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Influence of environmental conditions on the amount of N_2O released from activated sludge in a domestic waste water treatment plant

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Abstract. Waste water purification is characterized by intensive mineralization and nitrification processes. Because of the high O_2 demand, temporarily anaerobic conditions may be produced, and denitrification by nitrifying organisms as well as heterotropic denitrification may contribute to N_2O release. In situ measurements (1993–1994) suggest that N_2O is released from activated sludge in a domestic waste water treatment plant at an average rate of 1040 $\mu g\ m^{-2}\ h^{-1}$ with a range between zero and 6198 $\mu g\ m^{-2}\ h^{-1}$. The production of N_2O seems to be related to the concentration of NO_2^- and NO_3^- as well as to the pH. In the waste water about 75–200 $\mu g\ N_2O\ l^{-1}$ is dissolved. This N_2O is released after discharge into the receiving waters. The N_2O is produced essentially by nitrification rather than by heterotropic denitrification. On a long-term scale the increasing use of mechanical-biological waste water purification plants world-wide may add increasingly to the anthropogenic production of N_2O, although the present amount of N_2O produced is negligible compared to its global terrestrial production.
Key words. N_2O release; activated sludge; nitrification; denitrification; ozone destruction; greenhouse effect.

The release of N_2O from soils and water results from nitrification and denitrification processes[1–3]. The exact evaluation of N_2O production from soils and water is important, because nitrous oxide has been considered to be responsible for ozone destruction in the stratosphere and the greenhouse effect in the atmosphere[4,5]. Little is known about the contribution of aquatic ecosystems to the release of N_2O[6]. This is particularly true for anthropogenic waste water purification systems[3]. Sewage plants are characterized by intensive mineralization and nitrification processes which increase the demand for electron acceptors (O_2, nitrate, nitrite) considerably. Consequently N_2O production may be expected as a result of denitrification by nitrifiers[3,7] as well as by heterotrophic denitrification[3,8–10]. Denitrification (= nitrate/nitrite respiration) is an energy-conserving process leading to ATP formation, which occurs in aerobic bacteria under temporarily anaerobic conditions such as may occur in microsites in water and soils[8,9]. Particularly under conditions of reduced O_2 supply (intensive mineralization) and at relatively high concentrations of nitrite and nitrate, denitrification both by nitrifiers and by heterotrophic organisms may release relatively high amounts of N_2O. Waste water purification plants are rapidly expanding, particularly in the industrialized world. In Germany approximately 8800 plants are already in use[11]. The question arises to what extent and under what conditions N_2O is produced from such anthropogenic aquatic ecosystems.

Materials and methods

In situ N_2O emissions were quantified using open PVC chambers floating on an aerated fluid-bed tank (activated sludge) of the Giessen water purification plant, as described recently[3]. The waste water treatment plant of Giessen is a mechanical-biological activated sludge system with a pre-trickling filter to increase nitrification. The N_2O released from the aerated tank was collected in floating self-constructed open PVC covers (with 60 × 40 × 20 cm dimensions, 6 parallels). The atmosphere of the covers was transported continuously by a membrane pump (air stream of 90 $l.h^{-1}$) over silica gel and sodium hydroxide traps (to remove H_2O and CO_2, respectively) into columns filled with 2 mm pellets of 0.5 nm molecular sieve (Merck, Germany) to absorb N_2O. To obtain a homogeneous air stream, 2 uniformly perforated PVC plates (with holes, each of 0.8 cm diameter) were fixed perpendicularly to the air stream inside the chambers. At each sampling event the chambers were flushed for 2 h.

To compensate for the non-constant air fluxes caused by the waste water aeration device, the total air stream of 90 $l.h^{-1}$ was subdivided into a 20 $l.h^{-1}$ stream (for N_2O collection) and a 70 $l.h^{-1}$ bypass (to avoid an uncontrolled upfloating of the chambers). Both air streams were controlled by flow meters (Platon, Heidelberg, Germany). The nitrous oxide absorbed on the molecular sieve was desorbed in evacuated 1 l Erlenmeyer flasks containing 150 ml water[12]. A gas chromotograph equipped with an electron capture detector (ECD; Sigma 300, Perkin Elmer, Germany) was used to quantify N_2O[12]. Simultaneously with the N_2O measurements, the N_2O concentration of the ambient air used to flush the chambers, the water temperature, pO_2 (Oximeter 196, WTW, Weilheim, Germany), pH (pH-Meter 196, WTW, Weilheim, Germany), NO_3^--N[13] and NO_2^--N[14] as well as the BOD_5 (biological oxygen demand in 5 days; manometrically with the WTW BOD-analyzer Model 1002, Weilheim, Germany) were determined in samples taken close to the N_2O-measuring sites. For the quantification of N_2O dissolved in the waste water, samples of 1 liter were taken from the aeration tanks (at the waste water surface <5 cm, and at 50 and 100 cm depths; 6 replicates at each depth), and carried immediately in cooling boxes (ca. 4 °C) to the laboratory. Aliquots of 40 ml waste water were transferred to 100 ml Erlenmeyer flasks, which were closed airtight with a rubber septum seal. The samples were pasteurized in a waterbath (80 °C) over 70 min, firstly to stop further microbial N_2O formation, and secondly to drive out completely the N_2O dissolved in the waste water. The N_2O concentrations in 0.1 ml of the gas phase were quantified gas-chromatographically with an ECD as described[12], and calculated in ng N_2O ml^{-1} or kg N_2O per aeration tank. The multiple regression for evaluating parameters which influence the N_2O formation in waste water was carried out with the SPSS for Windows 5.0.

Results

In figure 1 the N_2O emissions throughout a period of 12 months are compared with the concentrations of nitrate

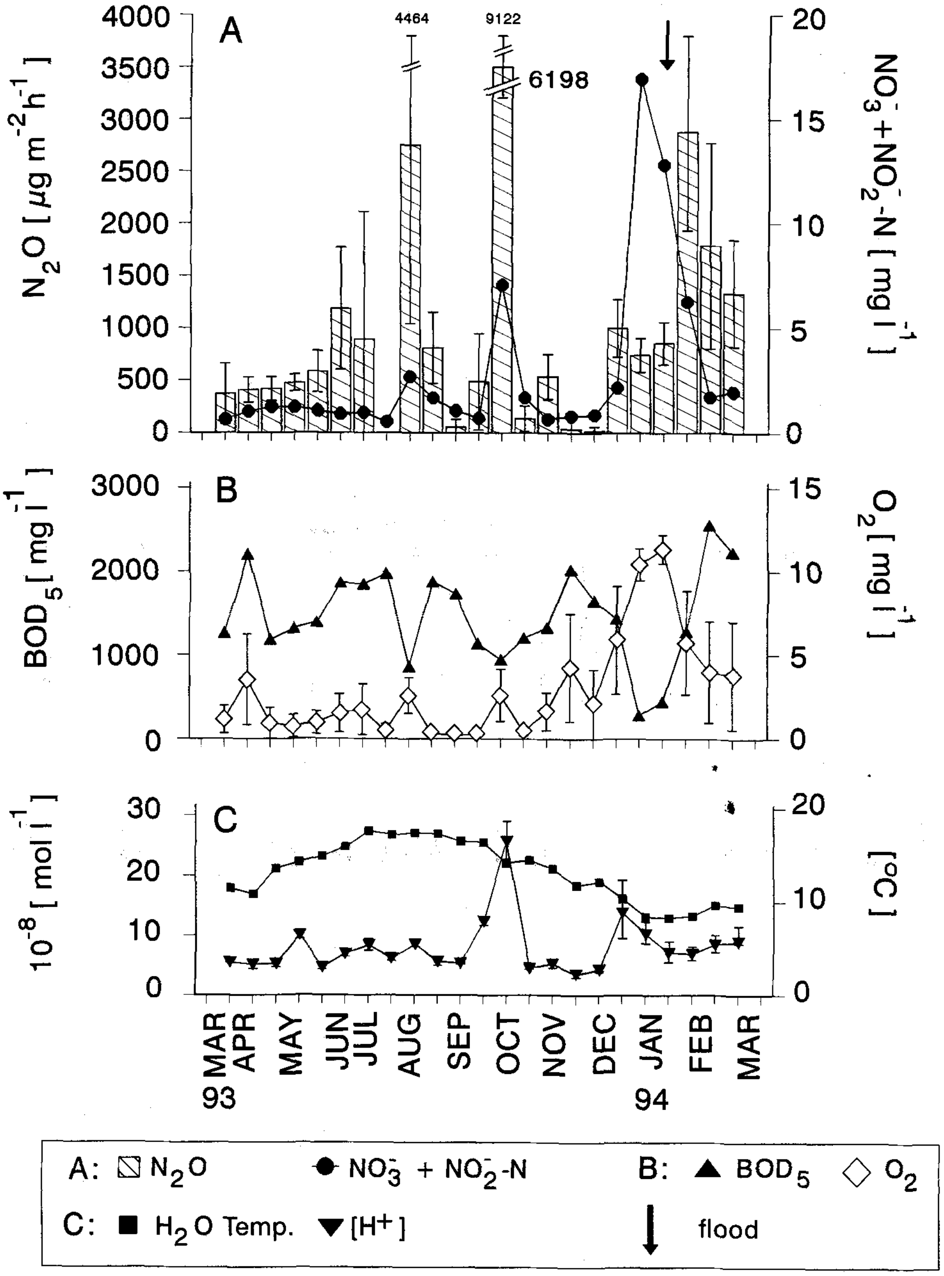

Figure 1. The annual in situ N_2O emission profile of an aeration tank in the waste water treatment plant of Giessen compared with *A* NO_3^--N + NO_2^--N concentration, *B* BOD_5, pO_2 and *C* temperature and $[H^+]$.

Table. Multiple correlation coefficients between the N_2O emissions and various physico-chemical properties of the tank throughout a 12 month period.

	NO_3^--N	+ $[H^+]$	+ NO_2^--N	+ O_2	+ BOD_5	+ Temp.
r^2	0.08	0.62	0.82	0.83	0.90	0.91
* r^2	0.79	0.87	0.91	0.91	0.93	0.93

* Excluding January 1994 data.

and nitrite as well as with the pO_2, BOD_5, pH and temperature of the activated sludge. The average total amount of N_2O released during 1993–1994 was 1040 $\mu g\ m^{-2}\ h^{-1}$ with a range between 0 and 6198 $\mu g\ m^{-2}\ h^{-1}$. Rough calculations suggest that the aerated tank of the Giessen waste water plant releases about 2.4 ± 1.3 kg N_2O-N into the atmosphere per year. There is a clear relationship between the intensity of N_2O produced and the concentration of nitrate plus nitrite in the water. The highest N_2O emission occurs at high nitrate-plus-nitrite concentrations, together with temporarily increasing pO_2 and proton activity (mol $H^+\ l^{-1}$). This may be ascribed to a decrease in easily decomposable organic matter as reflected by a drop in BOD_5 (figure 1B). These data indicate that N_2O is produced essentially by nitrifiers' denitrification rather than by heterotropic denitrification. The temperature, on the other hand, has little effect on the rate of N_2O released (figure 1C).

In the table the multiple correlations evaluating the influence of each single parameter out of various physico-chemical properties of the water on the N_2O emissions throughout the whole period are given. Correlations are given including and excluding the measurements of January 1994, when there were heavy rains and a massive dilution of the waste water. If the measurements of January 1994 are excluded, the multiple correlation (r^2) between N_2O release and the various parameters increased with the first 3 water properties considered (nitrate concentration, pH and amount of nitrite), but remains nearly unaffected if pO_2, BOD_5 and temperature are included. The table confirms the conclusions drawn in figure 1.

In figure 2 the N_2O released from activated sludge at the surface is compared to the amounts of N_2O dissolved in the tank water at 0.05, 0.5 and 1.0 m, respectively. The following conclusions can be drawn. First, the concentration of the dissolved N_2O ranges from 75 to 200 $\mu g\ l^{-1}$ waste water. Second, as the result of diffusion the N_2O concentration in the water increases from a depth of 1 m to 0.05 m at the subsurface. However, there seems to be no significant relationship between the amount of N_2O freed at the water surface and the concentrations at various water depths in the aerobic sludge tank.

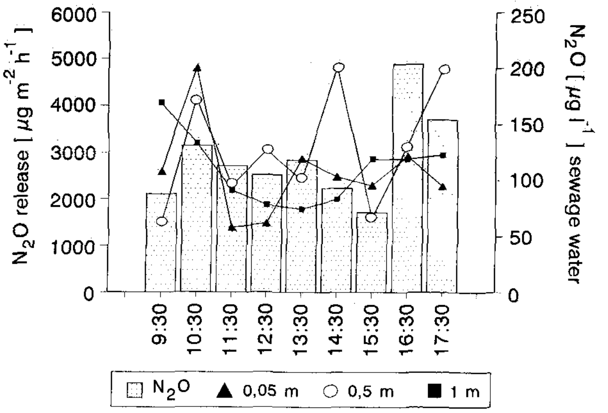

Figure 2. In situ N_2O emission during 25.1.1994 from aeration tank of the waste water treatment plant of Giessen compared with amounts of dissolved N_2O at 0.05, 0.5, and 1.0 meter depth.

Discussion

Domestic waste water purification plants with aerated sludge formation may contribute continuously to the release of N_2O into the atmosphere. If mechanical-biological waste water purification plants are installed world-wide in the next 10 to 30 years, this strategy will reduce nitrate pollution and eutrophication of our waters but may cause an increase in the global amount of atmospheric N_2O with all its consequences. At present the N_2O concentration of the atmosphere increases yearly by 0.2–0.3%[15,16]. An increase of 0.25% yearly corresponds to an additional amount of 3.5 Tg N_2O-N per year on a global scale. At present, the amount of N_2O released from terrestrial ecosystems (agricultural soils, grasslands and forests) on a global scale is estimated as ca. 5 Tg a^{-1} (ref. 17), and that from Germany as being in the range of 0.075 Tg a^{-1} (ref. 18). The waste water plant of Giessen is releasing about 0.001% N as N_2O from the total amount of N received (fig. 1). If this percentage is multiplied by the total amount of N accumulated in all German waste water treatment plants (0.4–0.5 Tg a^{-1})[19] approximately 4.5 Mg N_2O is being emitted yearly by our waste water purification systems. Compared to the estimates of release by the German or the global terrestrial ecosystems, this amount could be considered as insignificant. N_2O, however, is characterized by an atmospheric life time of 100 to 200 years and by a relative high potential for IR-adsorption[4,15,16]. In view of these features, this trace gas should not be underestimated as a potential global hazard on a long term scale, the more since local and global estimates of nitrous oxides from the various terrestrial ecosystems, oceans and combustions are scarce, and in fact essentially missing[20]. More in situ research is needed to quantify the release of N_2O from soils and aquatic systems. Finally, little is known about these ecosystems as sinks for nitrous oxide[4,17,18,20].

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