# 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 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 **unfavorable nutrient ratios**, and the measures taken to deal with them, are described in this report.

Be Right™

*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.*

# Nutrients in Activated Sludge

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 chemical oxygen demand (COD), biological oxygen demand (BOD), or total organic carbon (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 into 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 oxidize the carbon compounds, including reduced inorganic compounds. |
| BOD (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): A measure of organically bonded carbon; in contrast to BOD, TOC also includes the carbon in poorly biodegradable compounds. |
| TKN (Kjeldahl nitrogen): A measure of organically bonded nitrogen (organic N) and ammonium nitrogen ($NH_4$-N). |
| Total nitrogen TN: Includes organically bonded nitrogen, ammonium nitrogen ($NH_4$-N), nitrite ($NO_2$-N), and nitrate ($NO_3$-N). |

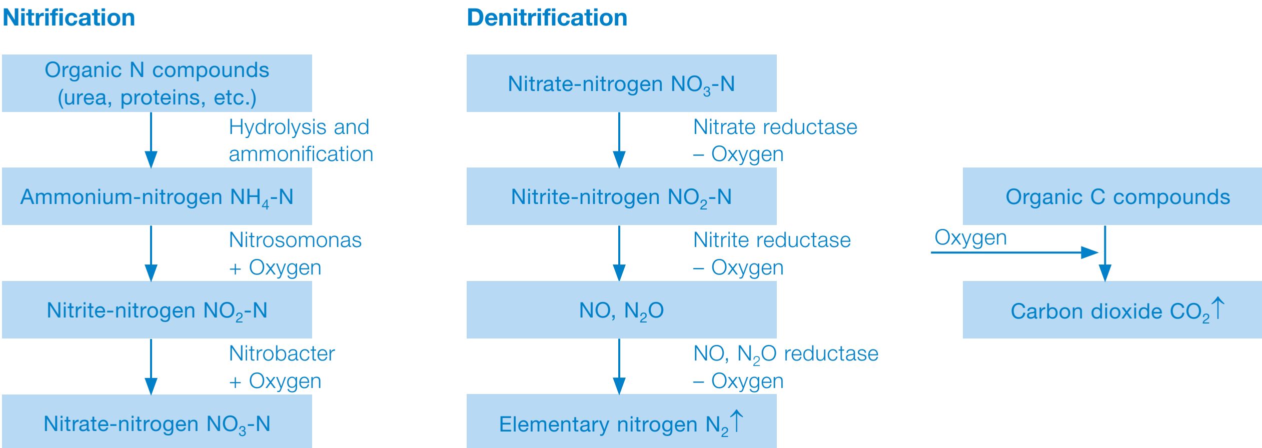


*Fig. 1: Degradation processes during nitrification and denitrification*

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 chemicophysical phosphate precipitation.

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

*Reagent-free probes are used for continuous 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.

## Sulfur

Septic domestic wastewater and some industrial wastewater contain reduced sulfur compounds (hydrogen sulfide, sulfides and thiosulfates). Sulfur is an indispensable component of proteins. In wastewater treatment plants, reduced sulfur compounds are not only oxidized chemically to sulfate but are also oxidized by some bacteria to form sulfur and, since this process generates energy, are stored inside cells as food reserves.

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

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

## C:N:P ratio (BOD: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.


*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 on-line nitrate measurement*

# Favorable and Unfavorable Nutrient Ratios

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: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 improvement, the addition of a readily degradable substrate (external source of carbon) should be considered.

Carbon sources for nutrient balancing include:

- Internal C = hydrolyzed or acidified primary sludge
- External C = industrial residues (from breweries, dairies, sugar industry) and industrial products (methanol, ethanol, acetic acid).

## COD:BOD Ratio

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


*The practical TNTplus vial tests are available for all key parameters*

*Table 2: Causes and effects of high sulfur concentrations*

| Causes/Origin of the Wastewater | Possible Consequences | Corrective Action |
|---|---|---|
| • High concentrations of sulfur compounds from chemical and protein processing industries (meat and poultry processing)<br>• Anaerobic processes in the sewerage system, which cause sulfur compounds to be reduced to hydrogen sulfide | • Corrosion in sewers and tank walls in wastewater treatment plants<br>• Neighbors suffer odor nuisance<br>• Increased growth of sulfur oxidizing filamentous bacteria (Type 021 N) | • Avoid blockages in the sewerage network<br>• 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 dwelling time in the sewerage network<br>• Far-reaching primary treatment of the wastewater<br>• Industrial wastewater with a high nitrogen content, e.g. from milk and meat processing | • Profuse development of filamentous bacteria (sludge bulking and foam)<br>• Insufficient denitrification | • Bypass the primary treatment<br>• Increase the denitrification volume while retaining sufficient volume for the nitrification (minimum sludge age of nine days) |
| **Nitrogen** | Low-nitrogen wastewater from:<br>• Paper industry<br>• Fruit and vegetable processing | • High COD/TOC values in the inflow of the wastewater treatment plant<br>• Filamentous bacteria | Balance the nutrient ratio by:<br>• Addition of N compounds (good-value industrial products such as urea)<br>• Addition of domestic wastewater, turbid water from digester |
| **Phosphorus** | • Landfill leachate, wastewater from fruit and vegetable processing | • Increased COD/TOC values in the outflow<br>• Filamentous bacteria | Balance the nutrient ratio by:<br>• Addition of P compounds (good-value industrial products such as phosphoric acid or phosphate fertilizers for the agricultural sector)<br>• Addition of domestic wastewater |

## 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: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.

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

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

*Table 4: Causes and effects of unfavorable COD:BOD ratios*

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

# 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 [$m^3$/d] | 10,000 |
| $BOD_{infl\ aer}$ [mg/L] | 110 |
| $TN_{infl\ aer}$ [mg/L] | 45 |
| $P_{tot\ infl\ aer}$ [mg/L] | 3.5 |
| $BOD_{infl\ aer.}$ : $TN_{infl\ aer}$ = 110:45 = | 2.45 |

*Table 6: Calculation of amount of nitrogen that is not to be denitrified (ΣNn.d.)*

| | |
|---|---|
| N incorporated in biomass (5 % of BOD 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)*

| VD/VAT | $C_{Deni}$ (Denitrification Capacity in kg $NO_3$-$N_D$/kg BOD) | |
|---|---|---|
| Volume Deni/Volume Aeration | 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 |

VD: Volume of the aeration tank used for denitrification

VAT: 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 | kg/kg | 0.70 | 0.96 | 1.35 |
| Density | kg/$m^3$ | 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$m^3$ 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

Unfavorable 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. TNTplus 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

1. Inflow to primary settling tank: determination and monitoring of the plant loading
2. Inflow to aeration tank: optimization of nutrient supply
3. Outflow from aeration tank: monitoring and optimization of C degradation performance, nitrification/denitrification and P elimination
4. Outflow from WWTP: monitoring of limit values, control of the WWTP

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

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

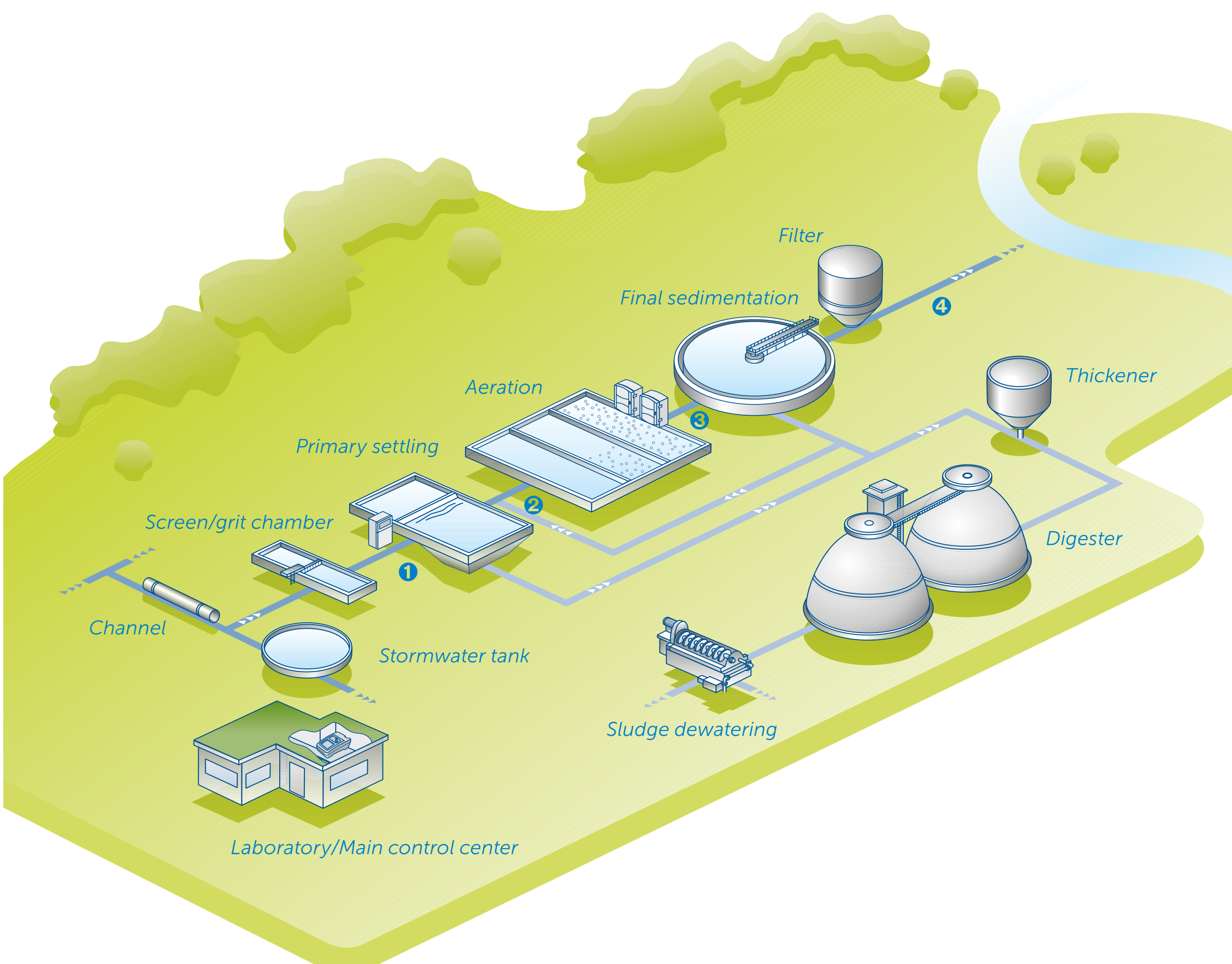


*Fig. 2: Schematic representation of a wastewater treatment plant with measurement locations for nutrient monitoring*

# 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 TNTplus tests; backlit graphic display with touchscreen |
| DRB 200 | Dry thermostat for standard and special digestions; preprogrammed digestions for the analysis of COD, total N, total P, TOC, organic acids, metals |
| TNTplus 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, DRB 200 thermostat and TNTplus vial 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<br>AN-ISE sc<br>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 SC 1000 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). |

***References***

*D. Jenkins, M. G. Richard, G. T. Daigger: Manual on the causes and control of activated sludge bulking, foaming, and other solids separation problems, Lewis Publishers, 2004*

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