PRACTICE REPORT
LABORATORY & PROCESS ANALYSIS
WASTEWATER TREATMENT
NUTRIENTS

Optimal nutrient ratios for wastewater treatment

To be able to comply with the legal requirements on treated wastewater, plant operators must control the treatment process carefully, so that they can intervene promptly to prevent → **limit values** from being exceeded. Besides chemical and physical methods, wastewater treatment is essentially based on → **biological treatment** by → **microorganisms** in activated sludge. Knowledge of the → **nutrient requirements** and the composition of the activated sludge are therefore needed if the plant is to operate at maximum efficiency. The causes and effects of → **unfavourable nutrient ratios**, and the measures to be taken to deal with them, are described in this report.

Author:
Dipl.-Ing. Michael Winkler
- Project Leader, Product Development and Customer Service
- BIOSERVE GmbH, Mainz

Nutrients in activated sludge

Laboratory analysis and process measurement technology support compliance with the limit values.

The workplace for laboratory analysis consists of a photometer, reagents and – depending on the parameter – a thermostat.

A balanced nutrient ratio is essential if the microorganisms are to function at maximum efficiency. The most important of these nutrients are carbon, nitrogen and phosphorus.

Carbon

Carbon is the principal component of the organic substances found in wastewater. It is biodegraded by the microorganisms in activated sludge under anaerobic conditions (bio-P), in an anoxic environment (denitrification zone) and in the aerated part of the biological stage (nitrification zone). The microorganisms use the carbon compounds to build their cell structures and to generate energy.

→ Carbon compounds are determined as COD, BOD_5 or TOC

Nitrogen

In the inflow of wastewater treatment plants, nitrogen is present in organically bonded form (organic N) and as ammonium nitrogen (NH_4-N). During biological wastewater treatment, organic N is converted to NH_4-N by the bacteria in the activated sludge. This NH_4-N and the NH_4-N from the inflow are converted to nitrite, which in turn is converted to nitrate (nitrification).

The nitrogen compounds that are not biodegraded in the activated sludge are converted under anoxic conditions (absence of dissolved O_2) to elementary nitrogen (denitrification). This escapes into the atmosphere as N_2.

→ Nitrogen compounds are determined as NH_4-N, NO_2-N, NO_3-N and TN (total nitrogen, which is important for balancing and outflow checks).

Phosphorus

The P load in the inflow of a wastewater treatment plant is made up of orthophosphate-phosphorus (PO_4-P), polyphosphates and organic phosphorus compounds. Together, they give the sum parameter 'total phosphorus' (P_{tot}).

$$\text{Organic compounds} + O_2 + \text{Nutrients} \xrightarrow{\text{Microorganisms}} \text{New cell material} + CO_2\uparrow + H_2O$$

Table 1: Important sum parameters for wastewater treatment

COD (Chemical Oxygen Demand); this corresponds approximately to the amount of oxygen required to completely oxidise the carbon compounds, including reduced inorganic compounds.
BOD_5 (Biological Oxygen Demand); this indicates how much elementary oxygen is consumed during five days of biodegradation by microorganisms under standard conditions.
TOC (Total Organic Carbon) is a measure of organically bonded carbon; in contrast to BOD_5, TOC also includes the carbon in poorly biodegradable compounds.
TKN (Kjeldahl nitrogen) is a measure of organically bonded nitrogen (organic N) and ammonium nitrogen (NH_4-N).
Total nitrogen TN (LATON) includes organically bonded nitrogen, ammonium nitrogen (NH_4-N), nitrite (NO_2-N) and nitrate (NO_3-N).

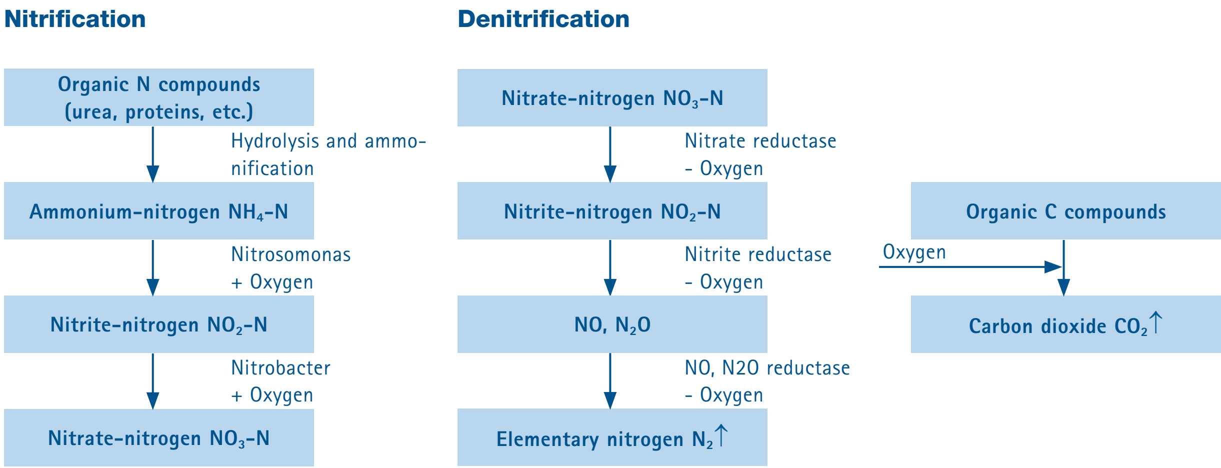


Fig. 1: Degradation processes during nitrification and denitrification

During biological wastewater treatment, polyphosphates and organically bonded phosphorus are converted to orthophosphate.

The P demand of the organisms is due to the special role of phosphorus in their energy metabolism. P is needed to form the cell membrane and DNA.

Some of the phosphorus in wastewater is eliminated biologically (bio-P). The rest can be removed by chemico-physical phosphate precipitation.

→ Phosphorus compounds are determined as ortho-PO_4-P (control of precipitation) and as P_{tot} (balancing, outflow monitoring)

Trace elements

Other trace elements needed to build cells – e.g. potassium, magnesium, manganese, iron, copper, zinc and nickel, and vitamins and growth factors – are usually present in municipal wastewater, or the microorganisms in the activated sludge provide them themselves.

Sulphur

Septic domestic wastewater and some industrial wastewater contain reduced sulphur compounds (hydrogen sulphide, sulphides and thiosulphates). Sulphur is an indispensable component of proteins. In wastewater treatment plants, reduced sulphur compounds are not only oxidised chemically to sulphate but are also oxidised by some bacteria to form sulphur and, since this process generates energy, are stored inside cells as food reserves.

High concentrations of reduced sulphur compounds in wastewater can, however, cause a number of problems (Table 2).

C:N:P ratio (BOD_5:TN:P_{tot})

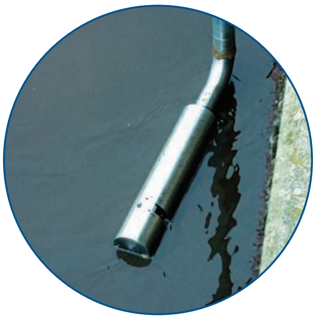
The content of the individual nutrients in wastewater should correspond to the needs of the bacteria in the activated sludge, and there should be a balanced relationship between C, N and P. This is crucial to the effectiveness of the biodegradation processes. During aerobic wastewater treatment, the C:N:P ratio should be in the range between 100:10:1 and 100:5:1.

Reagent-free probes are used for continuous monitoring.

Modern analysers are mounted directly on the edge of the tank and do not need a protective housing.

Favourable and unfavourable nutrient ratios

SC 1000 controller for up to eight sensors – also suitable for use as a network with, for example, Profibus



Partially immersed NITRATAX sc probe for online nitrate measurement

However, all sorts of industrial plants, regional differences in eating habits (disposal of different kitchen wastes through the drains), and the nature of the soil and drinking water cause wastewater to vary widely in its composition. Experience has shown that the C:N:P ratio in municipal wastewater is about 100:20:5.
The excess N and P compounds can usually be eliminated from the wastewater without any great difficulty using modern methods.

If the wastewater in the inflow to the biological stage is deficient in one of the main nutrients, a wide range of problems may occur (Table 3).

For efficient denitrification, a certain proportion of readily biodegradable C compounds must be present. After municipal wastewater has passed through the primary settling tank, it has a BOD_5:N ratio of 100:25 (=5). If the ratio falls below 100:40 (=2.5), the efficiency of the denitrification process is impaired, resulting in higher nitrate values in the outflow. If bypassing the primary treatment and increasing the denitrification volume fail to bring about any improve-

Table 2: Causes and effects of high sulphur concentrations

Causes/Origin of wastewater	Possible consequences	Corrective action
• High concentrations of sulphur compounds from chemical and protein processing industries (meat and poultry processing) • Anaerobic processes in the sewerage system, which cause sulphur compounds to be reduced to hydrogen sulphide	• Corrosion in sewers and tank walls in wastewater treatment plants • Neighbours suffer odour nuisance • Increased growth of sulphur oxidising filamentous bacteria (Type 021 N)	• Avoid blockages in the sewerage network • Add iron salts to the sewer (e.g. at the pumping stations)

Table 3: Causes and effects of nutrient deficiencies in the biological stage of wastewater treatment

Shortage of	Causes/Origin of the wastewater	Possible consequences	Corrective action
Carbon	• Long dwell time in the sewerage network • Far-reaching primary treatment of the wastewater • Industrial wastewater with a high nitrogen content, e.g. from milk and meat processing	• Profuse development of filamentous bacteria (sludge bulking and foam) • Insufficient denitrification	• Bypass the primary treatment • Increase the denitrification volume while retaining sufficient volume for the nitrification (minimum sludge age of 9 days)
Nitrogen	Low-nitrogen wastewater from: • Paper industry • Fruit and vegetable processing	• High COD/TOC values in the inflow of the wastewater treatment plant • Filamentous bacteria	Balance the nutrient ratio by: • Addition of N compounds (good-value industrial products such as urea) • Addition of domestic wastewater, turbid water from digester
Phosphorus	• Landfill leachate, wastewater from fruit and vegetable processing	• Increased COD/TOC values in the outflow • Filamentous bacteria	Balance the nutrient ratio by: • Addition of P compounds (good-value industrial products such as phosphoric acid or phosphate fertilisers for the agricultural sector) • Addition of domestic wastewater

ment, the addition of a readily degradable substrate (external source of carbon) should be considered.
Carbon sources for nutrient balancing include:
- Internal C = hydrolysed or acidified primary sludge
- External C = industrial residues (from breweries, dairies, sugar industry) and industrial products (methanol, ethanol, acetic acid).

COD:BOD$_5$ ratio

The ratio of these two sum parameters is a measure of the biodegradability of the wastewater pollution load. If the COD:BOD$_5$ ratio does not exceed 2:1, the biodegradability is said to be good. Higher values indicate the presence of poorly biodegradable substances.

Example

A municipal wastewater treatment plant with a high proportion of industrial wastewater has the following nutrient parameters in the inflow to the biological treatment stage (Table 5).

The BOD$_5$:N ratio of 2.45 is too low for adequate denitrification to occur. External carbon compounds should therefore be added. However, a number of calculations have to be carried out before this is done:

1. Amount of nitrogen that is not to be denitrified ($\Sigma N_{n.z.d.}$):

➔ see Table 6

2. Calculate the amount of nitrogen that can be denitrified with the wastewater:

With upstream denitrification and a V_D:V_{AT} ratio of 0.5, the denitrification capacity (according to Table 7) is C_{Deni} = 0.15 kg NO_3-N_D/kg BOD$_5$.

$S_{NO3\text{-}N,\,D} = C_{Deni} \times BOD_{5\,infl\,aer}$
$= 0.15 \times 110$ mg/L = 16.5 mg/L

This means that 16.5 mg/L NO_3-N can be denitrified with the existing biological treatment.

The practical LANGE cuvette tests are available for all key parameters.

In combination with analytical quality assurance, the measurement results are officially approved.

Table 4: Causes and effects of unfavourable COD:BOD$_5$ ratios

Causes/Origin of wastewater	Possible consequences	Corrective action
• Landfill leachate, wastewater from composting and residual waste treatment facilities and the chemical industry • Considerable reduction in BOD$_5$ in the long sewage network in summer • Intensive primary treatment of the wastewater	• Inadequate denitrification (high nitrate values in the outflow) • High COD in the outflow of the wastewater treatment plant • Deterioration of bio-P	• Addition of C sources to improve denitrification • Use chemicophysical methods (ozone treatment, activated carbon filter, membrane technology) for poorly biodegradable and non-biodegradable substances

If large numbers of samples have to be analysed, the automatic laboratory analysers offer valuable support.

Regulating the substrate dosage by means of NO_3-N measurements

Table 5: Average daily values of a municipal wastewater treatment plant

	Average daily values
Inflow [m³/d]	10,000
$BOD_{5\ infl\ aer}$ [mg/L]	110
$TN_{infl\ aer\ LATON}$ [mg/L]	45
$P_{tot\ infl\ aer}$ [mg/L]	3,5
$BOD_{5\ infl\ aer.}$: $TN_{infl\ aer}$ = 110:45 =	**2.45**

Table 6: Calculation of amount of nitrogen that is not to be denitrified ($\Sigma N_{n.d.}$)

N incorporated in biomass (5% of BOD_5 infl aer)	5.5 mg/L
$N_{org.e}$ (e = assumed target quantity in the outflow)	2 mg/L
NH_4-N_e (e = target quantity in the outflow)	0 mg/L
NO_3-N_e (e = target quantity in the outflow)	8 mg/L
Sum	**15.5 mg/L**

Table 7: Denitrification capacity in accordance with ATV-A131 (guideline values for dry weather and temperatures from 10 to 12°C)

V_D/V_{AT} Volume Deni/Volume Aeration	C_{Deni} (Denitrification capacity in kg NO_3-N_D/kg BOD_5)	
	Upstream denitrification	Simultaneous and intermittent denitrification
0.2	0.11	0.06
0.3	0.13	0.09
0.4	0.14	0.12
0.5	0.15	0.15

V_D: Volume of the aeration tank used for denitrification
V_{AT}: Volume of the aeration tank

Table 8: External carbon sources for calculating the necessary dosage

		Acetic acid	Methanol	Ethanol
COD	kg/kg	1.07	1.50	2.09
TOC	kg/kg	0.40	0.38	0.52
BOD_5	kg/kg	0.70	0.96	1.35
Density	kg/m³	1,060	790	780

In this example, 1 kg acetic acid is equivalent to 1.07 kg COD.

3. Calculating the external substrate requirement

The still to be denitrified N content is the total added nitrogen minus the amount of nitrogen that is not to be denitrified minus the amount of nitrogen that the plant can denitrify:

$S_{NO3\text{-}N,\ D,\ Ext} = TN_{Inflow} - \Sigma N_{n.d.} - S_{NO3\text{-}N,\ D}$
$= 45$ mg/L - 15.5 mg/L - 16.5 mg/L
$= 13$ mg/L

To denitrify the remaining 13 mg/L nitrogen, the microorganisms in the activated sludge must be provided with an additional source of carbon. A daily wastewater volume of 10,000 m³ has a nitrogen load of 130 kg. According to DWA Work Sheet A131, the external carbon requirement is 5 kg COD/1 kg NO_3-N. This means that, for complete denitrification to occur, 650 kg COD are needed per day. If the additional carbon is provided in the form of acetic acid, the data provided in Table 8 indicate that 607 kg would have to be added each day. The targeted dosage is based on the NO_3-N values.

Conclusions

Unfavourable nutrient ratios and high concentrations of individual substances reduce the degradation efficiency of biological wastewater treatment processes. Early recognition and continuous monitoring of critical parameters is therefore essential in order to enable plant operators to take rapid corrective action when necessary. Only in this way can compliance with legal outflow values be ensured and unnecessarily high wastewater levies be avoided. LANGE cuvette tests and continuously operating process measurement devices have demonstrated that they are indispensable aids to achieving greater transparency and reliability.

Typical measurement locations for the monitoring of nutrients in wastewater treatment plants

❶ Inflow to primary settling tank: determination and monitoring of the plant loading
❷ Inflow to aeration tank: optimisation of nutrient supply
❸ Outflow from aeration tank: monitoring and optimisation of C degradation performance, nitrification/denitrification and P elimination
❹ Outflow from WWTP: monitoring of limit values, control of the WWTP

The analysed nutrient parameter are (depending on the self-monitoring regulations):

→ **COD** (ggf. **TOC**)
→ **BOD_5**
→ **ortho PO_4-P**
→ **P_{tot}**
→ **NH_4-N**
→ **TKN** (Kjeldahl nitrogen: sum of NH_4-N and organic N)
→ **$N_{tot.inorg.}$** (inorganic N: sum of NH_4-N, NO_3-N and NO_2-N)
→ **TN_b** (total nitrogen: sum of organic and inorganic N)

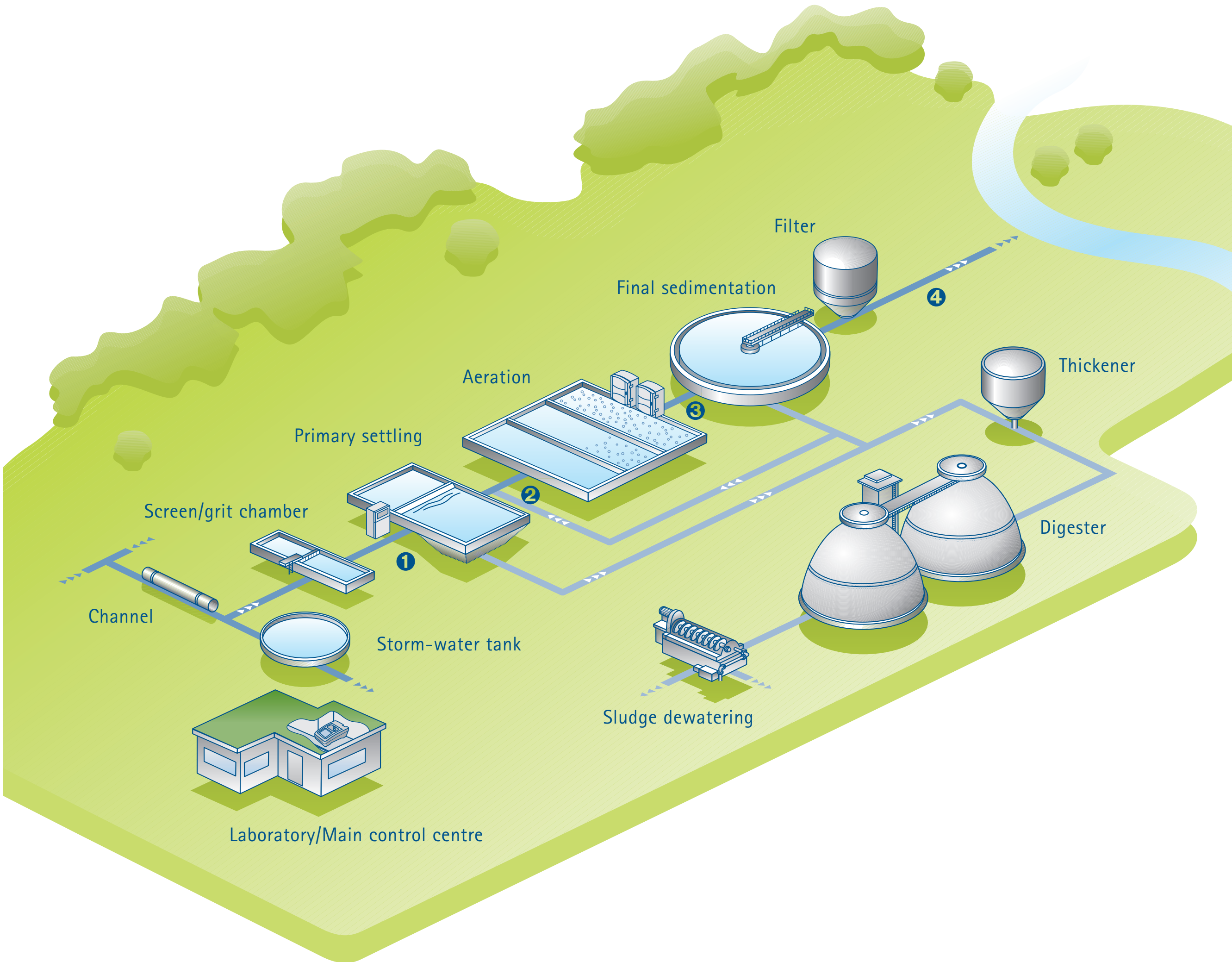


Fig. 2: Schematic representation of a wastewater treatment plant with measurement locations for nutrient monitoring

Optimal nutrient ratios with modern measurement technology

Measuring station for laboratory analysis

DR 3900	Compact and powerful spectrophotometer (320–1100 nm) with RFID technology for reliable and traceable measurement results in routine analyses and user applications; barcode reader (IBR) for automatic evaluation of LANGE cuvette tests; backlit graphic display with touch-screen
LT 200	Dry thermostat for standard and special digestions; preprogrammed digestions for the analysis of COD, total N, total P, TOC, organic acids, metals
Alternative	
HT 200S	High-temperature thermostat for fast digestion for the analysis of COD, total N, total P, metals in just 35 minutes; standard digestions for analysis of TOC
Cuvette tests	Ready-to-use reagents with maximum user safety; highly precise; approved method; more than 50 parameters and measuring ranges

Measurement station for laboratory analysis, with DR 3900 photometer, LT 200 thermostat and LANGE cuvette tests

Systems for online measurement

AMTAX sc	Process measuring instrument for continuous determination of the ammonium concentration in water and wastewater samples with a low solids content. The measurement is carried out by a gas-sensitive electrode.
PHOSPHAX sc	Process measuring instrument for continuous determination of the ammonium concentration in water and wastewater samples with a low solids content. The measurement is carried out using the vanadate-molybdate method.
AISE sc **AN-ISE sc** **NISE sc**	ISE probe for continuous in-fluid determination of the ammonium concentration (AISE sc, AN-ISE sc) and nitrate concentration (NISE sc, AN-ISE sc). The measurement is carried out using an ion-selective electrode (ISE) with automatic potassium and chloride compensation. Especially easy handling thanks to the CARTRICAL plus sensor cartridge.
NITRATAX sc	Process probe for determining the nitrate content directly in water, wastewater or activated sludge; no sampling required; self-cleaning; reagent-free method; variety of measuring ranges
SC 1000 Controller	A SC1000 controller system consists of a single display module and one or more probe modules. It is configured modularly to suit the customer's specific requirements and can be expanded at any time to include additional measurement locations, sensors, inputs, outputs and bus interfaces. Each module controls up to eight sensors.
Alternative	
SC 200 Controller	Controls up to two sensors (not for AMTAX sc or PHOSPHAX sc).

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