő: Gödöllői Agrártudományi Egyetem

KRISZT B., SZOBOSZLAY S., DOBOLYI CS. (1996): A Sreptomyces nitrosporeus N_2O termelésének (aerob denitrifikáció) vizsgálata. Agrokémia és Talajtan 45. (3-4), pp. 315-324.

M. V. FRONTASYEVA. S.S. PAVLOV (2000), Analitical investigations at the IBR-2 reactor in Dubna; Proceedings 2000 Workshop. Nuclear Data Production and Evaluation. Pohang Accelerator Laboratory. Pohang. Korea August 25-26.

M. V. FRONTASYEVA, HARMENS H, UZHINSKIY A AND THE PARTICIPANTS OF THE MOSS SURVEY (2019) Mosses as biomonitors of air pollution: 2015/2016 survey on heavy metals, nitrogen and POPs in Europe and beyond. UNECE ICP Vegetation. JINR Publishing Department, Dubna, R. ISBN 978-5-9530-0508-1. pp. 80.

NARAYAN KUMAR SHRESTHA, BEN W. THOMAS, XINZHONG DU1, XIYING HAO, JUNYE WANG, (2018): Modeling nitrous oxide emissions from rough fescue grassland soils subjected to long-term grazing of different intensities using the Soil and Water Assessment Tool (SWAT). Environmental Science and Pollution Research https://doi.org/10.1007/s11356-018-2719-2

ODILE HIRSCH (2007) User Manual ACTIVATM Family, HORIBA Jobin Yvon Reference 31

PAVLOV SS, DMITRIEV AY, FRONTASYEVA MV (2016) Automation system for neutron activation analysis at the reactor IBR-2. Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. J Radioanal Nucl Chem, 309, pp. 27–38.

RICARDO CHAGAS, MARTIN GERICKE, RICARDO B. FERREIRA, THOMAS HEINZE, LUÍSA M. FERREIRA (2020): Synthesis and characterization of dicarboxymethyl cellulose. Cellulose, 27, pp.1965–1974.

RENÁTA SÁNDOR, FIONA EHRHARDT, LORENZO BRILLI, MARCO CAROZZI, SYLVIE RECOUS, PETE SMITH, VAL SNOW, JEAN-FRANÇOIS SOUSSANA, CHRISTOPHER D. DORICH, KATHRIN FUCHS, NUALA FITTON, KATE

GONGADZE, KATJA KLUMPP, MARK LIEBIG, RAPHAËL MARTIN, LUTZMERBOLDK, PAUL C.D. NEWTON, ROBERTM. REES, SUSANNE ROLINSKI, GIANNI BELLOCCHI (2018): The use of biogeochemical models to evaluate mitigation of greenhouse gas emissions from managed grasslands. Science of the Total Environment, 642, pp. 292–306.

SIMARMATA T., BENCKISER G., OTTOW J.C.G. (1993): Effect of an increasing carbon: nitrate-N ratio on the reliability of acetylene in blocking the N_2O-reductase activity of denitrifying bacteria in soil. Biology and Fertility of Soils, 15, pp. 107-112.

SOUSSANA, J. F., TALLEC, T., BLANFORT, V. (2010): Mitigating the greenhouse gas balance of ruminant production systems through carbon sequestration in grasslands. Animal: An International Journal of Animal Bioscience, 4(3), 334–50. p. doi:10.1017/S1751731109990784

VELTHOF, G. L., and OENEMA, O. (1997): Nitrous oxide emission from dairy farming systems in the Netherlands. In: Netherlalnds Journal of Agricultural Science, 45, pp. 347–360. Available at: https://library.wur.nl/ojs/index.php/njas/article/viewFile/510/224.

WOOD JM. (1974) Biological Cycles for Elements in the Environment. Die Naturwissenschaften, 8, 357-364.