

The quest for sustainable nitrogen removal technologies

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Abstract In this paper the sustainability of current available and future nitrogen removal systems has been investigated. For the assessment of the sustainability six indicators were used; sludge production; energy consumption, resource recovery; area requirement and N_2O -emission. For the evaluation of the position of the individual nitrogen removal systems in the anthropogenic nitrogen cycle a broad outline for a life-cycle analysis has been presented.

Keywords Algal ponds; Anammox; constructed wetlands; denitrification; duckweed ponds; life-cycle analysis (LCA); nitrification; nitrogen cycle; resource recovery; sustainable processes; wastewater treatment

Introduction

For human life and health a diet with sufficient protein is essential. This results in a central position of man in the anthropogenic nitrogen cycle (Figure 1). The supply of protein food for the global population by agriculture is nowadays largely dependent on the use of synthetic nitrogen fertiliser produced from atmospheric N_2 by the Haber-Bosch process. In the last century the world's annual industrial output of nitrogenous fertiliser increased from 10 Mt N in 1960 to about 90 Mt N in 1998 (Figure 2). The global estimate for biological nitrogen fixation is in the range of 200–240 Mt N which shows that the anthropogenic mass flows for nitrogen have a major impact on the global nitrogen cycle (Gijzen and Mulder, 2001). However, the consumption of proteins will ultimately result in the discharge of the protein nitrogen in wastewater (Figure 1).

In view of the substantial contribution of the inorganic nitrogen in wastewater in the global nitrogen balance it is relevant to consider the sustainability of the current available nitrogen removal and cycling processes. The processes and technologies that will be considered in this paper are physical–chemical processes, conventional and advanced nitrification and denitrification in activated sludge systems, algal ponds, duckweed ponds and constructed wetlands. This paper presents further a framework to assess the sustainability of the individual processes and technologies. The process properties and criteria which have been evaluated are energy consumption in relation to the total nitrogen cycle, area requirement, process stability, sludge production, global or regional applicability, N_2O emission and resource recovery. Further, the aspect of dilution of sewage in the widely applied flush toilet will be discussed.

Indicators for sustainable nitrogen removal

For the assessment of the sustainability of wastewater treatment systems for N-removal in this study the following indicators have been used: sludge production; energy consumption; resource recovery; area requirement and emission of nitrous oxide (N_2O). In the literature there is general agreement on the relevance of minimising sludge production and maximising resource recovery for sustainability of treatment systems (Henze, 1997; Roeleveld *et al.*, 1997; Van der Graaf *et al.*, 1997). However with respect to energy consumption some authors conclude that the contribution of wastewater treatment in the total energy consumption is relatively low and therefore minimisation of the energy demand was

considered to be less relevant (Roeleveld *et al.*, 1997). However in this study the energy consumption for nitrogen removal is compared with the energy input in the total nitrogen cycle. For the assessment of the environmental impact of the alternative nitrogen removal processes a life-cycle analysis (LCA) has been made for the anthropogenic N-cycle. When the sustainability of total nitrogen cycle is discussed the aspect of dilution will be included.

Anthropogenic nitrogen balance

For a concise life-cycle analysis of the anthropogenic use of reactive nitrogen, the input and ultimate human output of nitrogen have been compared. At the end of the twentieth century the global annual input of nitrogen fertiliser in the human food chain was about 15 kg N per capita (Figure 3). A fraction of this nitrogen will be incorporated in vegetable or animal protein. The amount of protein in the human diet varies world-wide from 20 to more than 100 g protein per head daily. After human consumption ultimately a large fraction of the protein nitrogen will be excreted. Based on a nitrogen content in protein of 6.25 the daily human discharge is estimated at 5 to 16 g nitrogen per head per day. This is in agreement with reported typical values for human nitrogen excretion (Table 1).

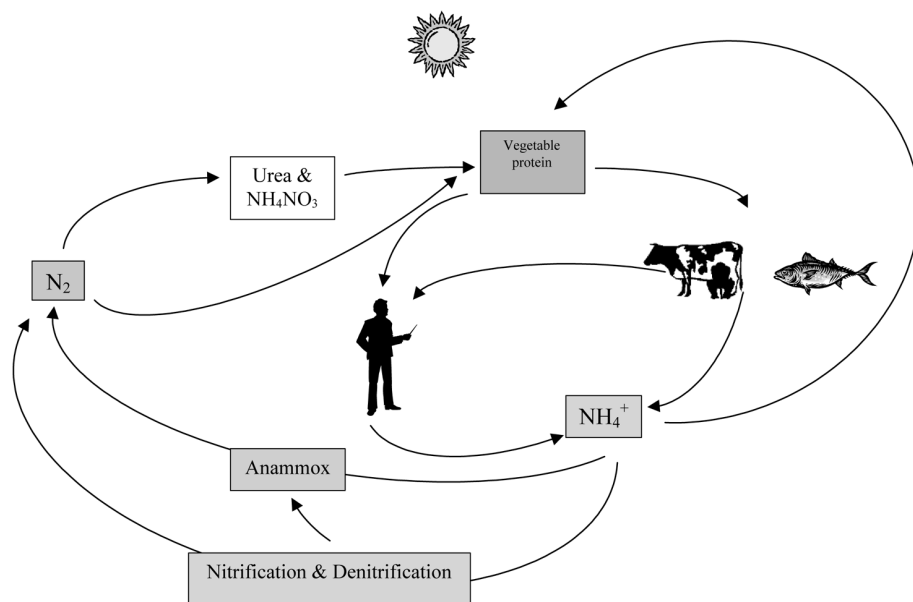


Figure 1 The anthropogenic nitrogen cycle

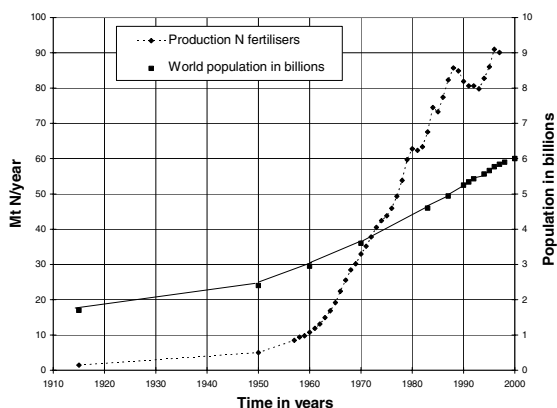


Figure 2 Global rise in population and production of nitrogen fertiliser (data FAO, 1966–1998)

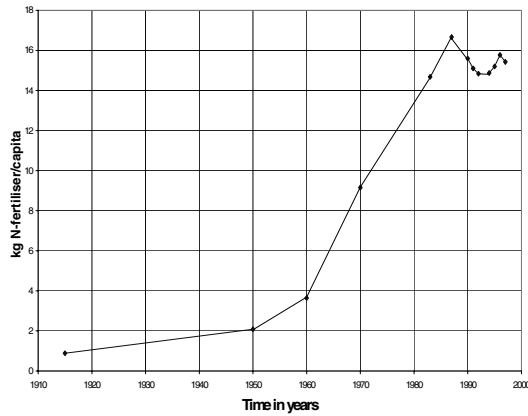


Figure 3 Development in the global annual production of nitrogen fertiliser per capita

Based on an average excretion of 13 g N per capita per day the annual excretion is 4.75 kg N per capita. Comparison of the global averages for input and output of N in the human food chain show that about 30% fertiliser nitrogen ends up in wastewater (Figure 4). However for Norway and The Netherlands the balance of fertiliser nitrogen input and human output through wastewater differ considerably from the global average (Figure 4). This confirms the presence of regional imbalances (Laegreid *et al.*, 1999).

In countries with intensive agriculture and factory farming (Norway and The Netherlands) only about 18% of the fertiliser nitrogen will end up in the wastewater. This means that in these European countries in theory with full nitrogen recovery from wastewater the agricultural demand for N-fertiliser can be met for only 18%. Due to the input of other sources such as imported cattle feed, wet and dry deposition and biological

Table 1 Typical values human nitrogen excretion

Faeces (g N/Capita.d)	Urine (g N/Capita.d)	Total (g N/Capita.d)	Reference
1.8–4.9	7.5–13.3	9.3–18.2	Gootaas, 1956
1.5	12.2	13.7	Pöpel, 1993
–	9.2–13.8	–	Larsen and Guyer, 1996

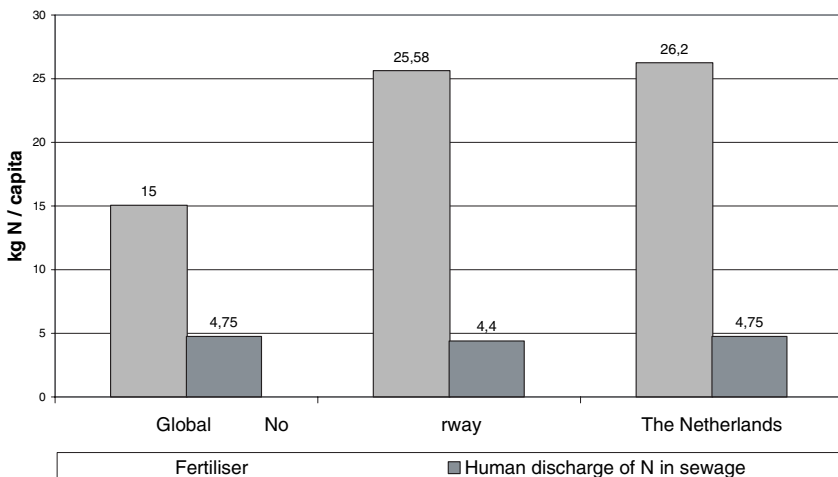


Figure 4 Comparison of the annual balance of N-fertiliser use and human N-discharge on global scale and on national scale in Norway (Bleken and Bakken, 1997) and The Netherlands (RIVM, 1991)

fixation, the contribution of anthropogenic nitrogen output via sewage in the total N-input is actually only about 10% (Bleken and Bakken, 1997). Measures aimed at an increase of the efficiency in the nitrogen cycle, such as the development of slow release fertilisers and improving the conversion efficiency in cattle feed are therefore considered to be more effective compared with resource recovery from sewage (Bleken and Bakken, 1997). On the other hand there will be regions with insufficient N-input where the contribution of N-recovery from sewage can be a relevant factor. This is in agreement with the suggestion of Larsen and Guyer (1996) to apply separate management of anthropogenic nutrient solutions in nutrient demanding nations.

Survey of nitrogen removal systems for wastewater

Wastewater concentration as factor in the selection of an optimal N-removal system

For the removal of ammonium from wastewater a wide variety of biological and physicochemical removal systems are available (Henze *et al.*, 1996; Priestley *et al.*, 1995). For a specific application the available alternatives will be evaluated on cost aspects, chemical and energy requirements, operational experience and process reliability. The selection of the most optimal alternative is generally based on cost-effectiveness. However in practice the selection of either a biological or a physicochemical method is determined by the nitrogen concentration of the wastewater. Three concentration ranges can be distinguished:

1. Diluted wastewater with an ammonium concentration $< 0.1 \text{ kg N/m}^3$. In this range biological N-removal is the preferred process based on cost-effectiveness. Domestic wastewater is within this range.
2. Concentrated wastewater with ammonium concentrations in the range $0.1\text{--}5 \text{ kg N/m}^3$. A typical example is sludge liquor for which after extensive investigations biological treatment was preferred (Janus *et al.*, 1997). Although ammonia stripping and producing MgNH_4PO_4 were identified as interesting alternatives for resource recovery these options were not cost-effective (Priestley *et al.*, 1995; Janus *et al.*, 1997).
3. Concentrated wastewater with ammonium concentrations $> 5 \text{ kg N/m}^3$. In this range physicochemical methods are technically and economically feasible. A successful example is the steam stripping of a wastewater with an ammonium concentration of 1.5% followed by ammonia recovery which has been in operation on industrial scale since 1985 (Harmsen *et al.*, 1986).

The concentration of wastewater is generally $< 2 \text{ kg N/m}^3$ thus biological treatment systems are preferred.

Survey of biological N-removal systems

For the biological N-removal systems which are investigated in this study the typical values of specific operational parameters are summarized in Table 2. The following N-removal systems are considered:

- Activated sludge with conventional nitrification and denitrification. Around the world the activated sludge system with nitrification and denitrification is the most widely used system for N-removal with many design variations (Henze *et al.*, 1996). In the nitrification process ammonium is via nitrite converted into nitrate: $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$. According to this reaction the oxidation of 1 kg N requires 4.57 kg O_2 . For denitrification the required COD/N ratio varies from 3–6.
- Activated sludge with nitrification denitrification via nitrite. In this process ammonium is oxidised into nitrite: $2\text{NH}_4^+ + 3\text{O}_2 \rightarrow 2\text{NO}_2^- + 4\text{H}^+ + 2\text{H}_2\text{O}$. The oxidation of 1 kg N requires 3.42 kg O_2 . Under anaerobic conditions nitrite is reduced into nitrogen gas and the required COD/N ratio is 2–4.
- Activated sludge with autotrophic N-removal. Recently the Anammox process in which

ammonium is oxidised under anaerobic conditions was discovered by serendipity (Mulder *et al.*, 1995). This process can be considered as an advanced biological nitrogen removal process in which nitrification and denitrification are integrated. Initially it was unknown whether nitrite or nitrate was used as electron donor however later it was found that in the Anammox process ammonium and nitrite are reacting and release nitrogen gas into the N-cycle (Strous, 2000). First ammonium must be oxidised to nitrite and then with Anammox the overall reaction of the autotrophic nitrogen removal process is: $4\text{NH}_4^+ + 3\text{O}_2 \rightarrow 2\text{N}_2$. According to this reaction the removal of 1 kg N requires 1.71 kg O_2 .

- Algal ponds. In algal ponds ammonia is assimilated into algal biomass according to the equation: $\text{NH}_3 + 5\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_5\text{H}_7\text{O}_2\text{N} + 5\text{O}_2$. The energy use in the algal pond is required for mixing and pumping. The highest value of the N-load is corresponding with the lowest efficiency.
- Duckweed ponds. From the applied N-load 41–68% is assimilated in duckweed (Alaerts *et al.*, 1996).
- Constructed wetlands. In constructed wetlands biomass is not recovered. The highest value of the N-load corresponds with the lowest removal efficiency.

Table 2 Typical values of specific operational parameters of biological N-removal systems

N-removal system	N-load (kg N/ ha.d)	Energy consumption (kWh/kg N)	COD/ N-ratio	Sludge/biomass production (kg d.w./kg N) ¹⁾	N _{total} removal efficiency (%)	Comments and references
Activated sludge conventional nitrification- denitrification	200–700 ²⁾	2.3 ³⁾	3–6	1–1.2	>75	Based on plants with typical load of 0,05–0,1 kg BOD/ kg d.w.d. Henze <i>et al.</i> , 1996
Activated sludge nitrification- denitrification via nitrite	200–700 ²⁾	1.7 ³⁾	2–4	0.8–0.9	>75	Abeling and Seyfried, 1992; Balmelle <i>et al.</i> , 1992
Activated sludge autotrophic N-removal	>200–700 ²⁾	0.9	0	<0.1	>75	Feasibility demonstrated for concentrated wastewater. Mulder, 1995; Seyfried <i>et al.</i> , 2002
Algal pond	15–30	0.1–1	6–7	10–15	23–78	El Hamouri <i>et al.</i> , 1995; Oswald, 1995; Polprasert, 1996
Duckweed pond	3–4	<0.1	28	20–26	74–77	System operated at 17–33°C. Alaerts <i>et al.</i> , 1996
Constructed wetland	3–26 ⁴⁾	<0.1	2–7	–	30–70	Hammer and Knight 1994; Haberl, 1995; Wittgren and Tobiasson, 1995; Meuleman, 1999

1. d. w. = dry weight

2. Calculated based on a conservative value of the aeration tank depth of 2 m and surface area aeration tank is 25% of total plant area

3. The given values are energy required for aeration and are exclusive energy in COD used for denitrification. Aeration efficiency is 2 kg O_2 /kWh

4. An exceptional high load of 112 kg N/ha.d was reported by Van Oostrom (1995)

Assessment of the sustainability of N-removal systems

Energy use for N-fixation and N-removal

The energy use of the alternative N-removal processes has been compared with of the energy use for N-fertiliser production (Figure 5). In the Haber-Bosch process nitrogen fixation with natural gas proceeds according to the equation: $3\text{CH}_4 + 4\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{CO}_2 + 8\text{NH}_3$. For the currently applied N-fertiliser production processes the energy use is 44.5 MJ/kg N which can be reduced to 34.5 MJ/kg N in production plants where best available technology is applied (Laegreid *et al.*, 1999). The energy required for nitrification was calculated from the data given in Table 2. The energy used for denitrification was calculated from the required COD. When resource recovery is applied the production of N-fertiliser will require an equivalent reduced amount of energy. The obtained results show that for conventional nitrification-denitrification the energy consumption for N-removal is 42.2 MJ/kg N. This is nearly similar with the energy use for N-fertiliser production. The energy required in the autotrophic N-removal process is 3.1 MJ/kg N which is only 7% of the energy required in the conventional process. By application of resource recovery the situation becomes more favorable, however it must be considered that the recovery and processing of the nitrogen from urine will require energy.

Recovery of reactive nitrogen versus denitrification

From the biological N-removal systems only the algal and duckweed pond system apply resource recovery, by using the produced algae and duckweed respectively. In the activated sludge systems the ammonium nitrogen is recycled as nitrogen gas. Direct recovery of ammonium from human wastewater is only feasible when the flush toilet and the collection and transport system for urine are modified fundamentally (Stoner, 1977; Larsen and Guyer, 1996). For the assessment of the environmental advantage of the resource recovery for nitrogen the energy use for N-fertiliser production has been compared with the energy use of the alternative N-removal processes (Figure 5). The energy use of the autotrophic N-removal process and the 20% resource recovery will come on a similar level after addition of the energy used for recovery.

Sludge production

The autotrophic N-removal process has lowest sludge production (Table 2).

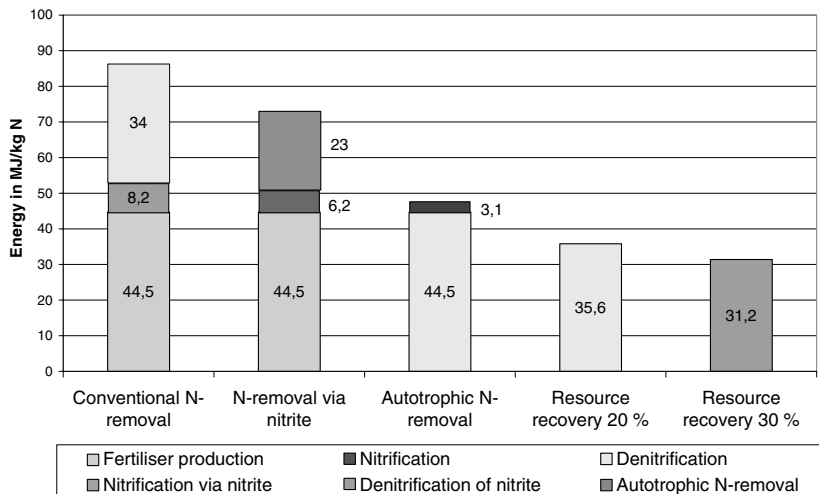


Figure 5 Comparison of the energy use for N-fertiliser production with the energy use of the alternative N-removal processes

Area requirement

For the individual N-removal systems the N-load, as measured for the area requirement, differs considerably (Table 2 and Figure 6). The wide range for the activated sludge systems is caused by differences in plant size. The average value of 450 kg N/ha.d is a factor 30–150 higher then for respectively the algal and duckweed pond systems. The higher loading rates are the result of faster biological processes which are possible due to the aeration. However because of this the energy use for the activated sludge systems is higher (Figure 6). In systems with the autotrophic N-removal process the energy use is reduced at similar N-load (Figure 6).

Emission of N₂O in the anthropogenic nitrogen cycle

At different stages of the anthropogenic nitrogen cycle emission of N₂O occurs. The global anthropogenic emission of N₂O is estimated at about 3 M ton N₂O-N/year (exclusive the contribution from combustion of fossil fuel, calculated from data in Pérez-Ramírez, 2002). Based on this figure it can be calculated that from the global annual production of nitrogen fertiliser of 90 Mton N about 0.3% will dissipate as N₂O. This value is lower then the emission of 0.5–2% given by Smil (2001). It is reported (Pérez-Ramírez, 2002) that this emission largely occurs in agriculture (50%), fertiliser production (6%) and wastewater treatment (21%). The emission of N₂O in wastewater treatment is largely determined by operational conditions and under unfavourable conditions like high load and low COD/N

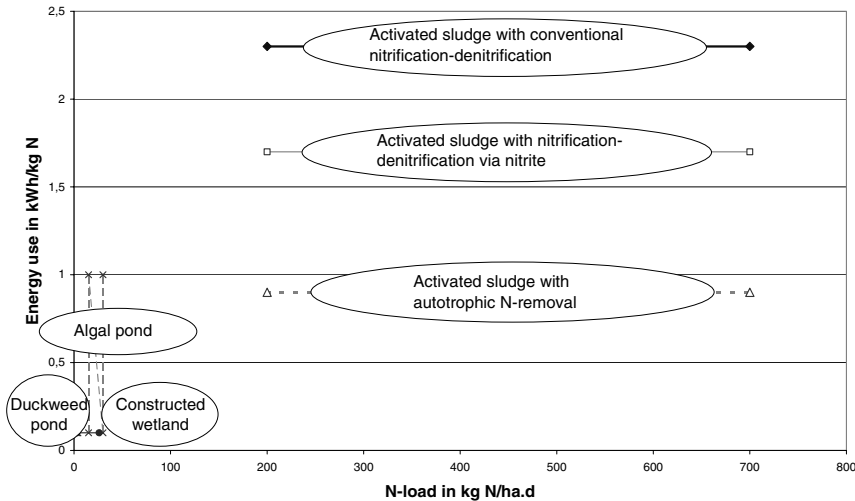


Figure 6 Comparison of energy consumption and area requirement of biological N-removal systems

Table 3 Matrix for the assessment of the sustainability of biological N-removal systems

N-removal system	Sustainability indicator				
	Sludge production	Energy consumption	Resource recovery	Area requirement	N ₂ O-emission
Activated sludge conventional nitrification-denitrification	--	---	-	+++	-
Activated sludge nitrification-denitrification via nitrite	-	--	-	+++	-
Activated sludge autotrophic N-removal	+	-	-	+++	-
Algal pond	+	-	+	--	-- ¹⁾
Duckweed pond	+	+	+	--	-- ¹⁾
Constructed wetland	+	+	-	--	-- ¹⁾

1. Based on prognosis because reliable data of N₂O emissions of these systems are not available

ratio's the emission of N_2 can contribute 10% in the total N-balance (Hanaki *et al.*, 1992). In high loaded constructed wetlands the N-load is frequently much higher than the nitrogen input in intensive agriculture which is around 100 kg N/ha.year. Therefore it is likely that a considerable part of the N-load is not taken up in plant production systems and more information is required with respect to the potential emission of nitrous oxide (Bouwman, 1998). Also the N-balances of algal and duckweed ponds must be checked for the emission of nitrous oxide.

Final evaluation

The sustainability matrix of the investigated N-removal systems show that the activated sludge system with autotrophic N-removal is the most sustainable process (Table 3). The next best is the duckweed pond system. The executed analysis of the nitrogen balances disclosed that on global scale there are regional imbalances with respect to N-input and output. In regions with serious shortages in N-input resource recovery must be developed and stimulated. On the other hand it is relevant to investigate expected future developments and to anticipate expected trends. With respect to the re-use of algae and duckweed for feed production the potential risk of accumulation of metals and organic micro-pollutants must be investigated.

Conclusions

- On a global scale regional conditions with respect to N-balance, climate, development differ considerably. As a result of this there is not one universal or paramount treatment system for N-removal from sewage. Regional conditions will determine which system is optimal under given conditions of climate, agricultural, environmental and economic development. This means that in a changing world the quest for sustainable N-removal techniques will continue.
- The process of autotrophic N-removal, which combines nitrification via nitrite and anaerobic ammonium oxidation is a very sustainable process because of: the minimal energy consumption, the absence of need for organic matter for denitrification, low sludge production and high N-load. However the autotrophic N-removal systems which are currently under development are applicable for ammonium concentrations of 100–500 mg N/l. For sustainable development it is relevant to investigate the feasibility of the autotrophic N-removal process for diluted wastewater.
- For high loaded constructed wetland systems, algal and duckweed ponds reliable data of the N-balance and the contribution of N_2O -emissions are not available. This information is required for a precise assessment of the sustainability of these systems.

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