Emission of greenhouse gases from constructed wetlands for wastewater treatment and from riparian buffer zones

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Abstract We measured N2O, CH4 and CO2 fluxes in horizontal and vertical flow constructed wetlands (CW) and in a riparian alder stand in southern Estonia using the closed chamber method in the period from October 2001 to November 2003. The average rates of N2O, CH4 and CO2 emission from the riparian gray alder stand were from 0.4 to 58 μg N2O-N m⁻² h⁻¹ and 0.1–265 μg CH4-C m⁻² h⁻¹, 55–61 mg CO2-C m⁻² h⁻¹, respectively. The average N2O-N emission from the microsites above the inflow pipes of horizontal subsurface flow (HSSF) CWs was 6.4–31 μg N2O-N m⁻² h⁻¹, whereas the outflow microsites emitted 2.4–8 μg N2O-N m⁻² h⁻¹. In vertical subsurface flow (VSSF) beds the same value was 35.6–44.7 μg N2O-N m⁻² h⁻¹. The average CH4 emission from the inflow and outflow microsites in the HSSF CWs differed significantly ranging from 640 to 9715 and from 30 to 770 μg CH4-C m⁻² h⁻¹, respectively. The average CO2 emission was somewhat higher in VSSF beds (140–291 mg CO2-C m⁻² h⁻¹) and at inflow microsites of HSSF beds (61–140 mg CO2-C m⁻² h⁻¹). The global warming potential (GWP) from N2O and CH4 was comparatively high in both types of CWs (4.8⁻⁹.8 and 6.8⁻¹⁶.2 t CO2 eq ha⁻¹ a⁻¹ in the HSSF CW 6.5⁻¹³.0 and 5.3⁻²⁴.7 t CO2 eq ha⁻¹ a⁻¹ in the hybrid CW, respectively). The GWP of riparian alder forest from both N2O and CH4 was relatively low (0.4⁻¹.0 and 0.1⁻⁰.30 t CO2 eq ha⁻¹ a⁻¹, respectively), whereas the CO2-C flux was remarkable (3.5⁻³.7 t ha⁻¹ a⁻¹). The global influence of CWs is not significant. Even if all the global domestic wastewater were treated by wetlands, their share in the trace gas emission budget would be less than 1%.

Keywords Carbon dioxide; constructed wetland; global warming potential; methane; nitrous oxide

Introduction Wetlands are considered as globally significant sources of greenhouse gases like methane (CH4; Bartlett and Harris, 1993; IPCC, 2001) and nitrous oxide (N2O; Martikainen et al., 1993). Numerous studies consider emissions and sequestration of carbon dioxide (CO2) in wetlands (Mitsch and Gosselink, 1993). Depending on meteorological and hydrological conditions, wetlands can be sources or sinks of carbon (Whiting and Chanton, 2001). Likewise, riparian buffer zones, as widely used ecotechnological measure to control water quality in agricultural catchments, have the potential to be hotspots of CH4 (Rush and Remmenberg, 1998) and N2O (Groffman et al., 2000) production in the landscape. Constructed wetlands (CW) for wastewater treatment have also been considered as sources of CH4 (Kadlec and Knight, 1996; Tanner et al., 1997; Wild et al., 2002; Mander et al., 2003) and N2O (Fey et al., 1999; Spieles and Mitsch, 2000; Tanner et al., 2002; Wild et al., 2002; Mander et al., 2003). Denitrification, as the microbial reduction of NO3⁻-N to NO2⁻-N and further to gaseous forms NO, N2O and N2 (Knowles, 1982), has been found in numerous studies as a significant process in nitrogen removal in both riparian buffer zones (Hanson et al., 1994; Groffman et al., 2000) and CWs (Spieles and Mitsch, 2000). However, in well aerated, yet moist conditions (soil water filled pore space at 40–60%), N2O can be emitted during the nitrification (Mosier, 1998). Both denitrification
and methane formation depend on the oxygen status of the soil or sediment. In this relation, the spatial and temporal variability of fluxes of both N2O (Brooks et al., 1997) and CH4 (Willison et al., 1998) is extremely high. Denitrification rates in soils are also influenced by carbon availability, nitrate availability, temperature and pH (Mitsch and Gosselink, 1993). CH4 is produced in anoxic soils and sediments, while well-drained soils act as a sink for atmospheric CH4 due to methane oxidation, through either ammonia oxidizers or methanotrophs (Hanson et al., 1994). Due to increasing human impact on global environment nitrous oxide is increasing in the atmosphere at a rate of about 0.3% yr\(^{-1}\), it has an atmospheric lifetime of about 120 years, a global warming potential of 296 relative to CO2 over a 100-year time horizon, and is responsible for about 6% of anticipated warming (IPCC, 2001). Methane in the atmosphere has a lifetime of 8.4 years, on a 100-year time horizon, CH4 has a global warming potential of 23 relative to CO2, and is responsible for about 20% of anticipated warming (IPCC, 2001). The main objectives of this research were: (1) to quantify N2O, CH4 and CO2 emission rates from two subsurface flow CWs for municipal wastewater treatment and in a grey alder forest in Estonia using the closed chamber method, and (2) to compare N2O, CH4 and CO2 fluxes and their global warming potential (GWP) from riparian buffers zones and constructed wetlands.

**Methods**

**Site description**

The Porijõgi riparian buffer zone site is a grey alder stand situated in the moraine plain of southeast Estonia (Tartu County, Sirvaku; 58° 13’ N, 26° 47’ E) in the right bank of a small river, the Porijõgi, which flows in a primeval valley where agricultural activities ceased in 1992. The landscape study transect in this valley crosses several plant communities: an abandoned field (last cultivated in 1992) on planosols and podzoluvisols; an abandoned cultivated grassland (last mowed in 1993) on colluvial podzoluvisol (dominated by Dactylis glomerata and Alopecurus pratensis); a 11-m-wide wet grassland on gleysol (two parallel communities, one dominated by Filipendula ulmaria, another by Aegopodium podagraria); and a 20–m-wide grey alder stand (Alnus incana) on gleysol. For a more detailed description, see Kuusemets et al., 2001. Description of the Kodijärve horizontal subsurface flow (HSSF) planted sand filter (constructed in October 1996, two beds each 25 × 6.25 × 1 m which are filled with coarse sand, purifies the wastewater from a hospital for about 40 population equivalents (PE); Figure 1B) is given by Mander et al. (2003). The hybrid treatment wetland system in Kõo, Viljandi County, Estonia consists of a two-bed vertical subsurface flow filter (VSSF; 2 × 64 m\(^2\), filled with crushed limestone, ø 5–10 mm, planted with P. australis), a horizontal subsurface flow filter (HSSF; 365 m\(^2\), filled with 15–20 mm crushed limestone, planted with T. latifolia and P. australis), and two free water surface wetland beds (FWSW; 3600 and 5500 m\(^2\), planted with T. latifolia). The system was constructed in 2000 for the purification of the raw municipal wastewater generated by about 300 PE. This wetland system showed a good purification, being for BOD\(_7\), total-N and total-P 88, 65 and 72% respectively. However, regarding the very high loading rate, the purification efficiency of the VSSF and HSSF part was only 57 and 31% of BOD\(_7\), 16 and 21% of total N, and 19 and 21% of total P correspondingly. The mean annual air temperature at the study sites varied from 5.0–5.5°C. In winter the lowest daily mean temperatures reach −207°C. The variation in long-term annual precipitation is 500–700 mm.

**Sampling and laboratory analysis**

The closed chamber method was used to measure N2O, CH4 and CO2 emission. Gas samplers (closed chambers; cover made from PVC, height 50 cm, Ø 50 cm, volume 651,
sealed by a water-filled ring on the soil surface, painted white to avoid heating during the application) were installed in 5 replicates in various parts of the studied systems: (1) in 3 different microsites (EDGE, WET and DRY; range of water table depth 45–95, 0–50 and 45–95 cm, respectively) in the Porijõgi riparian buffer zone (detail scheme of the study area is given by Mander et al., 1997), (2) on the inlet and outlet pipes of both beds,
in Kodijärve. In the hybrid wetland system in Kõo, 8 gas samplers were installed in the vertical flow filter (4 in each bed) and 15 in the horizontal flow filter (5 on two inlet pipes and 5 on the outlet pipe). At the end of the 1 hr measuring time gas samples were taken from the enclosures of samplers by previously evacuated gas bottles (100 ml). Gas sampling was carried out 15 times on the following time schedule: once a month in October and November 2001, and March, May to October and December 2002, January to March, July and November 2003. Simultaneously, the soil temperature and water depth in the sampling wells was measured, and the NH4-N and NO3-N concentration in soil samples was analysed using the Kjeldahl method (APHA, 1989). The trace gas concentration in the collected air was determined using the gas chromatographic system (electron capture detector and flame ionization detector) in the lab of the Institute of Primary Production and Microbial Ecology, Centre for Agricultural Landscape and Land Use Research (ZALF), Germany (for detailed description see Mander et al., 2003). Air and soil temperature, wind velocity, solar radiation and precipitation evapotranspiration were measured using a DAVIS Groweather automatic weather station installed close to the CW.

Statistical analysis
The normality of variables was checked using the Kolmogorov-Smirnov, Lilliefors’ and Shapiro-Wilk’s tests. In most cases of gas analyses the distribution differed from the normal, and hence non-parametric tests were performed. We used the Duncan Test, Wilcoxon Matched Pairs Test and the Mann-Whitney U-Test to check the significance ($\alpha = 0.05$ was accepted in all cases) of differences between the gas emission rates at different time and sites. The Spearman Rank Order Correlation was performed to analyse correlations between gaseous fluxes and environmental parameters.

Results and discussion
Spatial variation of gas emissions
The average flux of nitrous oxide from the microsites in the Kodijärve HSSF CW and Kõo hybrid CW ranged from 27 to 370 and from 72 to 500 $\mu$g N2O-N m$^{-2}$ h$^{-1}$, respectively (Figure 1A). In Kodijärve, according to the Wilcoxon Matched Pairs Test, significant differences were found in average N2O fluxes between the microsites: 325–350 $\mu$g N2O-N m$^{-2}$ h$^{-1}$ from chambers installed above the inflow pipes and 30–40 $\mu$g N2O-N m$^{-2}$ h$^{-1}$ from chambers above the outflow pipes. In Kõo, the VSSF beds emitted more nitrous oxide than the HSSF bed (405–510 and 70–165 $\mu$g N2O-N m$^{-2}$ h$^{-1}$, respectively), however, the differences were not significant. In the Poriõõi riparian forest, the WET microsite emitted significantly more N2O than the EDGE and DRY microsites (average values 30,9 and 8 $\mu$g N2O-N m$^{-2}$ h$^{-1}$, respectively; Figure 1A). On the other hand, decreasing water table level in the WET microsite in summer 2002 caused significant increase of N2O emission. The CH4 emission showed great variability in both space and time. The average methane emission from the microsites in the Kodijärve HSSF CW and the Kõo hybrid CW ranged from 30 to 9715 and from 770 to 5540 $\mu$g CH4-C m$^{-2}$ h$^{-1}$ respectively (Figure 1B). These values are about 2 magnitudes higher than found in natural boreal wetlands (MacDonald et al., 1998), 2–3 times higher than reported on re-flooded fens (Augustin et al., 1996) or constructed cat-tail wetlands (Wild et al., 2002), but 2.5–3 times lower than from fertilised wet grasslands on peat soils in the Netherlands (Van den Pol-Van Dasselaar et al., 1999), and up to 4 times lower than from the floodplain wetlands (Boon et al., 1997). With respect to the differences in CH4 flux between the microsites, we found quite a similar pattern with nitrogen gas fluxes. According to the Wilcoxon Matched Pairs Test, significantly more methane...
was released from the microsites situated above the inflow pipes of both HSSF CWs (up to 9720 µg CH₄-C m⁻² h⁻¹ in Kodijärve and 4630–5540 µg CH₄-C m⁻² h⁻¹ in Koo) than from the microsites above the outlet pipes (30–125 µg CH₄-C m⁻² h⁻¹; Figure 1B). This is consistent with the significant rank correlation between the water table depth and the CH₄ flux (Spearman R = -0.37). Likewise, this relationship has on many occasions been mentioned in other studies on wetlands (Boon et al., 1997). In the riparian alder stand, CH₄ flux was significantly lower than from the VSSF beds and the inflow microsites of HSSF CWs, varying from 14 to 144 µg CH₄-C m⁻² h⁻¹. The WET microsite showed significantly higher CH₄ emission values than the EDGE and DRY sites (Figure 1B).

In comparison with other gases measured, the CO₂ flux from soils showed the lowest spatial variation. Slightly higher CO₂ release was found from the microsites in the VSSF beds and above the inflow pipes of HSSF CWs (140–290 and 61–130 mg CO₂-C m⁻² h⁻¹, respectively), however, these differences were not significant (Figure 1C). In CWs, clear relation was observed between the BOD₇ value of wastewater and the average CO₂ release from the filter material. In both HSSF and VSSF beds of CWs, fluxes of measured gases were significantly positively correlated (Spearman R values ranged from 0.38 to 0.58 in Kodijärve, 0.45 to 0.61 in the VSSF beds in Koo, and from 0.20 to 0.31 in HSSF beds in Koo), whereas within the riparian alder stand no significant rank correlation between gas emissions was found (Spearman R = 0.05–0.09). Probably, the last finding is related to relatively high carbon storage in this riparian soil (4–5.3%; Mander et al., 1997). In filter beds of CWs, carbon can become limited due to intensive mineralization which reflects in correlation between the gaseous N and C fluxes. Similar trends have been reported by Paludan and Blicher-Mathiesen (1996) for a Danish freshwater wetland where high NO₃ loading results in an accelerated loss of gaseous C.

Temporal variation of gas emissions

According to the Duncan test, a significantly higher release of all gases from CWs was observed during the warmer period (Figure 2A–C), although the N₂O flux showed no significant correlation with soil and air temperature.

In the microsites above HSSF inflow in both Kodijärve and Koo, the time-dependence of CH₄ emission was extremely remarkable. It resulted in significant differences in average values of CH₄ fluxes from both HSSF CW in Kodijärve and hybrid CW in Koo in summer (5000–21900 and 1700–14400 µg CH₄-C m⁻² h⁻¹ in Kodijärve and Koo, respectively) and winter time (24–300 and 16–2000 µg CH₄-C m⁻² h⁻¹, respectively; Figure 2B). The very cold winter of 2002/2003 with air temperature from −15 to −25°C for almost two months apparently influenced both water purification efficiency and gas emissions. As with purification performance, the gaseous emission in spring and early summer was significantly lower than in autumn. In the riparian grey alder stand only the CO₂ emission varied in accordance to the variations of water and air temperature (Figure 2A–C). The average CO₂ emission varied from 13.6 ± 11.3 mg CO₂-C m⁻² h⁻¹ in January to 187.8 ± 56.3 mg CO₂-C m⁻² h⁻¹ in August. The emission of N₂O from the riparian zone showed highest values in January and March 2003 (up to 180 µg N₂O-N m⁻² h⁻¹ from the WET microsite) being relatively low during the rest of the study period (from −3.3 to 24 µg N₂O-N m⁻² h⁻¹; Figure 2A). Likewise, the results of some other investigations demonstrate that N₂O emission does not clearly depend on soil temperature, and the release of this gas from soil in cold periods can be as high or even higher in winter as in summer (Augustin et al., 1996; Fey et al., 1999). For instance, N₂O-N fluxes through the snowpacks in winter reached 112 µg N₂O-N m⁻² d⁻¹ (Brooks et al., 1997), which is comparable with the lower emission values from our study sites. In warm and
dry summer 2002, the N₂O emission from the riparian zone was significantly increasing with lowering water table level (Spearman R = 0.38). This effect has been in several studies on natural wetlands (Martikainen et al., 1993). The average CH₄ emission from the riparian alder stand varied from 0.1–29 to 1.2–265 µg CH₄·C m⁻²·h⁻¹ in winter and summer, respectively (Figure 2B). In our riparian study area, the snow-covered period emission of CH₄ is significantly smaller than reported by Wickland et al. (1999) for subalpine wetland sites of Rocky Mountains (23–73% of the annual fluxes).

In our study, the CO₂ emission is not connected with fluxes related to plant photosynthesis. Therefore, only data for cold periods are considerable as losses to the atmosphere. For calculating the net ecosystem CO₂ exchange, more advanced measurement technique is required. For instance, the eddy covariation technique allows to analyse full C balance in ecosystems (Shurpali et al., 1993). However, some studies on C sequestration in wetlands and forest ecosystems (Butnor et al., 2003) allow to estimate that about 50% of CO₂ released during the soil respiration in vegetation period, cycles back to the atmosphere. It is important to take it into consideration when calculating the GWP of CWs and riparian buffer ecosystems.

**Cumulated flux of greenhouse gases**

The cumulated emission of all studied gases from CWs varied from 16.3 to 21.9, from 230 to 295 and from 9100 to 9700 kg ha⁻¹·yr⁻¹ for N₂O-N, CH₄-C and CO₂-C, respectively. The emission level in Köö always exceeded the corresponding values in Kodijärve, which is probably due to the relatively high loading of the vertical flow system (only two beds of 64 m² for about 300 PE). In Kodijärve the nominal loading is only 20–40 PE per 312.5 ha. When properly functioning, however, the vertical flow system can have a relatively small area, although this seems to enhance N₂O emission. Regarding CH₄ flux, it is crucial to avoid clogging both vertical flow and horizontal flow filters: this might help in the case of a higher N₂ flux and correspondingly lower N₂O flux; however, it significantly increases methane emissions. Sometimes such clogging took place in both CWs studied, which probably led to high CH₄ emission values (Figure 1B).

The GWP of studied systems were calculated converting the fluxes of N₂O and CH₄ into CO₂ equivalents (eq; IPCC, 2001). In Kodijärve, the average N₂O flux from both beds was quite similar: 3.85 ± 7.10 t CO₂ eq ha⁻¹·a⁻¹ in the right bed and 3.85 ± 3.85 t CO₂ eq ha⁻¹·a⁻¹ in the left bed. Methane flux rates, however, showed significant differences, ranging from 0.69 ± 2.05 t CO₂ eq ha⁻¹·a⁻¹ in the right bed to 12.4 ± 26.3 t CO₂ eq ha⁻¹·a⁻¹ in the left bed. In Köö, the highest GWP of nitrous oxide was found in the vertical flow beds (12.4 ± 19.5 t CO₂ eq ha⁻¹·yr⁻¹), while the horizontal flow bed showed a high methane flux (9.13 ± 17.9 t CO₂ eq ha⁻¹·yr⁻¹). Both Kodijärve HSSF CW and Köö hybrid CW emit remarkable amounts of CO₂-C, N₂O-N and CH₄-C: 6.3 ± 6.4, 4.8 ± 9.8 and 6.8 ± 16.2 t CO₂ eq ha⁻¹·a⁻¹ in Kodijärve, and 6.8 ± 20.2, 6.5 ± 13.0 and 5.3 ± 24.7 t CO₂ eq ha⁻¹·a⁻¹ in Köö, respectively (Figure 3). The cumulated emission of N₂O and CH₄ in riparian alder forest in Porijögi was significantly lower than from the CWs (0.4 ± 1.0 and 0.1 ± 0.30 t CO₂ eq ha⁻¹·a⁻¹, respectively), whereas the CO₂-C flux was remarkable (3.5 ± 3.7 t ha⁻¹·a⁻¹).

**Figure 2** Temporal variation of emission rates of nitrous oxide (A), methane (B), and carbon dioxide (mean ± SD) from the Kodijärve HSSF CW, Köö hybrid wetland system and the Porijögi riparian grey alder stand averaged over all sampling sites. For better visualization, polynomial curves are added. Hidden values in part B: 1: 21890 ± 43570; 2: 18110; 3: 27425; 4: 14020 ± 17920; 5: 1030; 6: 14410 ± 14290; 7: 17570 (µg CH₄·C·m⁻²·h⁻¹)
When comparing the greenhouse potential of CH$_4$ and N$_2$O over a long time scale (100–500 years), one can speculate that due to the short adjustment time for CH$_4$ in the atmosphere (8.4 years; IPCC, 2001), the radiative forcing of CH$_4$ will fall relative to CO$_2$ (Whiting and Chanton, 2001). N$_2$O with its atmospheric lifespan of about 120 years and GWP value of 296 has, however, less expectable impact. Therefore, further investigations should concentrate on the factors that regulate N$_2$O and N$_2$ emission rates from constructed wetlands.

**Conclusions**

Gaseous emissions from constructed wetlands showed significantly higher values than those from riparian buffer zones. In CWs we found a remarkable variability in the average emission rates of N$_2$O-N, CH$_4$-C and CO$_2$-C ranging from 1 to 2600 μg m$^{-2}$h$^{-1}$, −1.7 to 87200 μg m$^{-2}$h$^{-1}$ and −6.1 to 1050 mg m$^{-2}$h$^{-1}$, respectively. In the riparian grey alder forest these values were −3.3 to 190, −5.9 to 805 and −3.9 to 290 mg% m$^{-2}$h$^{-1}$, respectively. Release of all gases studied was significantly higher during the warmer period, however there was no significant correlation found between the N$_2$O flux and soil/water temperature. Similar to the purification performance, gaseous emissions in spring and early summer were significantly lower than in autumn. The most intensive flux of N$_2$O and CH$_4$ was observed in chambers installed above the inflow pipes of horizontal flow beds. The vertical flow wetland did emit significantly more N$_2$O than the horizontal flow beds. Although the emission of N$_2$O and CH$_4$ from constructed wetlands was found to be relatively high, their global influence is not significant. Even if all the global domestic wastewater were treated by wetlands, their share in the trace gas emission budget would be less than 1%.

**Acknowledgements**

This study was supported by EU 5 FP RTD project EVK1-2000-00728 “PRocess Based Integrated Management of Constructed and Riverine Wetlands for Optimal Control of Wastewater at Catchment ScalE” (PRIMROSE), the Estonian Science Foundation project No. 5247, and the Target Funding Project No. 0182534s03 of the Ministry of Education and Science, Estonia.
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