Water quality and emission rates of greenhouse gases in a treatment reedbed

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Abstract

The aim of this study was to estimate water purification capacity and greenhouse gas fluxes in a semi-natural reedbed receiving effluent from a wastewater treatment plant (WTP) in Lihula, which is located on the southern border of Matsalu National Park, Estonia. The values of BOD_7 and COD in the treated water were low (<8 and <70 mgL^{-1} respectively), whereas the COD level increased within the reedbed. The average concentrations of ammonia N and total N significantly decreased from the WTP outflow to the reedbed outflow (from 6.8 and 9 to 0.2 and 1.2 mg L^{-1} respectively). Nitrate and nitrite N levels were low but decreased along the flow. The average concentration of both PO_4-P and total P in water decreased rapidly toward the reedbed outflow (from 2.8 and 3.2 to 0.04 and 0.09 mg L^{-1} respectively). Redox potential and dissolved O_2 saturation showed the lowest values in the reedbed inflow. The C, N, and P concentration in soil decreased from the reedbed inflow towards the outflow. The average N_2 and N_2O fluxes from the reedbed were relatively low, varying from 4.0 to 16.1 mg N_2 m^{-2} h^{-1} and from -5.0 to 3.7 μg N_2O m^{-2} h^{-1} respectively. The spatial-temporal variation of methane emission was great (10.5-16397 μg CH_4 m^{-2} h^{-1}), showing higher values in the inflow. The average CO_2 emission from the reedbed varied from 14.3 to 334 mg CO_2-C m^{-2} h^{-1}, being somewhat higher in the inflow area. Accumulation of C, N and P in soil, increasing COD values and falling redox potential/dissolved O_2 values in water, and higher CH_4 and CO_2 emission rates in the inflow site of the reedbed demonstrate the long-term impact of sewage loading.

Keywords: carbon dioxide, dinitrogen, methane, nitrous oxide, reedbed, semi-natural wetland, wastewater, water quality.

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1 Introduction

Over several decades, wetlands have become increasingly frequently used throughout the world for primary, secondary or tertiary treatment of municipal, domestic, industrial or agricultural wastewaters [1–4]. In many countries, (semi-)natural wetlands serve as sinks for treated sewage for polishing [2], peatland restoration [5]. Several authors report the high efficiency of the removal of both nitrogen and phosphorus by these systems over a long period [6], even receiving raw sewage [7, 8]. However, long-term loading with primarily treated or even untreated sewage will result in the accumulation of organic matter and heavy metals in wetlands, and saturation with phosphorus [2, 4, 9, 10]. In several cases, new conventional treatment plants have been constructed, and the wetlands serve as secondary or tertiary treatment systems [11]. Little is known, however, about how these wetlands perform as water purifiers in changed conditions.

Reedbeds used as wastewater treatment wetland systems are able to improve the quality of wastewater (reduce the content of suspended solids, organic, NH_3^-, NO_2^-, NO_3^-, N_{org}, PO_4^{3-}, P_{tot}, metals, pathogens and change pH etc.) through various processes [2]. In such processes, organic materials and nitrogen are largely removed through volatilization to various gaseous substances, such as CO_2, CH_4, N_2, N_2O, NO and NH_3. The gases are emitted from waterlogged soil either by diffusion through the water or by active transport through the culms of wetland plants. Many species of emergent macrophytes such as *Phragmites australis* possess a convective flow mechanism; oxygen is transported to the roots, and gaseous microbial by-products are emitted into the atmosphere from plant roots [12]. Constructed and (semi-) natural wetlands are claimed to be effective water purifiers that have lower maintenance costs than conventional systems [4], but at the same time wetlands can contribute to global warming by emitting three important greenhouse gases (GHG): carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) [13–24]. Nevertheless, we have not found in the literature data on GHG fluxes in reedbeds or other (semi-)natural wetland ecosystems used for the long-term after-treatment of municipal wastewater.

The objectives of this study were to (1) analyse the water purification efficiency of a reedbed ecosystem which has been used for decades as a sewage sink and nowadays receives effluent from a wastewater treatment plant (WTP), (2) estimate the fluxes of the main GHGs N_2O, CO_2 and CH_4, as well as N_2 in this reedbed, comparing fluxes of the same gases from an adjacent grassland and forest ecosystem with similar soil conditions.

2 Material and methods

2.1 Site description

The study area is located on the western coast of Estonia, close to the southern border of Matsalu National Park, in Läänemaa County. The tertiary treatment

system which we examine was designed for secondary wastewater treatment from the conventional treatment plant. The Lihula WTP (58°41’21’’N; 23°49’43’’E) was constructed in 1997. Before that, municipal wastewater from the town of Lihula and a food processing factory (totalling about 2500 population equivalents, PE) was treated using only three stabilization ponds, which were full of sediments and obviously malfunctioned [25]. In 1994 the food processing factory was closed down. The new WTP, using a rotating biological contactor, treats wastewater from about 50% of the households and municipal buildings of Lihula (potentially about 800 PE; 750 m^3 d^{-1}) [25]. In addition to the WTP, the wastewater treatment system we studied includes a stabilization pond connected to the WTP by a ditch, a ditch from the pond to semi-natural reedbed and a reedbed system that finally serves as the treatment wetland (Fig. 1).

The Lihula-Matsalu reedbed (7 ha), located about 2.6-3.8 km northwest from the WTP, is a former shallow bay in the Baltic Sea formed on the Silurian

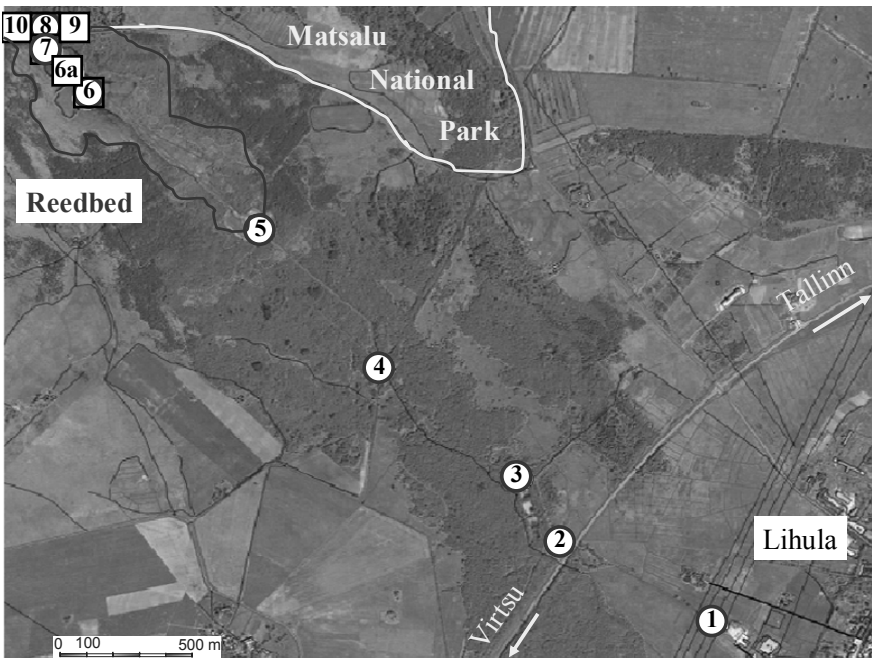

Figure 1: Location of sampling sites in the study area on the southern border of Matsalu National Park, Estonia: 1 – outflow from the wastewater treatment plant, 2 – stabilization pond inflow, 3 – stabilization pond outflow, 4 – inflow ditch (Inflow ditch), 5 – reedbed inflow, 6 – wet reedbed, 6a – dry reedbed, 7 – reedbed outflow, 8 – outflow ditch, 9 – forest, 10 – grassland. Circles – water sampling sites, quadrangles – gas and soil sampling sites. The names of the water sampling sites used in Figures 2–4 are given in parentheses.

bedrock of relatively soft limestones and marls, and covered by a thin till layer (0.5-2 m) of Weicshelian glaciation [26] that was repeatedly flooded and abraded by sea transgressions during the Holocene [27]. Due to postglacial uplift (up to 2.5 mm $year^{-1}$ in this particular region; [26]) the reedbed was isolated from the sea about 1000-1500 years ago. The soils of this flat reedbed plain are predominantly Mollic and Calcaric Gleysols [28] with clay content >60% [29]. The common reed (*Phragmites australis*), the dominant macrophyte of the reedbed, forms patch-like stands of different density, followed by a few patches of cattails (*Typha latifolia* and *T. angustifolia*), sedges (*Carex* spp.) and other aquatic macrophytes. The area is regularly flooded (for about 4-6 months of the year). Water flows through the reedbed, forming several pathways of various volume and depth (10-30 cm). Similar reedbeds 2-5 km north and northwest of the study area belong to Matsalu National Park, which was founded in 1957 as a nature reserve and was renamed a national park in 2004. In 1976 the Matsalu NP was included in the list of wetlands of international importance under the Ramsar Convention. For comparison gaseous fluxes from adjacent mixed forest (*Betula pendula, Pinus sylvestris* and *Picea abies* dominate in tree stand) on the complex of Rendzi-Gleyic Leptosols and Calcari-Gleyic Regosols, and a *Sesleria caerulea*-site type semi-natural grassland on Mollic Gleysol (Fig. 1; [28]) were measured. The water regime of both forest and grassland is influenced by the drainage ditch leading the water from the reedbed to the Penijõgi River and the Matsalu Bay.

2.2 Water sampling and analyses

The water quality measurement sites were located along the flow path of treated municipal wastewater and were as follows (Fig. 1): (1) outflow from WTP, (2) stabilization pond inflow (900 m from the WTP along the floodpath), (3) stabilization pond outflow (1100 m), (4) central course of connecting ditch (1970 m), (5) reedbed inflow (2560 m), (6) middle section of reedbed (wet and dry reedbeds; 3210 m)), (7) reedbed outflow (3470 m), and (8) outflow ditch (3770 m). The sampling was carried out in April, June, August and October 2007 and in August 2008. In October 2007 additional samples were taken from the outflow of the stabilization pond and from the inflow ditch (Fig. 1), because there was no water flow in the outflow ditch in August 2007. The samples were transported in 1 dm^3 polyethylene bottles to the lab (Laboratory of Tartu Environmental Research Ltd), where the analyses were begun within 24 h of collection. From all the water samples pH, BOD_7, COD_{Cr}, NH_4^+-N, NO_2^--N, NO_3^--N, total N, PO_4^{3-}-P, total P, SO_4^{2-} and Ca^{2+} were analyzed in accordance with the international methods for water analysis [30]. Dissolved oxygen and redox potential were measured in the field using a Marvet Junior Dissolved Oxygen Meter and CyberScan pH/mV/ºC Meter pH 300 Series.

2.3 Gas sampling and analyses

Short-time trace gas flux sampling was carried out using the closed-chamber method. The gas samples from the PVC chamber (diameter 50 cm, height 50 cm,

volume 65,5 l), which is white (to avoid heating during applications) and opaque (to avoid photosynthesis), were collected using previously evacuated flasks (100 mL) at 0 and 60 min after closing the top of the chamber. The surface area of each chamber was 0.196 m^2, and the chamber was placed on a water-filled ring that had been permanently placed in the soil before collection. The gas samples were taken in 5 replicates from the middle (from both - wet and dry sites) and outflow of the reedbed, in 3 replicates from the grassland and in 2 replicates from the forest near the outflow ditch in April, June and August, all in 2007 (Fig. 1). The concentration of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) in the samples was determined in the laboratory of the Leibniz Centre for Agricultural Landscape Research (ZALF) in Müncheberg, Germany using an automated gas chromatographic system (ECD and FID detectors, modified according to [31]). The emission rates of trace gases were calculated as the difference of gas concentrations between the beginning and the end of measurements, corrected for the area and volume of the chamber [32].

Dinitrogen (N_2) emission was measured using the He-O method [17, 19, 33, 34]. Intact soil cores (diameter 6.8 cm and height 6 cm) for analysis using the H-O method were taken from the topsoil (0-10 cm) under the gas sampler (closed chamber) sites after gas sampling was completed. Soil samples were weighted, kept at low temperature (4 ºC), and transported to the laboratory of ZALF. At the laboratory, the soil samples were placed in special stainless steel incubation vessels that could be sealed gas-tight to the surroundings. The soil cores within the incubation vessels were kept at the temperatures observed in the field. The N_2 was replaced with an artificial gas mixture (21.3% O_2, 78,6% He, 337 ppm CO_2, 374 ppb N_2O, 1882 ppb CH_4 and approximately 5 ppm N_2). The new flow equilibrium was established by continuously flushing the vessel headspace with artificial gas mixture at 10 ml per minute for 12 hours. N_2 concentration was measured in the continuous gas flow 1 hour after closing the incubation headspace. The emission rate of N_2 was calculated as the difference in gas concentrations (final accumulation value minus start continuous flow value) [34].

2.4 Soil sampling and analysis

In August 2008 soil was sampled from four gas sampling sites (6, 6a, 9, and 10, Fig. 1) as complex samples (20-30g soil sampled from five microsites located in a 0.5m radius circle, mixed, dried at 60^{o}C, and considered as one sample) from 0-10cm and 30-40cm depths. In the Laboratory of Tartu Environmental Research Ltd the nitrogen and carbon concentration was analysed using the Elemental analyser, and phosphorus concentration using the ICP-OES spectrometer.

Soils from the inflow part were mostly Calcaric Gleysols with somewhat higher Ca concentration than the Mollic Gleysols that are predominant in the outflow part of the treatment reedbed.

2.5 Statistical data analysis

The normality of water and gas quality variables was verified using the Lilliefors' and Shapiro-Wilk's tests. Most of the water quality characteristics

were normally distributed, whereas the gas fluxes showed skewed distributions. An analysis of variance (One-way ANOVA) was carried out for all data. The STATISTICA 7.0 software was used and the level of significance of α=0.05 was accepted in all cases.

3 Results and discussion

3.1 Performance of the Lihula wastewater treatment plant

The actual loading of the WTP is only 80-100 m^3 d^{-1} (the projected value is 750 m^3 d^{-1}), which is partly due to overestimated loading rates, leaking old pipe systems, the slower connecting of consumers to the WTP, and partly because of a decreasing number of inhabitants in Lihula town [25]. Therefore the average water quality in the outflow from the WTP met the quality requirements for COD, BOD_7 and total N (Table 1).

Table 1: Average values of main water quality indicators in the outflow from the Lihula WTP and water quality standards (mg L^{-1}) for treated wastewater in Estonia [35].

	COD	BOD_7	Total P	Total N
Average WTP outflow	52	7	1.9	8.9
Quality standards	125	25	2 (1)*	10**

* In parenthesis is the standard for sensitive water bodies.

** Recommended standard for constructed wetland outflow; for sources <10000 inhabitants, official standard is not established.

Nevertheless, the average total P level in the outflow was up to two times higher than the quality standards require for effluents discharged into sensitive water bodies like the Penijõgi River and shallow Matsalu Bay (Table 1). In June and August 2007 the total P levels in the WTP outflow exceeded the standard fourfold: 4.1 and 4.9 mg L^{-1} correspondingly.

3.2 Water quality

The saturation of dissolved oxygen in water showed high values in the outflow of the WTP and the inflow to the stabilization pond (on average up to 80%, Fig. 2), which shows that the purification process in the rotating biological contactor is almost aerobic. The lowering of the O_2 concentration in the outflow from the stabilization pond and the connecting ditch shows that the removal of sediments from the pond will be necessary in the near future.

A slight increase in the average level of dissolved oxygen saturation in the reedbed inflow (up to 60%) and continued increase within the reedbed (up to 80%) may indicate a dissolution effect from groundwater and lateral inflow. Redox potential followed a similar pattern to dissolved oxygen saturation (Fig. 2), however, due to high standard deviation values, this change was not

significant. On the other hand, predominating negative values point to facultative conditions (-100 – 15 mV) in the reedbed water [2].

Throughout the whole sampling session, the values of BOD_7 and COD_{Cr} in the reedbed were below the standard values, and maximum values were observed to be 9.7 and 99 mg L^{-1} respectively (Fig. 2). Because of the degradation of organic matter, however, one could expect some increase in these variables. The concentrations of BOD_7 and COD_{Cr} in WTP outflow and in the stabilization pond inflow and outflow were generally low and decreased towards the reedbed outflow. Relatively high BOD_7 and COD values in the inflow to the reedbed may indicate the influence of sediments rich in carbon compounds accumulated here during the loading of the system by raw or unsatisfactory treated wastewater between the 1960s and the 1990s. Similar effects have been mentioned in analogous treatment wetland systems [9–11].

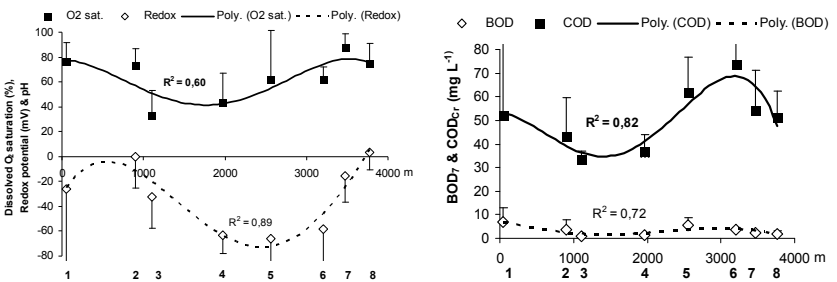

Figure 2: Variation in the average values of dissolved oxygen saturation (%) and redox potential (mV) (left), and levels of BOD_7 and COD_{Cr} (mg L^{-1}; right) along the flow path of treated municipal wastewater from Lihula from April to October in 2007 and August in 2008. Error bars indicate standard deviation values. 1–8: water sampling sites (see Fig. 1). For significant trendlines ($p<0.05$), determination coefficients (R^2) are given.

The main form of mineral nitrogen is ammonia nitrogen, the concentration of which was higher in the WTP outflow and the inflow to the stabilization pond. This indicates that the WTP may have problems with mineralization of organic N and nitrification of NH_4. Due to the suitable aerobic conditions (diffusion and photosynthesis) for the nitrification process in the stabilization pond and possible N uptake by plants in the inflow ditch, however, the average concentrations of ammonia N and total N decreased significantly from WTP outflow to reedbed outflow (from 6.8 and 9 to 0.2 and 1.2 mg L^{-1} respectively; Fig. 3). The average nitrate and nitrite N levels were low (from 0-0.15 and 0.05 to 0.8 mg L^{-1}), but decreased along the flow. Somewhat higher NO_3-N concentrations in the outflow from the stabilization pond and in the reedbed inflow (Fig. 3) indicate varying conditions of nitrification and denitrification that may be influenced by dissolution and differences in soil microbial activity between the vegetation

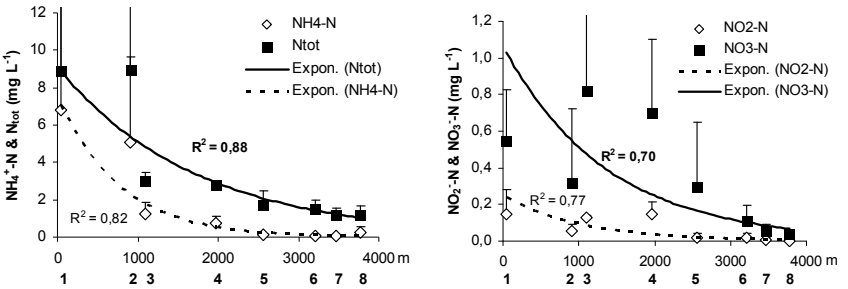

Figure 3: Variation of average values and standard deviations (error bars) of concentrations of nitrogen components along the flow path of treated municipal wastewater from Lihula from April to October 2007 and August 2008. For further explanation, see Figures 1 and 2.

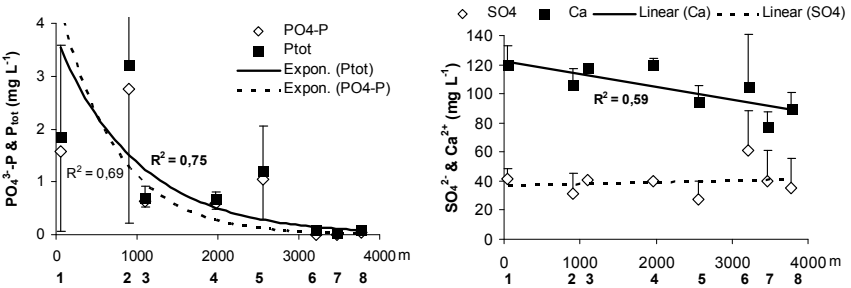

Figure 4: Variation of total phosphorus and PO_4^{3-}-P (left), and Ca^{2+} and SO_4^{2-} along the flow path of treated municipal wastewater from Lihula from April to October 2007 and August 2008. For further explanation, see Figures 1 and 2.

patches. The main form of N in the reedbed was organic nitrogen ($N_{org} = N_{tot} - NH_4\text{-}N - NO_2\text{-}N - NO_3\text{-}N$): 0.50-1.78 mg N L^{-1}, which is presumably caused by decay of plant litter.

The average concentration of both PO_4-P and total P in water decreased rapidly toward the reedbed outflow (from 2.8 and 3.2 to 0.04 and 0.09 mg L^{-1}, respectively; Fig. 4), whereas the initial concentrations of total P in June and August 2007 in the outflow of Lihula WTP and in the inflow to the stabilization pond extended the established quality standard (Table 1), and were 3.3 and 4.1 mg L^{-1} and 4.9 and 9.0 mg L^{-1} respectively.

The concentration of P_{tot} in reedbed inflow in June (2.4 mg L^{-1}) also exceeded the standard level. In August this value was lower (1.6 mg L^{-1}) than the limit, but still high in the reedbed inflow. Total P concentrations were very low in the middle section and outflow of the reedbed and in the outflow ditch. Most likely phosphorus was removed from water by co-precipitation with $CaCO_3$ [36, 37].

The decreasing trend of dissolved Ca along the flow path also supports this theory. The high pH value in this treatment system is due to the Ca-rich environment (Silurian marls and limestones and calcareous till as the main geological features; [26]), which is the main factor for P sedimentation in the system. Although several reports from Ca and Al-rich environments suggest that semi-natural treatment wetlands can remove P over a long period [6–8], it may become a problem in a few years, when P in the wetland soil returns to the water if the overloading continues [38].

There was a slight increase in pH values in the reedbed, from 7.2 - 8.8. This increase may come from the fact that in open water zones within wetlands, which can develop high levels of algal activity and in turn create a higher pH value [39]. Relatively high sulphate values (13-81.5 mg SO_4 L^{-1}) in the reedbed may be caused by temporarily anaerobic conditions in the reedbed soil (Fig. 4; see also [40]).

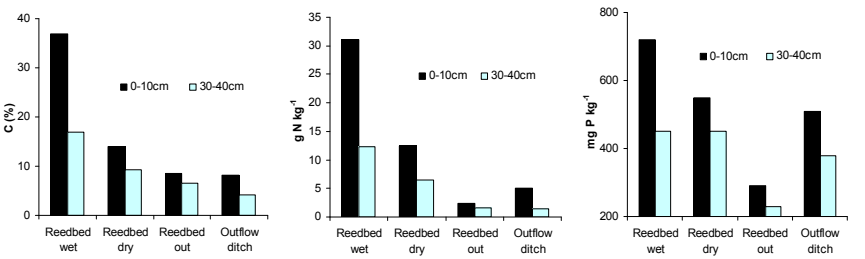

Figure 5: Average soil carbon, nitrogen and phosphorus concentrations in the treatment reedbed formed on Calcaric and Mollic Gleysols.

3.3 Carbon, nitrogen, and phosphorus pattern of soils

The carbon, nitrogen, and phosphorus concentration in soils showed higher values than the average for Calcaric and Mollic Gleysols in grasslands and coastal meadows in Estonia (8-10% C, 2-5 g N kg^{-1}, and 0.2-0.4 g P kg^{-1}; [29, 41]). The soil pattern also demonstrates the long-term effect of wastewater loading to the reedbed: the C, N, and P concentrations in both topsoil (0-10cm) and at a depth of 30-40 cm decreased from the reedbed inflow towards the outflow, ranging from 37 to 4.2%C, from 31 to 1.4 g N kg^{-1}, and from 720 to 230 mg P kg^{-1} (Fig. 5).

3.4 Emissions of CO_2, CH_4, N_2O and N_2 in the reedbed

3.4.1 CO_2

The average CO_2 emission from the reedbed varied from 14.3 to 334 mg CO_2-C m^{-2} h^{-1}. The highest CO_2 emission rates were registered in June in the wet part and in the outflow part of the reedbed (Fig. 6). These values are significantly higher than those observed for boreal natural ombrotropic and transitional bogs in Fennoscandia (from -385 to 10.5 mg CO_2-C m^{-2} h^{-1}; [42–45]), at the same level as emission values from boreal drained bogs (58.6-315 mg CO_2-C m^{-2} h^{-1}),

and somewhat lower than those registered from boreal drained fens (120-744 mg CO_2-C m^{-2} h^{-1}; [43, 46, 47]).

Comparatively high CO_2 emission values were also registered in boreal organic agricultural soils in Finland (from 45 to 95 CO_2-C m^{-2} h^{-1} in a grassland and arable land respectively; [48]), in a drained grassland on peatland soil in the Netherlands (167-250 mg CO_2-C m^{-2} h^{-1}; [49]) and in a drained boreal spruce forest (533-611 mg CO_2-C m^{-2} h^{-1}; [50]).

The variation of the CO_2 flux rate from the forest was 19.7 – 234 mg CO_2-C m^{-2} h^{-1} and from the grassland 11.4 – 81.8 mg CO_2-C m^{-2} h^{-1} (Fig. 6).

3.4.2 CH_4

The reedbed only emitted relatively small amounts of methane, but spatial and temporal variability was high. The average CH_4 emission varied from 10.5 to 16397 μg CH_4 m^{-2} h^{-1} from April to August (Fig. 6).

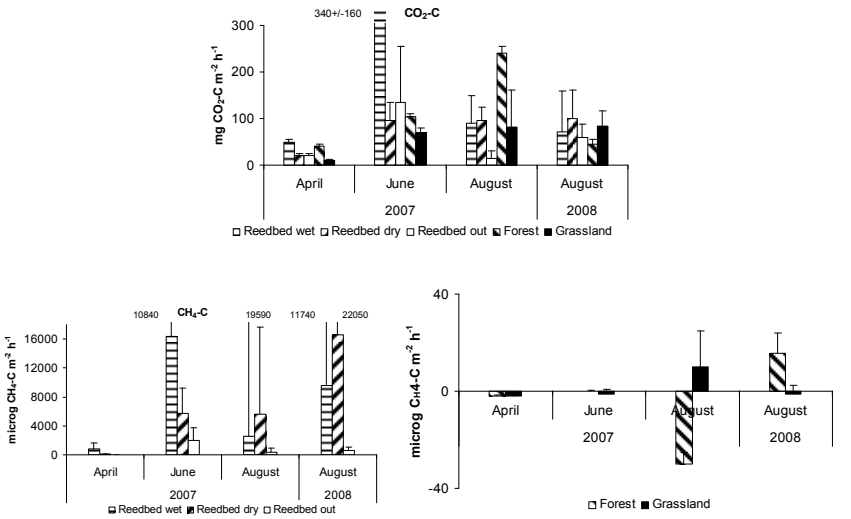

Figure 6: Average emission rates (standard deviation is indicated with error bars) of CO_2 and CH_4 from the reedbed, forest and grassland of the Lihula-Matsalu study area.

This variability is explained by the differences in temperature and changes in the water table (in April 0-10 cm above the soil surface and in June and August 0-10 cm below the soil surface). The decrease of the water table in the reedbed during summer increased methane emission in both wet and dry reedbeds, but decreased in the outflow of the reedbed. Flooding can reduce methane emission, probably by blocking the primary sites of methane release in the lower part of the reed plant stems [51]. The CH_4 fluxes from forest (from -29.0 to -0.8 μg CH_4 m^{-2} h^{-1}) and grassland (from -1.4 to 8.5 μg CH_4 m^{-2} h^{-1}) were significantly lower than from the reedbed (Fig. 6). This is clearly due to the impact of the drainage ditch.

The CH_4-C fluxes measured in the reedbed were in the same range as values gathered in pristine boreal bogs and fens (23-4623 μg CH_4 m^{-2} h^{-1}; [47]), higher than values from drained boreal wetlands (from -83 to 570 μg CH_4 m^{-2} h^{-1}; [46, 47]), and significantly lower than those registered in wastewater treatment wetlands (27600-528000 μg CH_4 m^{-2} h^{-1}; [16, 52]). Pools in raised bogs can show extremely high CH_4-C emission values in summer (up to 131875 μg CH_4 m^{-2} h^{-1}; [53]). Also, *Phragmites* stands in boreal lakes (85900 μg CH_4 m^{-2} h^{-1}; [54]) and on Mollic Gleysols (up to 25432 μg CH_4 m^{-2} h^{-1}; [55]), rewetted fens (up to 9000 μg CH_4 m^{-2} h^{-1}; [32]) and small marshes within the agricultural landscape (up to 11575 μg CH_4 m^{-2} h^{-1}; [56]) can show high CH_4-C emission values, whereas drained marshes converted to agricultural fields demonstrate significant CH_4 uptake (up to 120 μg CH_4 m^{-2} h^{-1}; [57]). Except for some riparian alder forests [58], boreal and temperate forests oxidize CH_4 [59] even when treated with sludge [60].

Pulsing hydrology can significantly influence CH_4 fluxes, in most cases lowering emissions [61].

In August, during the maximal plant growth in reedbed, the CH_4-C emissions were possibly underestimated because the reed plants might mediate methane fluxes [61–63].

3.4.3 N_2O and N_2

The average N_2 and N_2O fluxes from the reedbed varied from 7.1 to 16.1 mg N_2 m^{-2} h^{-1} and from -5.0 to 3.7 μg N_2O m^{-2} h^{-1} respectively (Fig. 7). The highest values of N_2, 19.8 g N_2 m^{-2} h^{-1} and N_20 19.0 μg N_2O m^{-2} h^{-1}, were registered in April in the forest. In the grassland, N_2 and N_2O emission rates were relatively low, 6.8 – 7.4 mg N_2 m^{-2} h^{-1} and 0.1 – 0.6 μg N_2O m^{-2} h^{-1} respectively. Higher nitrous oxide emission values from the forest are probably influenced by the nearby drainage ditch. It is known that the change in wetland water regime significantly influences GHG fluxes, decreasing the CH_4 emission [64] and increasing N_2O [46, 65] and CO_2 emissions [49, 66]. In most cases, pulsing water regime increases N_2O emissions [67], although there are also contradictory results [68]. Some investigations show that *Phragmites* plants can mediate N_2O emission [69], whereas other have not found any relationship between the reed plant biomass and N_2O emission [70].

There are not many literature sources on N_2 emissions from wetland or forest ecosystems. Teiter and Mander [19] and Mander et al. [18, 58] demonstrated high N_2 emission rates (up to 1200 kg N_2-N ha^{-1} yr^{-1}) and high N_2 : N_2O (up to 2000) ratios in both HSSF CW and riparian alder forests, which indicates that in these ecosystems the denitrification process lasts to the very end, and not much N_2O is formed. Data on dinitrogen emission and the N_2:N_2O ratio gathered in this study are comparable with those presented in the literature [18, 19, 58]. Surprisingly, other forest ecosystems studied for dinitrogen fluxes show very low N_2 emission values and very low N_2:N_2O ratios [71].

Values of N_2O-N emission from our study are significantly lower than the values observed in various CWs for wastewater treatment (up to 17,000 μg N_2O m^{-2} h^{-1}; [13, 14, 16, 17, 72]), lower than those reported from drained boreal

peatlands (2-331 μg N_2O m^{-2} h^{-1}; [47]) and comparable with flux values reported on pristine boreal peatland ecosystems (1.14-27.4 μg N_2O m^{-2} h^{-1}; [42, 65]), Antarctic tundra soils (0.81-1.36 μg N_2O m^{-2} h^{-1}; [73]), temperate meadow grasslands (7.9-41 μg N_2O m^{-2} h^{-1}; [74]) and semi-natural grasslands (16.9-46 μg N_2O m^{-2} h^{-1}; [75]).

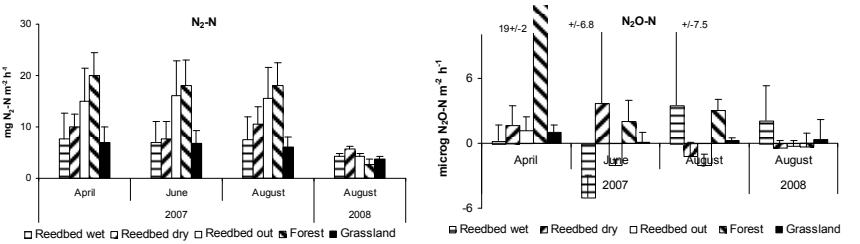

Figure 7: Average emission rates (standard deviation is marked as error bars) of N_2 and N_2O, from the reedbed, forest and grassland of the Lihula-Matsalu study area.

Grasslands [76] and wetlands with altered water regime [77] show higher N_2O-N emission (up to 184 μg N_2O m^{-2} h^{-1}). Forests emit low amounts of nitrous oxide (from low consumption up to 35 μg N_2O m^{-2} h^{-1}; [78, 79]), whereas deciduous forests tend to emit more than coniferous forests [80].

Several studies suggest that a large amount of N_2O can be emitted from various soils, even at temperatures below 0°C [81, 82]. The main mechanism for N_2O in frozen soil is denitrification [83], whereas N_2O can be produced in unfrozen water films in an anaerobic soil matrix in frozen soil [84]. Emission of N_2O in winter may account for more than half of the annual emission in boreal and temperate areas [85, 66]. Freezing and thawing cycles significantly increase N_2O emissions [87, 88]. Grasslands in intensive agricultural use demonstrate high N_2O emissions, especially on organic drained soils (up to 7.1 kg N_2O-N ha^{-1} yr^{-1}; [48]), in pastures (up to 24.5 kg N_2O-N ha^{-1} yr^{-1}; [89]), and after intensive fertilization (up to 15.9 kg N_2O-N ha^{-1} yr^{-1}; [90]).

Investigations have found that the constantly high water table in soil and substrates is an important precondition for N_2 emission [91, 92].

3.5 Approximation of gas emission values for yearly base

According to the temporal pattern of GHGs found in constructed wetlands [19], we estimated the annual average emission values of the studied gases in the Lihula-Matsalu treatment reedbed (Table 2). Our short-term investigation characterizes the average vegetation period pattern of GHG emissions [17]. Concerning the CH_4 and N_2 fluxes, we multiplied the calculated vegetation period values by the coefficient 0.5 [17], whereas N_2O emissions are assumed to be at about the same level in both cold and warm seasons [93].

In our study, CO_2 emission is not connected with fluxes related to plant photosynthesis. Therefore, the results cannot be considered losses to the

atmosphere. Although the CO_2 emission is known to increase during the freezing-thawing cycles, as is the case with N_2O-N emission [94], we assume that there is no significant flux of CO_2 in winter, and that the non-considered C fixation in photosynthesis can compensate about 75% of emission. Therefore, for approximation we multiplied the calculated vegetation period values of CO_2-C emissions with the coefficient 0.25 (Table 2). However, considering analogous studies on gaseous carbon fluxes from constructed wetlands [18], one can assume that the fixation of atmospheric CO_2 to plant tissues via photosynthesis and binding in soil microorganisms could compensate emissions in the vegetation period. In a horizontal subsurface flow (HSSF) constructed wetland (CW), the annual sequestration of C in different years was 484 and 649 kg C per 312,5 m^2 wetland area, while CO_2-C emissions were 120 and 230 kg C per wetland area [18].

Table 2: Estimated annual average emission rates of carbon dioxide, methane, nitrous oxide and dinitrogen from the reedbed (kg ha^{-1} yr^{-1}).

	CO_2-C	CH_4-C	N_2O-N	N_2
Reedbed wet	3020	0.30	0.02	290
Reedbed dry	1700	0.30	0.08	370
Reedbed out	1250	0.03	-0.07	560
Forest	2360	0	0.52	640
Grassland	1350	0	0.04	260

The C balance in a restored natural peatland in the Netherlands showed quite analogous results to the HSSF CW: the annual ecosystem exchange of CO_2 for the years 2002-2004 varied from -232+/-57 to -446+/-83 g C m^{-2} yr^{-1}, whereas the variation of ecosystem respiration was from 866+/-666 to 924+/-711 g C m^{-2} yr^{-1} [95]. However, a significantly lower density of *Phragmites* stands and phytomass value in Lihula-Matsalu reedbed (unpublished data by M. Maddison) allows one to estimate that the C fixation in plants is 3-4 times lower than in the above-mentioned HSSF CW. The wet inflow part of the reedbed is probably a source of CO_2-C, whereas in the outflow part and drier areas, emission and uptake might be balanced (see Table 2). Similarly, investigations in afforested boreal organic (former) agricultural soils show that the C accumulation in the developing tree stands can partly compensate the relatively high C loss from the soil [96].

4 Conclusions

Our data suggest that the reedbed studied can effectively polish the sometimes unsatisfactory treated wastewater effluent. The values of BOD_7 and COD, as well as all forms of nitrogen in the treated water were low (<8 and <70 mg L^{-1} of BOD and COD respectively, <10, <8, <1.0, and <0.2 mg L^{-1} for total N, NH_4-N, NO_3-N, and NO_2-N, correspondingly), whereas the average concentrations of all nitrogen forms significantly decreased from WTP outflow to reedbed outflow.

The concentration of phosphorus in the effluent of the wastewater treatment plant, which appears to be higher than established for sensitive receiving water bodies standards (1 mg P L^{-1}), decreased rapidly toward the reedbed outflow. Ca-rich soils will presumably guarantee P removal for a longer period.

Accumulation of C, N and P in soil (concentration of all components in both topsoil and to a depth of 30-40cm decreased from the reedbed inflow towards the outflow), increasing COD values and lowering redox potential/dissolved O_2 values in water, and higher CH_4 and CO_2 emission rates in the inflow site of reedbed demonstrate a long-term impact of sewage loading.

The average N_2 and N_2O fluxes from the reedbed varied from 4.0 to 16.1 mg N_2 m^{-2} h^{-1} and from -5.0 to 3.7 μg N_2O m^{-2} h^{-1} respectively. Although the spatial-temporal variation of methane emission was great (10.5-16397 μg CH_4 m^{-2} h^{-1}), showing higher values in the inflow part in June, the average emission value of methane is relatively low and comparable to natural wetland areas. Unexpectedly, N_2O fluxes from the reedbed were even lower. It coincided closely with relatively high N_2 emission values. This demonstrates that the denitrification process in this wetland ecosystem can be completed until the last product, which is least harmful to the atmosphere.

The average CO_2 emission from the reedbed varied from 14.3 to 334 mg CO_2-C m^{-2} h^{-1}, being somewhat higher in the inflow area. Our rough calculations based on published materials on analogous systems make it possible to estimate that the fixation of atmospheric CO_2 to plant tissues via photosynthesis and binding in soil microorganisms can compensate emissions in the vegetation period.

Further management of the stabilization pond (removal of the sediment), replacement of leaking sewage pipes and the sustainable harvesting of reed in the reedbed for construction and energy production are preconditions for the sustainable management of the Lihula-Matsalu reedbed.

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