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Review

Nitrification and me – A subjective review

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ABSTRACT

Based on the subjective experience of the author it is discussed how the nitrification processes served as an important basis for the development of today's understanding and mathematical models for many wastewater treatment processes (activated sludge, biofilm reactors) and self-purification processes in rivers. Besides being an important process for the protection of receiving waters, nitrification served as a proxy for the understanding of the behavior of a narrowly defined group of microorganisms growing on known substrates under environmental conditions. Until the upcoming of readily available microbial genetic techniques, nitrification was the single most studied microbial process in environmental engineering.

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1. Introduction

Nitrification was the single most important process in our development of today's theoretical understanding of biological wastewater treatment processes. It is an important process in wastewater treatment plants however research on this process has two entirely different aspects:

1. In order to protect receiving waters we elaborate the engineering information required for establishing reliable nitrification performance of biological wastewater treatment systems and an understanding of nitrogen transformation in receiving waters. *Here the goal is making full scale use of the nitrification process in order to achieve improved water pollution control.*
2. We use the nitrification processes to follow the behavior and performance of specific, narrowly defined groups of microorganisms in an otherwise ill-defined mixed population. Alternatively we follow the transformation of a specific compound (ammonium) in a complex chemical matrix (wastewater). *Here nitrification is just a proxy for learning more about the detailed behavior of microorganisms and pollutants in general.*

In this report I am trying to analyze how these two aspects evolved over the last decades and specifically how they have affected my own research and perception of these aspects of engineering biological processes in the environment and in wastewater treatment systems.

Do not expect a careful, detailed, broad and well balanced review of nitrification. Rather accept this report to bear to a large extent the color of my subjective analysis and experience. I think that stepping back and trying to understand how science in this area evolved over the decades may teach us how to proceed successfully into the future. If I can contribute to this end I have more than reached my goal.

2. Nitrification – catalyst for the change of the paradigm

For many decades empirical ratios such as mean hydraulic residence time, volumetric loading, food to microorganism ratio (F/M), etc. served as the basis for sizing the reactors of biological treatment plants (trickling filters, activated sludge tanks). Beginning in the mid 1950s and heavily influenced by chemical engineers, sanitary engineers began to analyze their systems based on systems analytical methods, mass balances, transformation processes and transformation rates, kinetics and stoichiometry, reactor hydraulics etc. This change of the paradigm allowed or improved productive communication between engineers and natural scientists.

Nitrification as a transformation process which is easily identified and perfectly serves water pollution control was a very welcome example to demonstrate the advantages of the new tools. For over 30 years many new concepts were introduced and first demonstrated with the aid of nitrification.

Thus we ''owe'' a lot to this process which supported to a large extent the development of today's understanding and technological know how in biological wastewater treatment.

3. Nitrification before my time

''Before parameters such as BOD, COD, and organic carbon were used to judge the efficiency of a wastewater treatment system, a high degree of nitrification in a secondary effluent was assumed to be an indicator of a well-treated sewage'' (Gujer, 1974). Nitrification was initially not seen as a necessity from the point of view of the receiving water but was rather experienced as a cause of eutrophication and nuisance (Fair and Geyer, 1954). Obviously nitrification activity was here used in lieu of better alternatives to judge the progress of the treatment process and not in order to judge the load of reduced or oxidized nitrogen on receiving waters.

The introduction of the chemostat by Monod (1950) and Novick and Szilard (1950) laid ground for the understanding and mathematical modeling of continuous microbial culture systems. Garrett (1958) seems to be the first author who related microbial growth to the wasting rate of activated sludge; he realized the direct relationship between wasting rate and washout of a group of microorganisms. In his report he writes: ''*The monthly averages of the total nitrite-plus nitrate–nitrogen ranged from 0.2 to 0.7 ppm. This is not a significant amount of oxidized nitrogen, and is probably a result of wasting solids at a rate more rapid than the maximum rate of growth of the nitrifying organisms under the conditions in the aeration tanks.*''

A substantial step in understanding nitrification in the activated sludge process is due to a research group at the British Water Pollution Research Laboratory (Water Pollution Research, 1964). Here Downing et al. (1964) developed a comprehensive theoretical concept for the design of nitrifying activated sludge plants based on kinetic concepts and reactor technology. Wuhrmann (1964) substantiated this concept and introduced the German term ''Schlammalter'' (sludge age) in the context of washout of nitrifiers. Other authors report on more empiric studies of nitrification and did not yet integrate the upcoming theoretical approaches (see e.g. Balakrishnan and Eckenfelder, 1969).

By 1970 the use of the synonymous terms Solids Retention Time (SRT), Mean Cell Residence Time (MCRT) or Sludge Age (SA, its meaning was revised after its first definition based on incoming solids) in modeling and design of nitrifying activated sludge plants have been firmly established (see e.g. Lawrence and McCarty, 1970) and became part of modern sanitary engineering education. By 1975 the first fully dynamic models of nitrification became available (Lijklema, 1973 or Poduska and Andrews, 1975), with supporting data based on experimental work with artificial sewage.

Physical/chemical treatment options for nitrogen removal were studied and realized in a few full scale plants in the early 1970s. Breakpoint chlorination, ion-exchange (on clinoptilolite) and air-stripping of ammonia (NH_3) were considered to be competitive. The fact that processes, specific for ammonium removal, were studied extensively indicates that ammonium (and nitrate) started to be recognized as a problem in water pollution control.

In 1975 USEPA produced a then rather advanced *design manual for nitrogen control* which describes the state of the art at this time: Complex treatment schemes such as three sludge systems (high loaded activated sludge for COD removal, separate system for nitrification and a third system fed with methanol for denitrification) and rather involved physical–chemical processes are documented in this manual. The introduction to this manual states: ''*This manual could not have been produced five years ago* (1970) *because of the state of nitrogen control technology at that time.*'' It is interesting to follow up on this manual. USEPA (1993) published ''*an update and a revision of the original 1975 edition*''. It states: ''*Since the first manual's publication, the trend in nitrogen control technology applications has been overwhelmingly in favor of biological processes, with only a few instances in which physical/chemical processes have been implemented.*''

Thus when I started my career in process engineering of wastewater treatment in 1971 as a young PhD candidate, secured design information for biological nitrification was still lacking. It was however rapidly developed throughout the 1970s. My own first contribution was a steady state model for nitrification in the contact stabilization activated sludge process (Gujer and Jenkins, 1975).

4. Nitrification becomes a task for water pollution control

Discharge requirements for ammonium, nitrite and nitrate started to be enacted in the 1970s. In Switzerland the first wastewater treatment plant for which nitrification became required was the Werdhölzli plant of the city of Zurich, where less than 2 gNH_4–N m^{-3} in more than 80% of the 24 h flow proportional composite samples had to be reached above 10 °C. In 1973 the city of Zurich announced an international competition for the design of the extension of its wastewater treatment plant. From this competition with world wide participation it became clear that secured design information for many of the proposed process alternatives was lacking and full scale experience was still rather scarce (Wiesmann, 1982).

As a young sanitary engineer, I was assigned the task to develop the design criteria for the extension of the Werdhölzli plant with the aid of pilot plants that were available at the Swiss Federal Institute for Water Resources and Water Pollution Control (Eawag) directly on the main sewer feeding into the treatment plant. The challenge of this project was a major factor in the future development of my career.

5. Nitrification in the activated sludge process

5.1. *Sampling frequency makes the difference*

The performance of pilot plants as well as full scale plants is typically monitored based on 24 h composite samples. It is only recently that reliable on-line sensors became available which provide much higher time (and possibly space) resolution. In the 1970s, when automatic sampling was hardly available and all monitoring was based on wet-chemical

analysis, data with high temporal resolution were scarce and expensive to obtain.

In the context of the pilot tests for the extension of the wastewater treatment plant Werdhölzli in Zurich we performed a detailed and then very costly sampling procedure with 2 h composite samples in the influent and grab samples in the effluent of the biological reactor of a single CSTR type activated sludge process with partial nitrification (Fig. 1). The fact that we sampled the effluent of the biological reactor rather than the effluent of the plant (secondary clarifier), where concentration fluctuation would be hydraulically attenuated, proved to be very rewarding. The immediate breakthrough of ammonium upon the increased loading in the morning hours (urine) clearly revealed that nitrification is a highly dynamic phenomenon which cannot easily be described based on static models. These results lead me into dynamic simulation which remained a central topic of my research for years to come.

My first dynamic model (Gujer, 1977) concentrated on the prediction of the nitrification activity of activated sludge. Receiving waters were included with some simple complete mixing models and allowed to predict diurnal variation of ammonium (NH_4^+), ammonia (NH_3) and nitrate (NO_3^-) throughout the year.

In 1975 it was necessary to develop a FORTRAN code, specific for this case, and implement it on the high capacity main frame of the Swiss Federal Institute of Technology. Altogether this was an effort which required several weeks. Today, using advanced simulation tools, a similar model and program would be available within hours. In addition, systems analysis tools (sensitivity, parameter estimation, etc.) would be available to support and simplify model development and identification (Gujer, 2006).

5.2. *A "safety factor" controls design*

Lawrence and McCarty (1970) introduced the concept of a safety factor (SF) in the design of activated sludge plants which relates the solids retention time chosen for the design to the solids retention time at which complete failure of the plant (complete washout of the relevant organisms) would result. Later it was shown (USEPA, 1975) that it is reasonable to choose SF in excess of the ratio of the daily peak ammonium load divided by the daily average ammonium load (L_{max}/L_{avg}). This became an important relationship in many design procedures for nitrifying activated sludge systems. It allowed including many specific local conditions into the design: Diurnal load variations, design temperature, expected inhibition, sludge production, etc. For the design of the Werdhölzli treatment plant a combination of experimental and modeling results yielded Fig. 2. Here SF is defined as:

$$SF = \mu_{max} \cdot SRT$$

where μ_{max} is the maximum specific growth rate of ammonium oxidizers under design operating condition (temperature, dissolved oxygen, pH, inhibitors) which stands for the maximum activity of the nitrifying population. SRT is the expected aerobic solids retention time for the design loads of COD, TSS and P, it is related to the size of the nitrifier population in the system.

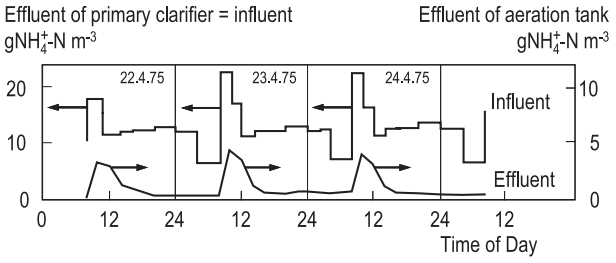

Fig. 1 – Diurnal variation of ammonium concentration in the influent and effluent of the aeration tank of a pilot plant operated for the design of the biological wastewater treatment plant Werdhölzli in Zurich. The plant was operated at a sludge age of 5.4 d, the samples were collected at temperatures around 13 °C, the aeration tank was completely mixed. Adapted from Gujer and Erni (1978).

5.3. *Long term and short term temperature effects are comparable*

An important aspect of long term dynamic simulation of activated sludge plants is the question how microorganisms respond to short term (diurnal variation) and long term (seasonal) temperature change. We answered this question with the aid of pilot plants that we operated at different temperatures close to the washout of nitrifying organisms. Nitrification efficiency was maintained at about 50%, excess sludge removal was increased or decreased based on daily analytical result. In addition the nitrification activity of biomass grown at different temperatures (6 and 14 °C) was evaluated after a rapid change of the temperature (hours). As indicated in Fig. 3, it turned out that the long term maximum growth rate and the short term activity of the biomass both increased by a factor of 0.11 $°C^{-1}$. In mathematical modeling this allows using just one temperature dependency for nitrifying biomass, independent of the time frame of the temperature change.

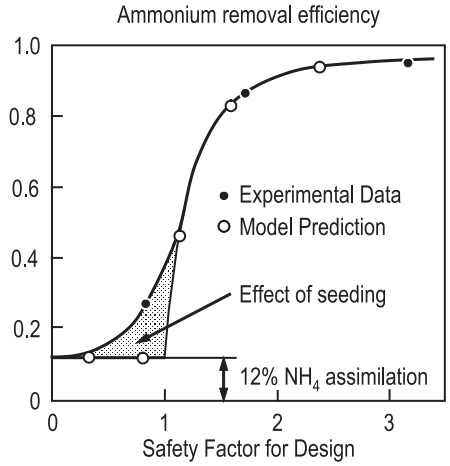

Fig. 2 – Nitrification efficiency as a function of the safety factor for design of the Werdhölzli treatment plant. Basis is a diurnal ammonium load variation by a factor of 2 (diurnal peak to average load). Developed for winter conditions, 8–12 °C. Adapted from Gujer (1977).

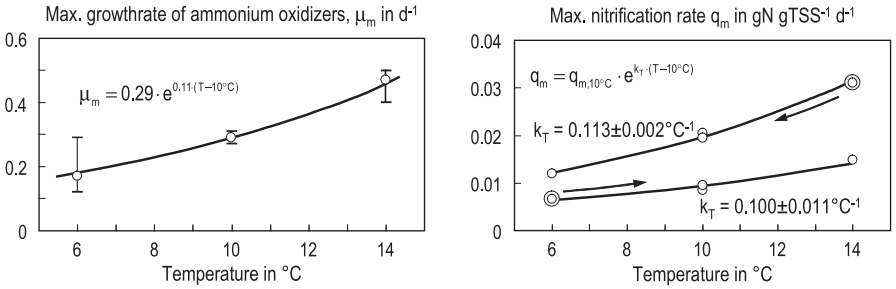

Fig. 3 – Long term (left) and short term (right) effects of temperature on ammonium oxidizing organisms. Growth rates are based on 12 weeks of operation of 3 pilot plants close to washout of the organisms at 6, 10 and 14 °C. Short term effects are based on batch results with activated sludge grown at 6 and 14 °C. Adapted from Gujer (1977).

5.4. *Inhibition of nitrification*

Early reports on nitrification in activated sludge processes typically included the remark that industrial wastewater may have inhibited nitrification if not fully then at least partially. Even though heavy metals and some organics are known to inhibit the growth of nitrifying organisms (Tomlinson et al., 1966), my personal experience (without scientific proof) deviates from the above remarks. This was the time when oxygen electrodes were not available and dynamic behavior of biological systems was poorly understood and resulted in poor operating strategies frequently far from ''steady state''. Thus frequent periods of lack of oxygen, poor control of SRT and time dependant ammonium loads may have been the dominant cause of reports on the inhibition of nitrification. Today, with more reliable control of oxygen concentration, reports on inhibition are less frequent. In addition raw wastewater in industrialized countries is under permanent control such that toxic compounds must not be expected with high frequency. Personally I have yet to find a case where an industrial effluent can be demonstrated to be the cause of reduced nitrification.

Gujer and Boller (1978) report on the effect of different *chemicals for the precipitation of phosphorus* in activated sludge plants (pre-precipitation and simultaneous precipitation) on nitrification. We found a reduced maximum growth rate of nitrifying organism when Ferrous Sulfate ($FeSO_4$) was used as a precipitant but we could not identify any mechanism which caused this apparent inhibition.

In addition we found a weak effect of *digester supernatant* on the maximum growth rate of ammonium oxidizing organisms. Digester supernatant is an important recycle stream which may contain reducing, inhibitory (sulfur) compounds when directed back to the wastewater treatment plant. We tested the effect of such recycling with a pilot plant which was operated close to washout of nitrifying organisms (see above). As indicated in Fig. 4 the effect of digester supernatant is only small but statistically significant. A typical NH_4-load in the supernatant is in the order of 10–20%, depending on the sludge thickening and dewatering processes applied.

5.5. *Process control*

Equipped with a calibrated and field tested dynamic model for nitrification in activated sludge systems Gujer and Erni (1978) could simulate the effect of hydraulic flow scheme, ammonium load balancing, limitation of nitrification by oxygen and some process control strategies. Given the process is supported by sufficient dissolved oxygen, ammonium load balancing was proven to be by far the most efficient means for improving nitrification performance. An example of such load balancing by digester supernatant is given in Fig. 5: Growing more nitrifiers during the night prepares the activated sludge to better deal with high loads during peak loading situations. Since digester supernatant is rich in ammonium (roughly 700 gN m^{-3}) it proves to be very efficient to store this liquid and recycle it in the best possible moment. Bringing it back to the treatment plant when it is generated (typically during working hours when raw sludge is fed to the digesters or when digested sludge is dewatered) would only add to the peak load and would thus bleed through the plant. In addition any inhibitory effects of digester supernatant (Fig. 4) would have fewer consequences during low load rather than high load periods.

Load balancing is an early version of what was later termed *waste design*, a term which stands for the generation of wastewater amenable to improved or optimal treatment (Larsen and Gujer, 2001).

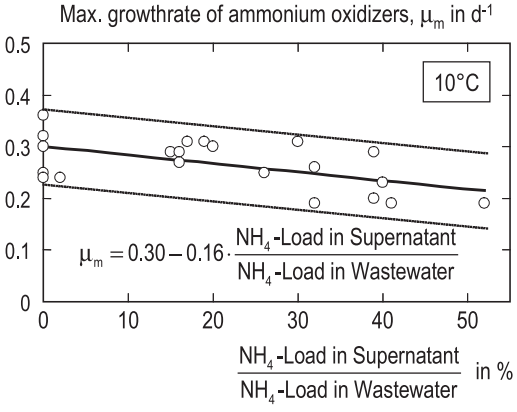

Fig. 4 – Effect of digester supernatant on maximum growth rate of ammonium oxidizing organisms. Each point is the weekly average growth rate of activated sludge operated close to washout. Ammonium is used as the tracer for an unknown possible toxic compound. Adapted from Gujer (1976a).

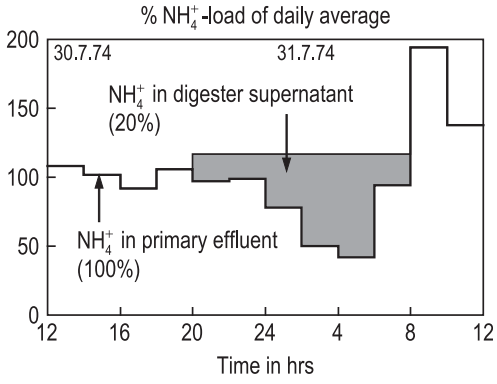

Fig. 5 – Balancing of ammonium load with digester supernatant in order to enhance the nitrifier population (Gujer and Erni, 1978).

Today the IWA Task Group on Benchmarking of Control Strategies for WWTPs (http://www.benchmarkwwtp.org/, see also Copp, 2002) provides a fully developed framework for testing alternative control strategies for nitrification/denitrification in an activated sludge plant. In the latest version of this framework load balancing is included in the defined options however the flow scheme itself cannot be optimized.

5.6. *Peak shaving*

Since nitrifying biological treatment must typically be designed for peak ammonium loads, it is advantageous trying to even out the ammonium load throughout the day not only by using ammonium-rich recycle streams from sludge handling but potentially directly at the source.

Urine separation toilets were introduced in Sweden in the early 1990s in order to recycle valuable nutrients in a concentrated separate stream (Kirchmann and Pettersson, 1995; Hanæus et al., 1997). The concept and the consequences of urine separation for improved water pollution control were introduced and discussed by Larsen and Gujer (1996). Rauch et al. (2003) suggest separating urine at the source, storing it and randomly discharging it to the sewer. This will result in an even ammonium load on the treatment plant (peak shaving) which will improve nitrification performance and could even enhance denitrification. Combined with a strategy to withhold urine during rain events, ammonium in combined sewer overflow (CSO) could be reduced to further enhance water pollution control. Such activities which optimize the composition of wastewater in view of efficient wastewater treatment are summarized today under the terms *waste design* and *source control* (Larsen and Gujer, 2001).

5.7. *Geography affects the performance of wastewater treatment*

The load variation in the influent to the treatment plant is the result of the convolution of time dependent input of pollutants into the sewer and the residence time distribution of the sewage in the sewer (Fig. 6). Whereas concentric catchments lead to large load variation, linear and very large catchments lead to load equalization. Since diurnal load variation controls to a large extent the nitrification performance of biological treatment processes, resulting load equalization in linear or large catchments is advantageous.

Fig. 7 summarizes the extreme 2 h ammonium load relative to the daily average from a variety of catchments. Since the safety factor (SF) for the design of nitrifying treatment plants is typically chosen in the order of the ratio of the maximal to average Load (L_{max}/L_{avg}) this figure provides important design information. The choice of SF according to Fig. 7 has the interesting and desired feature that SF and thus the solids retention time becomes larger the smaller the treatment plant and thus the less professional and more difficult the operation.

5.8. *Design concepts must be revisited*

Dominguez and Gujer (2006) discuss the evolution of the wastewater treatment plant Werdhölzli in the period of 1985–2003. The plant was initially designed for nitrification (see above) and included simultaneous precipitation of phosphorus. The design loads chosen exceeded observed loads by about 15%. The treatment concept relied on the idea that an old existing activated sludge plant could be used to pretreat about 50% of the primary effluent in order to facilitate nitrification in a new second stage activated sludge process.

Over the 18 years in question, the population of the city of Zurich decreased rather than increased by about 20%. Many large, wastewater producing industries (brewery, milk processing plant, slaughterhouse, etc.) left the city. Phosphate was banned in textile detergents which resulted in less sludge production from precipitation. Groundwater infiltration into the sewers was drastically reduced and drinking water consumption decreased by 33% which allowed reducing the maximum hydraulic load of the treatment plant and thus resulted in an increase of the allowable activated sludge concentration. The old activated sludge process was taken out of operation, pre-denitrification with 28% of the volume was introduced in the new plant without extending reactor volume. A second wastewater treatment plant of the city of Zurich was taken out of operation and the wastewater was fed into the Werdhölzli plant, this added an extra 20% to the load. Temporarily deicing fluids from Zurich airport were treated as well. And so on.

We realized from this analysis that a wastewater treatment plant is a ''living organism'' and will hardly ever be operated in the way and with the performance it was designed for. Over the short period of 18 years the boundary conditions as well as the flow scheme of the Werdhölzli plant changed dramatically. The future is difficult to predict and our design concepts should consider this uncertainty.

5.9. *Nitrification kinetics depends on many environmental factors*

Holienčin (1996) developed a kinetic model for the production of nitrite in the context of nitrification in the activated sludge process. Due to the many environmental factors involved, this model is complex and cannot be presented here. A summary

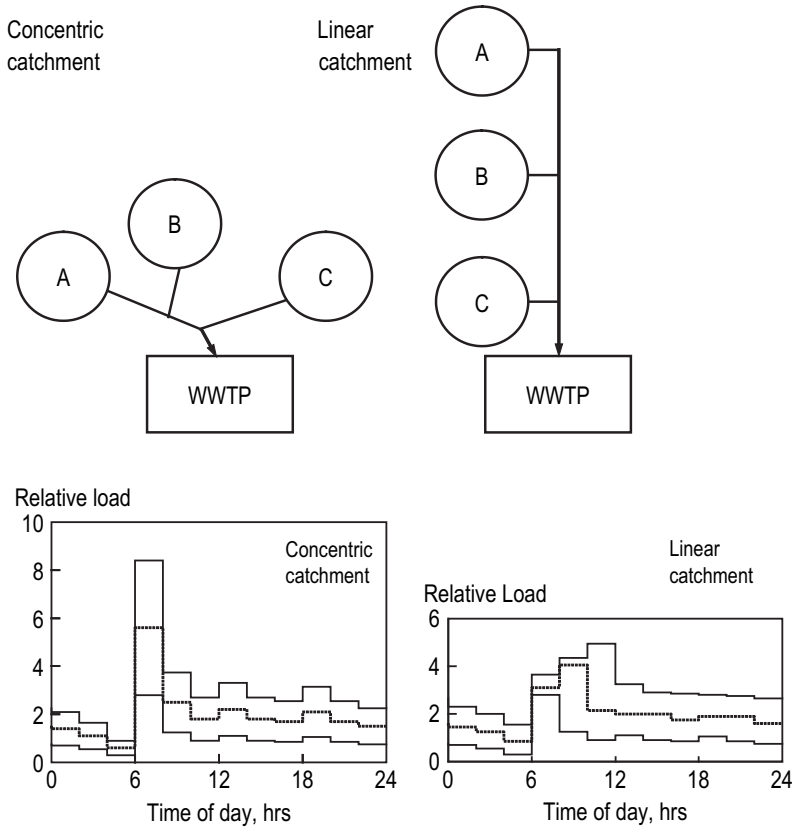

Fig. 6 – Concentric or linear arrangement of urban areas affects diurnal variation of pollutant loads in wastewater treatment plants.

of the trends is given in Tables 1 and 2. They relate to the following simple model for two step nitrification:

$$r = r_{max} \cdot \frac{S}{K_s + S}$$

with

r = rate of oxidation of ammonia or nitrite [gN m^{-3} d^{-1}]
r_{max} = maximum value of r under operating conditions
S = concentration of substrate (NH_3 or NO_2^-) [gN m^{-3}]
K_S = saturation coefficient for true substrate.

5.10. *Detailed understanding of ammonium oxidation requires enzyme kinetics*

Manser et al. (2006) analyzed decay processes of nitrifying bacteria under aerobic and anoxic conditions. They found large differences in apparent decay rates under aerobic conditions (large rates) and anoxic conditions (rates close to zero). However in order to interpret their batch results in detail, they had to introduce the dynamics of enzyme saturation of the organisms. Under aerobic conditions at 20 °C they found a decay rate of enzymatic activity of ammonium oxidation of $k_{decay} = 3\ d^{-1}$ and a regeneration of this activity in the presence of ammonium of $k_{synthesis} = 30\ d^{-1}$. Under anoxic conditions the decay of enzymatic activity was negligible.

Most of today's dynamic models for the activated sludge process do not include enzyme dynamics. For most practical purposes Manser et al. (2006) conclude that the approach chosen in ASM3 (Gujer et al., 1999; see below), which differentiates between biomass decay rates under aerobic and anoxic conditions, is sufficient.

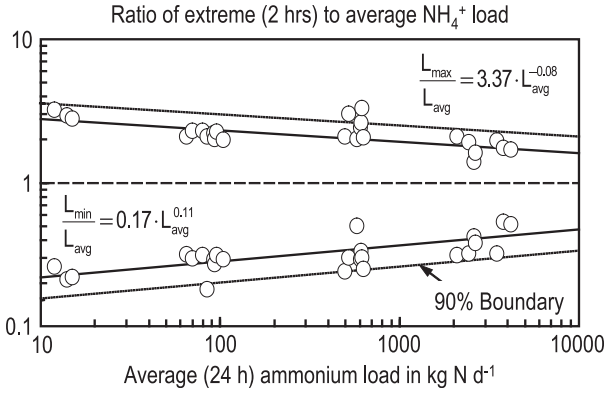

Fig. 7 – Extremes of diurnal ammonium load variation in the influent to wastewater treatment plants as a function of average load or size of the treatment plant. Assuming 10 gN cap^{-1} d^{-1} the X-coordinate covers the range of 1000–1,000,000 population equivalents. Adapted from Gujer and Erni (1978).

Table 1 – Effects of environmental conditions on max. activity (r_{max}) and saturation coefficient K_S of ammonium oxidation (nitritation).

Parameter	r_{max}	K_S	Remark
NH_3 (ammonia)	Yes	No	True substrate
NH_4^+ (ammonium)	No	No	In equilibrium with NH_3, depending on pH and temperature
HNO_2	Yes	No	Non-competitive inhibition
NO_2^- (nitrite)	No	No	In equilibrium with HNO_2, depending on pH and temperature
HNO_3	No	No	
NO_3^- (nitrate)	No	No	
pH value (H^+ activity)	Yes	Yes	pH range 6.2–8.0: non-competitive inhibition by H^+, K_S increases with increasing pH
Temperature	Yes	No	
O_2 (dissolved oxygen)	Yes	No	We do not have our own results for K_S
Alkalinity	Yes	No	Affects pH inside flocs (diffusion limitation)
Organic substrate	Yes	No	Indirect effect, reduced O_2 available inside flocs
Hydraulic retention time	Yes	No	Affects biomass concentration
Solids retention time	Yes	No	Activity decrease due to decay at elevated SRT

Adapted from Holienčin and Gujer (1996).

Table 2 – Effects of environmental conditions on max. activity (r_{max}) and saturation coefficient K_S of nitrite oxidation (nitratation).

Parameter	r_{max}	K_S	Remark
NO_2^- (Nitrite)	Yes	No	Most probably true substrate
HNO_2	Yes	No	Non-competitive inhibition
NO_3^- (Nitrate)	No	Yes	Competitive inhibition
HNO_3	Yes	No	Non-competitive inhibition
NH_3 (Ammonia)	Yes	No	Very weak dependency
NH_4^+ (Ammonium)	No	No	
pH value (H^+ activity)	Yes	No	pH range 6.2 to 8.0: Only weak at elevated pH values
Temperature	Yes	Yes	
O_2 (dissolved Oxygen)	Yes	Yes	We do not have our own results for K_S
Alkalinity	Yes	No	Weak indirect effect from nitritation due to pH change inside flocs
Organic Substrate	Yes	No	Indirect effect, reduced O_2 available inside flocs
Hydraulic retention time	Yes	No	Affects biomass concentration
Solids retention time	Yes	No	Activity decrease due to decay at elevated SRT

Adapted from Holienčin and Gujer (1996).

5.11. *Interaction of nitrification and denitrification may cause loss of nitrous oxide (N_2O)*

In the process of heterotrophic denitrification some N_2O is produced as an intermediary product. Since separate denitrification reactors are not aerated this N_2O is only stripped to a very small degree in a following nitrification reactor. More critical is the situation in plants operated with simultaneous or alternating nitrification/denitrification. These systems combine elevated nitrite and low oxygen concentrations with gas stripping, a situation which was identified as critical (von Schulthess et al., 1994).

Later von Schulthess and Gujer (1996) measured N_2O production in a full scale activated sludge process under different operating conditions. We concluded that not more than 0.072% of the incoming nitrogen is released to the atmosphere as N_2O if nitrification (2 $gO_2\,m^{-3}$) and denitrification (0 $gO_2\,m^{-3}$) are optimized separately. In a national balance, this would be a negligible amount.

However Poth and Focht (1985) demonstrated that *Nitrosomonas europaea* which is present in activated sludge, especially under ammonium-rich conditions (Manser et al., 2005a; Manser, 2005), is able to denitrify nitrite to N_2O under low oxygen, high nitrite conditions. Several researchers have demonstrated that this mechanism contributes substantial amounts of N_2O to off gas and dissolved nitrogen in effluents of biological treatment. Thus today's trend towards simultaneous nitrification/denitrification may start to emit large amounts of N_2O, a very undesirable greenhouse gas, even considered in the Kyoto agreement. N_2O emission from nutrient removal plants is presently under scrutiny by many researchers and may prove to be rather more complex than identified in the limited studies of a single PhD student.

6. Dynamic activated sludge models

A first generation of dynamic models for nitrification in the activated sludge process was developed in the 1970s (see above). An important input came from the research group around Gerrit v. R. Marais at the University of Cape Town (UCT). This group started to develop models with a broad scope, integrating degradation of soluble, colloidal and particulate organics, nitrification, denitrification as well as oxygen consumption and sludge production in cascades of mixed reactors, first for steady state (Marais and Ekama, 1976) and later for dynamic behavior (Dold et al., 1980).

In 1982 Poul Harremoës, then Vice-President of IAWPR, initiated the IAWPR Task Group on Mathematical Modeling for Design and Operation of Biological Wastewater Treatment. Based on the advanced work of the group from UCT this task group developed the family of activated sludge models known today as ASM1 to ASM3 (see Henze et al., 2000, for the documentation of the models and Gujer, 2006, for an appreciation of their development).

One of the major contributions of this task group was the so called *matrix notation* which allows communicating rather complicated integrated mathematical models in a well organized and condensed format which was first developed by Gujer (1985). Today it appears that this family of ASMs is broadly accepted as state of the art models for the activated sludge process. Initial acceptance of these models related to a large extent to the success of these models in predicting

nitrogen transformations (nitrification, denitrification). In the meantime these models (especially ASM2d) have reached a level of complexity which is difficult to handle routinely by consulting engineers. Their responsible application and adaptation is still the task of highly experienced engineers. But applied by specialists they truly help to improve plant design.

Calibration of ASMs is tedious and often done by ad hoc tuning procedures. Brun et al. (2002) developed a systematic approach which allows identifying the most important model parameters and their interdependencies. Such a procedure is however at this time not readily available for practical engineers; the resources of time, required software as well as the theoretical background for well founded interpretation of the results are barely available. Today such techniques are primarily applied in research and development environments. In addition it appears that many experimental results are heavily influenced by uncharacterized hydraulic deficiencies of reactors. Calibration concentrates however on the adaptation of the biokinetic models, thus, hydraulic deficiencies may be mimicked by adapted biological parameters, not exactly a productive procedure in dynamic modeling.

Definitely it was the positive experience with dynamic models of nitrification in activated sludge processes which provided ample motivation to step into the development of the more comprehensive and integrated models. Presently a further valuable contribution is developed by the IWA Task Group on Good Modeling Practice which is working on ''Guidelines for Use of Activated Sludge Models''. Whether this will facilitate and improve the application of the rather detailed and complex models remains to be seen.

7. Biofilm models

First models which explicitly considered diffusion of pollutants in the depth of biofilms appeared in the mid 1970s (Williamson and McCarty, 1976; Harremoës, 1976). The model by Williamson and McCarty was able to deal with electron acceptor as well as electron donor. These first models could not deal with the competition of different groups of microorganisms. Thus an *a priori* prediction of nitrification performance in the presence of organic substrates was not possible.

Whereas in suspended growth reactors the competition between different groups of organisms (say nitrifiers and heterotrophs) is rather easy to model and to understand, this competition becomes more involved when organisms grow attached inside a biofilm. What is the activity of organisms buried in the depth of a biofilm? How can slow growing autotrophic organisms be enriched when rapidly proliferating heterotrophic organisms grow close to the surface of a biofilm? Biofilm models must combine transformation and transport processes whereas suspended growth models are typically based on the assumption of complete mixing, which is a very simple description of complicated transport processes.

Mueller et al. (1978) provide an early report on the performance of a rotating biological contactor (RBC) with simultaneous degradation of BOD and nitrification (Fig. 8). Clearly heterotrophic activity is located in early, upstream reactors whereas nitrification sets in once soluble BOD is degraded. The distribution of the relative biomass depends on the composition of the external wastewater. Based on this observation Wanner and Gujer (1984) developed a steady state model which successfully described the competition between autotrophic and heterotrophic organisms within a biofilm. The model was qualitatively validated with the data of Mueller et al. (1978) and later expanded into a fully dynamic model describing species competition in biofilms (Wanner and Gujer, 1986). These models predict the distribution of different particulate fractions of biomass as well as pollutant concentrations over the entire biofilm (Fig. 9).

Fruhen et al. (1991) worked with a highly controlled system and obtained experimental evidence that this mixed culture biofilm model allows to describe the competition of nitrifiers and heterotrophic organisms in a biofilm rather well. Changes in the external substrate composition had dramatic effects on the nitrification performance of a biofilm and on species distribution within the biofilm.

An application of this model to a rotating biological contactor (RBC) is provided by Gujer and Boller (1990). It is based on a model similar to ASM1 but includes nitrite from nitrification. It is used to discuss the consequences of different operating strategies and possible problems of continuous operation.

The model is generally applicable for the description of competing microorganisms in fixed biomass (biofilms). It teaches us the controlling factors which affect the relative abundance of organisms competing for space and substrate within biofilms.

8. Experiments with biofilm systems

8.1. *Laboratory systems*

Siegrist and Gujer (1987) used a laboratory scale biofilm reactor to simulate a trickling filter. The process of nitrification which is heavily pH dependent was used to demonstrate mass transfer effects within biofilms. A closed chamber allowed exposing the biofilm to different atmospheres (O_2, N_2, CO_2) and together with the choice of alkalinity (buffer capacity, HCO_3^-) in the influent the drop of pH across the biofilm could be controlled. Model predictions closely matched biofilm behavior. We learnt how to combine diffusion, reaction and pH equilibrium models.

8.2. *Rotating biological contactors*

From our modeling efforts (see above) we derived that high nitrification rates in trickling filters or rotating biological contactors (RBC) could be achieved if heterotrophic organisms would be excluded from biofilm reactors as much as possible, thereby high nitrifier biomass density within the biofilm could be reached. We compared the nitrification performance of an RBC after high rate activated sludge treatment without nitrification but with and without tertiary filtration to remove residual TSS. The idea was that TSS in the effluent of the

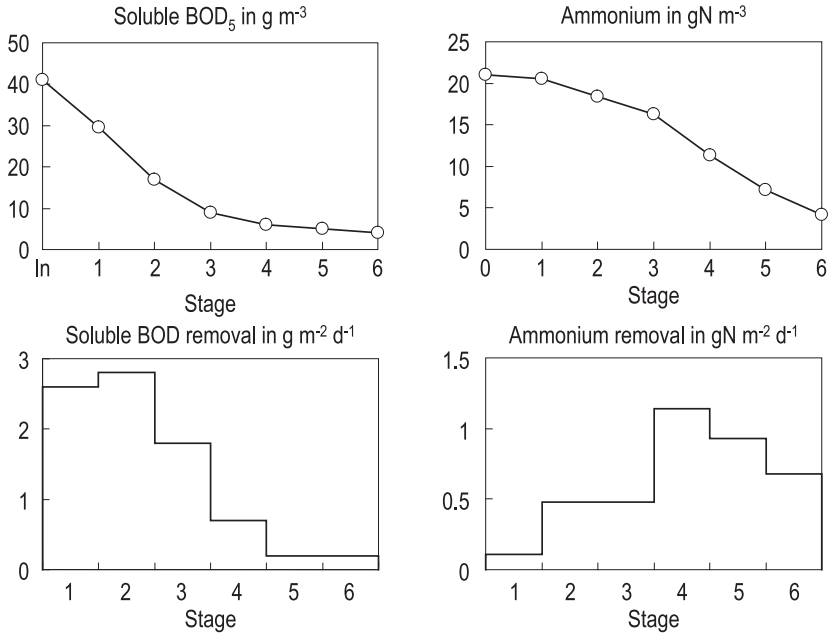

Fig. 8 – Experimental results obtained from a nitrifying rotating biological contactor operated with six stages in series. Data from Mueller et al. (1978), adapted from Wanner and Gujer (1984).

secondary clarifier would only dilute the biomass in the biofilm and would thereby reduce nitrification performance.

The results of pilot tests are given in Fig. 10. Clearly filtration held back the heterotrophic organisms and resulted in the expected positive effect. Unfortunately this effect was not sustained in full scale equipment: the production of nitrifying biomass was smaller than its consumption by higher organisms (worms, snails, fly larvae) and nitrification activity was periodically lost due to predation. In addition the secondary, non-nitrifying treatment step contains a large volume of ammonium-rich wastewater. During storm events, this water is rapidly flushed into the tertiary nitrification plant which has only a small water volume. This instantaneous increase in load cannot typically be handled by such a tertiary system and results in massive bleeding of ammonium. Thus full scale performance did not match our expectations.

We learnt from this experiment that on the one hand models are useful to develop new technology. However on the other hand we had to realize that not all aspects of full scale operation can successfully be piloted at reduced scale and in limited time periods.

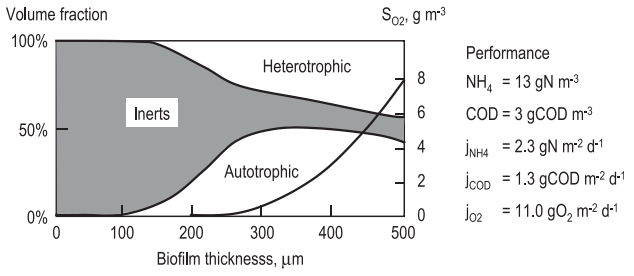

Fig. 9 – Relative biomass distribution over the depth of a biofilm and oxygen concentration profile. Adapted from Wanner and Gujer (1984).

8.3. *Tertiary trickling filters*

In trickling filters, the biomass has a fixed position within the reactor whereas the wastewater passes by. Nitrifying organisms can only grow when their substrate is available and since diurnal load variation and temperature may result in a lack of substrate in the lower part of the filter, biomass development is not usually distributed evenly over the depth.

In pilot experiments with a plastic media tertiary trickling filter for nitrification Boller and Gujer (1986) found the situation indicated in Fig. 11. The biomass in the lower part of the trickling filter is exposed to ammonium for about 1 h d^{-1}. Under these conditions biomass predation and decay are important relative to biomass growth. Thus, nitrification

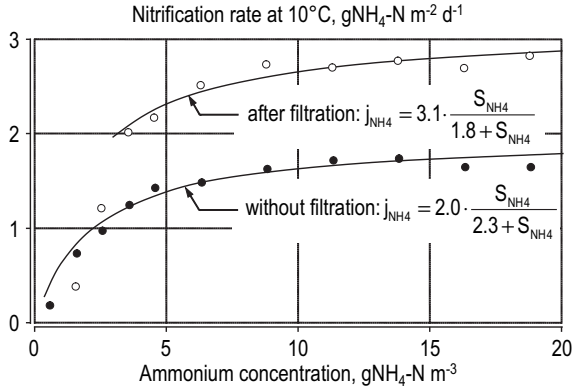

Fig. 10 – Nitrification rate of a tertiary RBC after high rate, non-nitrifying biological pretreatment. Suspended solids in the secondary effluent were either left in the effluent or removed by filtration. Rates are adjusted to 10 °C. Figure adapted from Boller et al. (1990).

activity in the lower parts of the filter is reduced. This is especially critical in autumn, when temperatures decrease. At elevated temperatures biofilm regions at the low end have hardly been exposed to ammonium, thus no biofilm activity could develop. With decreasing temperature this reactor region is now required in order to reach full performance, however it will take weeks until an active biofilm is available.

The suggested strategy to deal with this problem is to cut the filter in two sections, what is the first section one week then becomes the second the other week and vice versa. Such a strategy allows developing a substantial biofilm throughout the entire reactor system even under summer conditions, when only half the reactor volume would be sufficient. However, a first full scale design which relied on this strategy, was abandoned due to high cost. The strategy was transferred to a tertiary RBC plant, where the reversal of flow direction was implemented rather than providing a two stage process.

In tertiary trickling filters biomass production and thus biomass accumulation is rather small. Gujer and Boller (1984) report on massive invasions of higher organisms (trickling filter fly larvae, Psychodidae, and some worms, Naididae) which were grazing on this biomass and virtually wiped out the nitrification performance of tertiary trickling filters for extended periods of time. This problem was overcome by increasing the hydraulic load of the trickling filter, a strategy causing extra operating costs (pumping energy).

The pilot experience with tertiary trickling filters led to the development of a rather simple but efficient mathematical model for the design of this technology (Gujer and Boller, 1986). The model deals with the competition of oxygen and ammonium and readily allows adjusting pilot experience to different temperatures. Even though this technology has never found broad application I still use this model in class to teach simple but meaningful biofilm models.

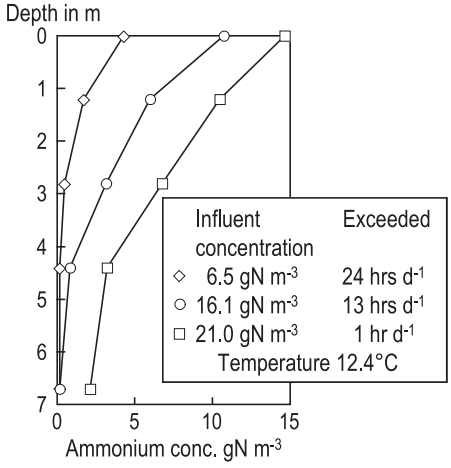

Fig. 11 – Diurnal variation of ammonium concentration profiles over the depth of a tertiary nitrifying plastic media trickling filter (from top to bottom). Different concentration profiles are exceeded for the indicated time during the day. Example: At a depth of 1.2 m 6 gN m^{-3} are exceeded during 13 h d^{-1} when the influent varied between 6.5 and 21 gN m^{-3} (Boller and Gujer, 1986).

8.4. *Dual media sand filters*

Sand filters after nitrifying biological treatment units accumulate nitrifiers and may thus be prepared for additional nitrification. The advantage of using a tertiary trickling filter for nitrification is twofold, (i) the biomass is highly enriched in nitrifiers and (ii) the effluent contains rather elevated concentrations of oxygen. Pilot tests revealed that a sand filter operated after a tertiary trickling filter with an effluent rich in oxygen could nitrify up to 1.7 gN m^{-3} (see Fig. 12, Boller and Gujer, 1986), a substantial amount considering that discharge requirements in Switzerland typically are 2 gNH_4–N m^{-3}. In addition this amount of nitrification has a very positive effect on nitrite too, especially in summer, when ammonium is low and nitrite may be elevated (s.a. Fig. 15). These results were obtained even directly after backwashing, indicating that some nitrifying biomass adheres to the filter material.

8.5. *Hybrid systems outcompete two stage processes*

Today, two stage biological systems rely on optimized management of biomass and substrates. Matsché and Moser (1993) report on the performance of a two stage hybrid activated process which combines the biomass of the second, nitrifying activated sludge system with the sludge in the first system in order to improve nitrogen control (nitrification and denitrification). Later this concept has been implemented successfully in an adapted version in the main wastewater treatment plant of Vienna (Wandl et al., 2006). Here an optimal management of primary effluent (denitrification in the second stage), final effluent (nitrate, denitrification in the first stage), activated sludge from the second biological treatment step (nitrifiers, nitrification in the first step) and sludge from the first activated sludge process (sorbed organics for denitrification in the second step) leads to substantial improvements of nutrient removal performance.

In our own research we followed the concept of separating the individual functions (organics removal by activated sludge and nitrification in fixed biomass reactors). This concept stems from a period when denitrification was

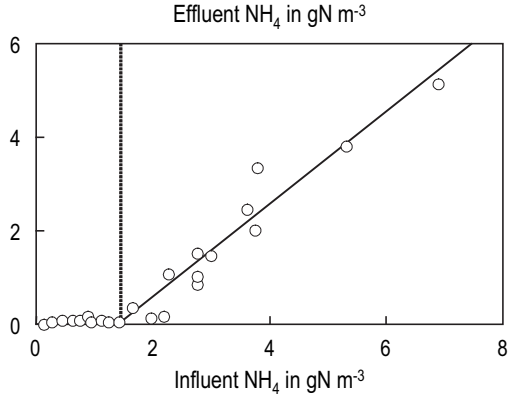

Fig. 12 – Correlation between influent and effluent ammonium concentration in a nitrifying dual media sand filter after a nitrifying tertiary trickling filter (Boller and Gujer, 1986).

hardly considered in Switzerland. Clearly its performance comes nowhere near the potential of the highly integrated hybrid systems. However optimized control of such a system might only be available on large, professionally operated plants.

8.6. *Summary on tertiary nitrification*

Initially many biological wastewater treatment plants were designed for BOD removal only. First generation activated sludge processes in Switzerland typically did not nitrify even in summer. It was tempting to develop end of pipe type technology which could nitrify the effluent of such a plant. Thus, we developed design information for several alternative technologies for tertiary nitrification (see Boller et al., 1994). It turned out that none of these technologies were ever applied in more than a handful of applications. The rapid development of nutrient removal technology in the 1990s made tertiary nitrification soon obsolete.

We learnt that predicting the future is difficult at best.

9. Nitrification in receiving waters

It is not sufficient to predict nitrification performance of wastewater treatment but it is rather essential to understand the fate of nitrogen in the receiving waters as well.

Fig. 13 shows the length profile of some nitrogen species along a small creek close to steady state. The anaerobic influent must first be aerated and after 200 m the process of nitrification becomes clearly visible. Nitrite is first produced and accumulates. As ammonium is degraded to sufficiently low levels nitrite follows suit and is itself degraded again to low residual levels. Here only high spatial resolution of the data can reveal these details.

Fig. 14 shows the diurnal variation of the ammonia (NH_3) concentration in a river about 1.5 km below the discharge of the effluent of a partially nitrifying treatment plant. The synchronization of temperature, pH and ammonium load by sunlight results here in extreme variations of the toxic compound.

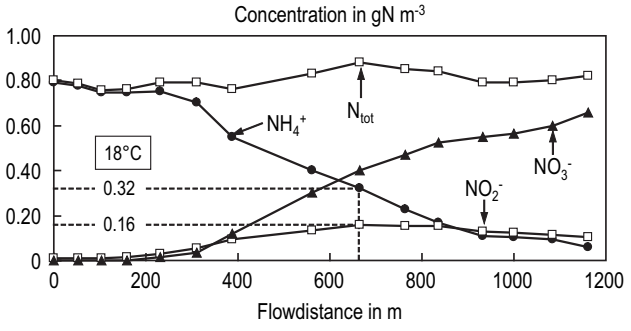

Fig. 13 – Length profile of mineral nitrogen species in a small creek. The creek drains the anaerobic hypolimnion of an eutrophic small lake, becomes reaerated and then nitrification sets in (unpublished, provided by M. Koch). Dashed lines relate to the example in Fig. 15.

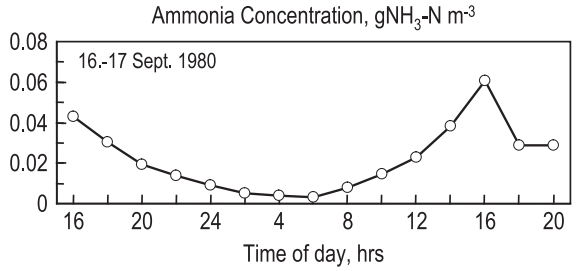

Fig. 14 – Diurnal variation of ammonia concentration in the river Birs, 1.5 km below a partially nitrifying wastewater treatment plant. Variation is affected by temperature, photosynthesis (pH), and ammonium load all synchronized by sunshine as is the oxygen concentration (unpublished, provided by B. Hurni).

Good interpretation of water quality in receiving waters thus requires a detailed understanding of the processes not only in the treatment plants but also by self-purification (and self-polluting as in the case of nitrite) processes within the receiving waters themselves. Two aspects complicate this endeavor:

- In creeks and small rivers the biomass responsible for self-purification processes is concentrated in fixed biomass (biofilms) on the surfaces of the sediment and the leaves of macrophytes. Thus modeling its behavior requires developing some biofilm models for nitrification, subject to the extra complication of competition of abundant hetero- and phototrophic bacteria and algae. In addition growth surfaces vary enormously over the seasons because leaf surface of macrophytes depends heavily on sunshine.
- Whereas activated sludge reactors typically are modeled as a series of completely mixed compartments a river resembles more a plug flow type reactor. Thus non-stationary mathematical models of rivers typically result in partial differential equations.

A first simple model (Gujer, 1976b) allowed quantifying ammonium oxidation in small rivers as a function of growth surfaces, temperature and competing organisms. Later this model was extended to predict the maximum nitrite concentration that is reached in such rivers due to the oxidation of ammonium (Gujer, 1978). Since nitrite is toxic for fish we must understand the dynamics of this compound or else our investment into nitrification of wastewater might not be successful in restoring natural fish populations.

Based on the model of competition of ammonium and nitrite-oxidizers Fig. 15 indicates the maximum nitrite concentration that will be reached in the context of self-purification processes. Dashed lines in Fig. 13 at 650 m are repeated in Fig. 15, thus it becomes possible to estimate the maximum nitrite concentration that may be reached.

Fig. 16 shows the results from a continuous monitoring exercise of ammonium and nitrite in the river Glatt in Switzerland (Berg, 1991). This river was at the time heavily loaded with non-nitrified secondary effluent. Clearly nitrite becomes a significant problem with increasing temperature

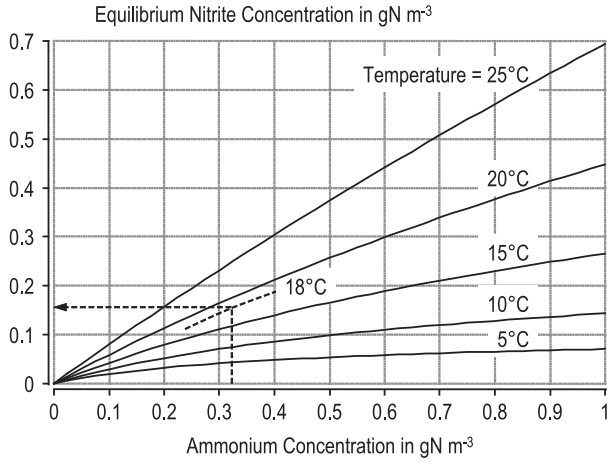

Fig. 15 – Equilibrium nitrite concentration in small rivers derived from a model suggested by Gujer (1978). Dashed lines relate to the example in Fig. 13.

and in summer may potentially be more of an ecological threat than ammonia.

Jancarkova et al. (1997) quantified the distribution of nitrifying biomass in a shallow stream. Depending on the local hydraulic situation, they found very significant amounts of active biomass deep in the loose sediment of the river. In addition a very significant fraction of the biomass was eroded and self-purification capacity was lost during a storm event. Understanding self-purification thus requires us to know the "hydraulic history" of the river, to consider the exchange of river water between bulk and sediment and to include erosion and regrowth processes of biomass. All together a formidable task at least.

I learnt from these examples that only a holistic understanding of technical (wastewater treatment) and ecological systems (self-purification, toxicity) can be the basis in generating successful proposals for environmental protection.

10. Immission standards for nitrogen species

It is not the task of environmental engineers alone to suggest immission standards for receiving waters but rather do we expect ecologists and ecotoxicologists to support us in this endeavor. In view of the costs of nitrogen control it became however a necessity to have arguments for or against nitrification at hand – and immission standards are strong arguments.

Table 3 summarizes possible limits based on the following arguments for the choice of maximum allowable ammonium concentration in receiving waters under Swiss conditions (Gujer, 1978):

- Allowing 20% of the oxygen saturation concentration to be consumed for the nitrification of river water after infiltration into groundwater;
- Limiting the ammonium concentration to 0.5 $gNH_4\,m^{-3}$ to protect possible surface water use for water supply (equal to drinking water tolerance values in EU and Switzerland);
- Accepting the limiting value of 0.02 $gNH_3\text{–}N\,m^{-3}$ as suggested by the European Inland Fisheries Advisory Commission (EIFAC, 1970) for the protection of freshwater fish and applied in the EU;
- Choosing a temperature and pH value typically observed on sunny afternoons, when pH is the highest due to photosynthesis;
- Considering toxicity of nitrite which might arise from nitrification (Fig. 15);
- Considering the effect of chloride ion (Cl^-) on nitrite toxicity for fish as suggested by Müller (1990) and derived from EIFAC (1984): The higher the chloride concentration, the lower the toxicity of nitrite.

Based on the arguments in Table 3 the Swiss ordinance on water pollution control (GSchV, 1998) prescribes that the ammonium concentration (NH_4–N plus NH_3–N) should not exceed 0.4 $gN\,m^{-3}$ in the receiving water below 10 °C and should be below 0.2 $gN\,m^{-3}$ above 10 °C. These values are a compromise between ecological requirements and cost of wastewater treatment. In many situations they are difficult to reach.

11. Nitrification as a case

11.1. *From* Nitrobacter *to nitrite-oxidizing bacteria (NOB)*

Wagner et al. (1996) demonstrated with the aid of molecular techniques (FISH) that *Nitrobacter* spp. cannot be the main

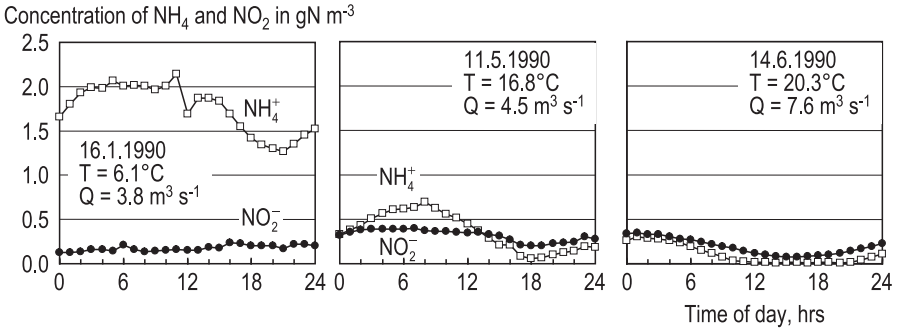

Fig. 16 – Ammonium and nitrite concentration over 3 full days in January, May and June in the river Glatt. Data provided by M. Berg (s.a. Berg, 1991).

Table 3 – Basis for immission standards for ammonium in receiving waters in Switzerland (s.a. Gujer, 1978; Müller, 1990; EIFAC, 1984).

Reasoning	Tolerance		Allowable ammonium concentration in $gN\,m^{-3}$ River water temperature	
			10 °C	20 °C
Protection of groundwater	20% of O_2 saturation reserved for nitrification ($4.57\ gO_2/gNH_4$–N)		0.49	0.40
Protection of water supply	Tolerance concentration for drinking water in Switzerland and EU $0.5\ gNH_4\,m^{-3}$		0.39	0.39
Limiting ammonia concentration for protection of local fish $0.02\ gNH_3$–$N\,m^{-3}$ (average)	$0.02\ gNH_3$–$N\,m^{-3}$	pH = 8.0	1.0	0.49
		pH = 8.5	0.33	0.17
		pH = 8.75	0.20	0.10
Limiting the nitrite concentration depending on local chloride concentration for the protection of fish, considering nitrification	$<10\ gCl^-\,m^{-3}$	$0.02\ gNO_2$–$N\,m^{-3}$	0.1	0.05
	$10–20\ gCl^{-1}\,m^{-3}$	$0.05\ gNO_2$–$N\,m^{-3}$	0.2	0.1
	$>20\ gCl^{-1}\,m^{-1}$	$0.10\ gNO_2$–$N\,m^{-3}$	0.5	0.2

organisms responsible for the oxidation of nitrite to nitrate in typical biological wastewater treatment plants. Until then it was assumed by environmental engineers that *Nitrosomonas* and *Nitrobacter* are the responsible organisms for nitrification. I suspect many engineers assumed these organisms to be well defined entities growing on well defined and easily accessible substrates. These assumptions made nitrification the ideal process for following the behavior of a specific organism within the mixed population that makes up activated sludge. In these studies frequently it is not nitrification that is of interest but nitrification is only a proxy for the analysis of species behavior in mixed cultures.

Today careful engineers use the term ammonium oxidizing organisms (AOB) and nitrite-oxidizing organisms (NOB) rather then giving specific names to the catalysts of these processes. Nevertheless experience with these processes remained valid, independent of the more advanced microbiological findings.

The unique situation that simple experiments (respiration in batch tests, nitrite and nitrate production rates, etc.) allowed to establish kinetic and stoichiometric information, develop mathematical models for activated sludge population dynamics and dynamic system behavior, biofilm models, etc. was extremely helpful in the development of models for activated sludge processes and attached growth systems. Today many models of mixed culture mixed substrate interactions actually follow the lines first calibrated and validated with the processes of nitrification.

The lack of quantitative microbial techniques to follow different groups of organisms and their activity in the activated sludge made it necessary for engineers to use nitrification as a readily and easily quantifiable process for the development of many models. I am convinced that nitrification was a blessing for engineers involved in the development of mathematical models.

I foresee that in the future when molecular microbial techniques become more and more quantitative and readily available, these techniques will partially replace the use of nitrification as a source for further understanding of the interplay of substrate and microbial populations. But there are still questions to be answered with the aid of domesticated nitrifying organisms. In addition nitrification is such an easy to understand and well behaved system that it will remain important in the education of generations of engineers.

11.2. *Nitrification as an indicator for micropollutant degradation*

Nitrification performance of a biological wastewater treatment plant can easily be followed and is today a frequent requirement in many industrialized countries. In contrast, degradation of micropollutants is difficult and costly to follow and is not routinely included in plant performance control. Clara et al. (2005) demonstrate that at solids retention times typically used in nitrogen removal plants many micropollutants are efficiently degraded. Thus nitrification efficiency is a valid indicator for micropollutant removal. For some micropollutants like EE2 it may even be the nitrifiers themselves which are responsible for their degradation (Forrez et al., 2009).

As mentioned early in this review, nitrification has for a long time served as an indicator for good secondary treatment. With its importance related to micropollutants this indicator function may get value again.

11.3. *The case of bioaugmentation*

It is tempting (and is even patented, US Patent 5811009) to pregrow nitrifying organisms with warm ammonium-rich liquids originating e.g. from sludge handling (supernatants from digesters operated at 35 °C) and then to add these organisms to an activated sludge reactor in order to augment the nitrifier concentration and thus to obtain better performance from a given, highly loaded reactor.

With the aid of FISH (Fluorescent In Situ Hybridization) Manser (2005) demonstrated that different organisms are enriched in ammonium-rich liquids (R-strategists: *Nitrosomonas europaea* and *Nitrobacter*) and in domestic wastewater

with lower ammonium concentrations (K-strategists: *Nitrosomonas oligotropha* and *Nitrospira*). With experiments and based on simulations Manser concluded that the R-strategists are rapidly washed out from the activated sludge and the use of the extra nitrogen for load balancing (Fig. 5) would actually result in better plant performance, however at the cost of extra oxygen input into the reactor.

Simply working with oxygen electrodes and ammonium, nitrite and nitrate analysis would not necessarily lead to this conclusion (see patent application). In this case molecular microbiological techniques lead directly to an explanation of a not *a priori* expected result. Using the activated sludge with nitrifiers grown in the activated sludge process itself as an influent into a reactor where a warm, concentrated ammonium solution is nitrified, appears to be a more successful strategy. Salem et al. (2003) simulated this strategy based on ASM1 and predicted a very positive effect which was later validated in full scale (Salem et al., 2004; Krhutkova et al., 2006). The initial simulations did however not differentiate between alternative possible groups of nitrifiers. It is only with the full scale validation that these predictions became valuable.

11.4. *The case of conventional activated sludge versus membrane bioreactors*

It is not *a priori* clear that the experience with conventional activated sludge systems (CAS), where biomass is retained based on sedimentation, can directly be transferred to membrane bioreactors (MBR). Here biomass is quantitatively retained and does not have to settle. It is well possible that under these differing operating conditions different organisms with different properties are enriched. Manser et al. (2005a) used FISH and found only minor differences between the two systems for both ammonia-oxidizing and nitrite-oxidizing bacteria.

Kinetic parameters differed between the two systems. Apparent Monod saturation coefficients for nitrifiers are larger in CAS than in MBR systems. Manser et al. (2005b) explain these differences with mass transfer effects. In CAS the flocs are larger than in MBR systems. The longer diffusion paths result in a larger apparent saturation value. Thus some kinetic parameters are system specific.

11.5. *Model structure uncertainty*

In calibrating our mathematical models we frequently assume that the mathematical structure of our models provides a good image of reality. Daebel et al. (2007) analyzed the residuals (deviations) between experimental observation and model prediction for some respiratory tests with nitrifiers. We found systematic deviations (autocorrelated residuals) which go back to structural deficiencies of our models. We concluded that by using standard least square procedures for parameter identification, parameter uncertainty is underestimated.

Neumann and Gujer (2008) follow up on this problem based on artificial data and conclude that we do not yet have the techniques to deal with parameter uncertainty in view of structural problems in our mathematical models. Especially environmental engineers are suffering from this situation, since frequently their models are only crude approximations of the fine details of reality.

Today we do not have a scientific strategy to deal with model structure uncertainty. Pragmatic approaches are to add extra noise to the data until structural problems are masked or to thin out data until structural problems cannot be identified any more.

11.6. *Kinetic parameters are stochastic variables*

Mathematical models for biological wastewater treatment such as the family of Activated Sludge Models No. 1–3 (ASM1, ASM2, ASM3) typically are assumed to be deterministic and based on fixed parameter values (which may however have to be calibrated for a specific situation and system). Using nitrification we could argue that different groups of nitrifiers exist under the operating conditions of an activated sludge system, which is genetically open to the environment. Thus, it is well possible that over time different groups of organisms may be enriched in the activated sludge. This would then result in apparent time dependent kinetic parameters if nitrification is modeled with only one ''species'' of organisms. In addition varying activated sludge floc size could lead to variable diffusion limitations inside the flocs which from a macroscopic point of view would be identified as a variable value of Monod saturation coefficients.

Daebel et al. (2007) identified the saturation coefficient for ammonium oxidizing (AOB) and nitrite-oxidizing (NOB) bacteria in activated sludge from a conventional activated sludge plant with sedimentation and a membrane bioreactor (MBR). The kinetic parameters varied over time (Fig. 17) and since flocs were smaller in the MBR than in the CAS the parameters were also different for the two systems. Since the variation of the kinetic parameters is statistically highly significant, we must assume that such parameters are not constant in time but may be subject to time dependent stochastic processes (effects of processes not captured with today's models).

At this moment it is unclear what the consequence of such results is, but we might have to accept that our nice deterministic models capture only a small fraction of the complex behavior of activated sludge.

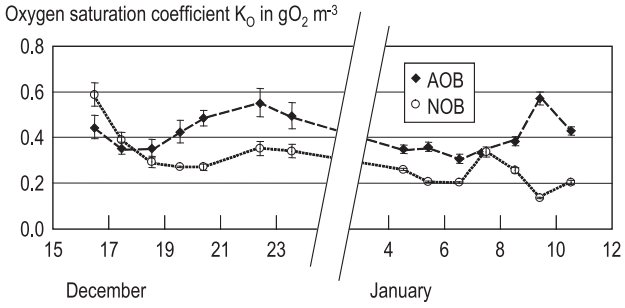

Fig. 17 – Temporal variation of the oxygen saturation coefficient (Monod model) of ammonium (AOB) and nitrite (NOB) oxidizing bacteria in a continuously operated membrane bioreactor plant (MBR). Expected value and 95% confidence region of a lognormally distributed parameter value. Adapted from Daebel et al. (2007).

11.7. *Batch tests may not yield reliable kinetic information*

Mass transfer and utilization of oxygen strongly interfere. What we observe on a macroscopic level (using an oxygen electrode) is quite different from what microorganisms inside flocs experience. Results obtained from a batch test in which both AOB and NOB are active (test spiked with ammonium) and a test in which NOB activity dominates (spiking nitrite only) may result in different apparent Monod saturation coefficients for oxygen. Since AOB consume much more oxygen than NOB, mass-transfer may result in different oxygen concentration profiles inside the flocs (Manser et al., 2005b). The situation gets even more complicated when heterotrophic activity must be considered.

The same applies to saturation coefficients of nitrite: If nitrite is supplied from the outside of the flocs by spiking, we must expect a larger apparent saturation coefficient than when nitrite is produced from ammonia by AOBs, when nitrite might actually diffuse out of the flocs.

11.8. *Chemical nitrification*

In special cases microbial and chemical nitrification processes are strongly interlinked. Trying to nitrify a highly concentrated ammonium-nitrite solution Udert et al. (2005) found the oxidation of ammonium to nitrite to be catalyzed by microorganisms which reduced the pH far below 5.5. In the resulting solution conditions developed which induced chemical oxidation of nitrite to nitrate and a final pH below 3.

It is presently not known where such processes are of importance; nitrogen emission from acid soils is a candidate. The interesting aspect of these experiments is the simultaneous activity and interaction of significant microbial and chemical processes.

11.9. *Nitrification provides evidence for the anammox process*

Nitrification has the favorable property that substrates (educts) and products of the process can quite easily be followed and analyzed with the aid of mass balances. This is not the case with the degradation of organic compounds where carbon dioxide (CO_2) may easily be lost to the atmosphere and may interact with the carbonate buffer system.

Siegrist et al. (1998) operated a tertiary rotating biological contactor (RBC) for the nitrification of the pretreated effluent from a hazardous-waste landfill. The influent contained a minimum of organic substrate nevertheless up to 70% of the ammonium which was nitrified was lost in the process. This unexpected result led these authors to the discovery that anammox bacteria have developed in their system. Clearly this observation would have been difficult without the possibility to follow substrate and product of the expected processes.

11.10. *Ammonium as a reactive tracer*

Engineers frequently use inert tracer compounds in order to obtain experimental information on reactor hydraulics (hydraulic residence time distribution). It is rather difficult to derive information on reactor internal mixing from such experiments since time constants for internal mixing are considerably shorter than mean hydraulic residence times, thus internal mixing is masked by the averaging process of mixing of the tracer. If reactive tracers are used their time constants (mean life expectancy) may be much shorter, thus following their concentration inside the reactor may yield more information on mixing processes.

Using ammonium and dissolved oxygen as reactive tracers Braun and Gujer (2008) used on-line electrodes inside the reactor and found oscillations of these two compounds with different frequencies. A low frequency ($1\ h^{-1}$) related to problems in the aeration control, a high frequency ($9\ h^{-1}$, Fig. 18) with a period of approximately 7 min originated from problems with macroscopic internal mixing. These oscillations affect the performance of the biological reactor. They are not typically contained in our models but might actually be quite common in biological wastewater treatment, where mixing energy is costly and thus kept to a minimum.

The time constants of nitrification are such that ammonium and related also oxygen can be used to identify such problems with reasonable effort. With non-reactive tracers we could not identify these problems with the same resolution and reproducibility.

When we use data on treatment performance from pilot or full scale plants, such mixing effects may affect the results but may not be realized because typically we do not measure state variables routinely within our reactors. In the process of calibration of our models for dynamic simulation we primarily adjust kinetic and stoichiometric parameters but seldom improve the hydraulic reactor models. Thus defects of reactors are copied onto kinetic parameters. The value of these parameters for the simulation of another system is then questionable.

The question arises: to what degree can models calibrated with results from pilot plants be extrapolated to full scale plants under design?

12. Open questions and outlook

Nitrite is a known toxic compound for fish and thus is an important aspect of water pollution control. The reliable

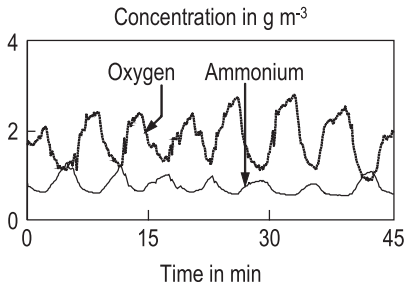

Fig. 18 – Oscillations of ammonium and dissolved oxygen concentrations in a non-optimized activated sludge reactor caused by internal, macroscopic mixing processes. Adapted from Braun and Gujer (2008).

prediction of nitrite in the effluent of biological treatment systems is however still an open problem: Unexpected spills of high concentrations of nitrite are frequently observed. The problem is not to develop a model structure but rather to understand the variation of the kinetic parameters. It might well be that only stochastic models for parameters or alternatively structured biomass (microorganisms with cell internal structure) will be successful in capturing some of these phenomena.

Reaching very low ($\ll 2\,gN\,m^{-3}$) residual ammonium concentrations in the effluent of activated sludge plants is sometimes difficult, especially when diurnal load variations are high. We do not yet have a full understanding of these problems. Here too it may be necessary to include cell internal structure (organism activity) to explain our experience. In addition a further understanding of predation, decay and lysis processes under different redox conditions might be required. Sometimes the cause is related to poorly characterized hydraulic mixing conditions in the aeration tank.

The economics of wastewater treatment could be improved if nitrification were stopped with the production of nitrite only. Nitrification would be cheaper (oxygen supply) and denitrification would be more efficient. At the low temperatures of urban wastewater we do however not yet have the technology to stop nitrification at the level of nitrite. In addition nitrous oxide production is related to high nitrite concentration.

Sensor technology has made significant progress in the last decade. Broad application of such technology combined with advanced control strategies has the potential to provide us with vastly different treatment technologies. The full potential of this development has not yet been developed.

Increasingly anaerobic ammonium oxidation (anammox) is recognized to be an important process of the nitrogen cycle in dilute natural systems. Kuypers et al. (2003) state: *In fact, the widespread occurrence of ammonium consumption in suboxic marine waters as well as in sediments suggests that anammox bacteria could have an important but as yet neglected role in the oceanic loss of fixed nitrogen*. Whereas anammox is increasingly used for the removal of nitrogen from highly concentrated ammonium solutions (Kuenen, 2008), we have yet to see a substantial application of this process for the treatment of dilute wastewater. Anaerobic treatment with production of methane followed by nitritation combined with anammox would be an interesting combination for urban wastewater in many situations, especially in warm climates.

13. Do we stand on the brink of a new paradigm again?

Today we have a solid understanding of what I would call the backbone of biological wastewater treatment which is responsible for the removal of the macro-nutrients from urban wastewater: TSS, COD, nitrogen and phosphorus. There will still be further valuable developments but compared to the second half of the 20th century I do not expect advances in in-depth understanding at the same rate. What lies ahead of us is more the development of detailed understanding of the behavior of specific chemicals (micropollutants, …), specific groups of organisms (filaments, anammox, …), novel treatment technologies (membranes, anaerobic processes, granular biomass, …) and of detailed engineering methods (computational fluid dynamics, CFD, …). At the same time there is a trend away from an interest for highly integrated, large, centralized sewer and prototype treatment systems to the development of more decentralized and smaller, potentially even industrially produced units. In addition we learnt to admit that there will remain some uncertainty in engineering design and we rapidly find techniques to quantify this uncertainty and to integrate it into our decision processes.

The transition from general understanding of bulk performance of publicly owned wastewater treatment plants towards the specific behavior of individual entities in small, possibly industrially produced and privately owned treatment units requires a new approach with new tools. On the one hand new stakeholders will be involved and their interest and potential must become understood and considered. On the other hand new specific techniques (microbial, chemical and engineering) will become available which will allow for very specific and detailed results however at considerable cost. Combining these two aspects requires the consideration of societal relevance and thus more transdisciplinary work. The glory of time of gaining generally valid information from analyzing nitrification as a proxy for many important processes slowly vanishes, the new paradigm however still waits to be explicitly defined.

14. Conclusion

There is no doubt, ammonium is today recognized as an important quality parameter in receiving waters and nitrification is the dominant process to rid wastewater of ammonium. Thus nitrification is here to stay and a detailed understanding of this process is key to modern wastewater treatment. By now the organisms responsible for nitrification of urban wastewater are domesticated and a broad suite of technologies is available for their productive application.

Mathematical models, which are an important tool for design and optimization of biological treatment units have been developed and are used on a broad scale. The future will result in some refinement but not necessarily in an entirely new structure.

Nitrification can easily be quantified thus it has served as a proxy to learn about many problems of biological wastewater treatment processes. Today we increasingly get more specific chemical and microbiological techniques which reduce the importance of working with nitrification.

Definitely open questions remain in the context of nitrification of dilute and concentrated nitrogen solutions. I am convinced that research and development will continue in this exiting field of environmental engineering.

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