

1. NITROGEN COMPOUNDS AS POLLUTANTS

1.1. The Role of Nitrogen in The Environment

Nitrogen compounds are becoming increasingly important in waste water management, because of the many effects that nitrogenous material can have on the environment. Nitrogen, in its various forms can deplete oxygen due to nitrification, fertilize aquatic plant growth, exhibit toxicity toward aquatic life, affect chlorine disinfection efficiency and present a public health hazard. These effects will be reviewed further in Section 1.4.

This volume is about the nitrogen removal processes applied in environmental technology. A detailed description of all processes, biological as well as physical-chemical, will be presented, but obviously the selection of environmental technology must be based not only upon what the technology can offer, but also upon which problems we need to solve. Before we can make the final selection of the proper technology, we need to answer a chain of questions:

1. What are the concentration and form(s) of the pollutants in the ecosystem in focus?
2. Are these concentrations and forms changed over time? If "yes" due to what processes? Can these processes be controlled?
3. What are the sources of the pollutants? Which sources are point sources and which sources are non-point or diffuse sources?
4. What is the geographical distribution of the problem(s)? Are the problems local, regional or global? The answers to this question require in most cases that a local, regional or global cycle of the pollutant is set up.

Figure 1.1. gives a flow chart of a procedure showing how to get from emission of mass and energy to a solution of the related environmental problems. Emission is translated into imission and concentration. The effect and impact of a concentration of a compound or energy is found by considering all the chemical, physical and biological processes that take place in the ecosystem. This step will often require the application of ecological models as a management tool, as the

processes are interactive and an overview is difficult to obtain without a synthesizing instrument as modelling; see Jørgensen (1988). This evaluation leads us hopefully to an acceptable ecological solution by the use of ecological engineering or environmental technology. The former attacks the problem in the ecosystem, which is often needed, when the cause of the problem is coming from non-point sources; the latter attempts to reduce or dilute the emission at the point source. This volume focuses on the environmental technological solutions to nitrogen removal, although the application of biological removal processes in nature, i.e., in the ecosystems, also will be touched upon, as these processes are in principle the same processes, such as the biological processes characterizing the biological nitrogen removal processes in environmental technology.

The three steps in the procedure presented in Fig. 1.1 concerned with ecosystems are the most complex ones. They require a very comprehensive ecological and environmental scientific knowledge, which often must be synthesized in a model in order to give applicable answers to the crucial environmental problems. It would require a second volume of this book to discuss in detail the nitrogen in the environment, but a brief discussion of these problems seems necessary to present the frames of the environmental technology available for nitrogen removal - or to touch upon the problems behind the possible solutions presented in parts B (removal of nitrogen by biological methods) and C (removal of nitrogen by physical-chemical methods) of the volume. Section A is a necessary part of this volume to avoid the separation of "the problem" and "the solution," which should always be avoided in environmental management. An integration of the two sides of environmental issues should always be attempted, and it is facilitated in the case of nitrogen pollutions by the fact, that many of the biological, chemical and physical processes used for nitrogen removal in environmental technology are, as mentioned above, the same as the processes that take place in nature. The following sections of this introductory chapter will consequently focus on:

- the global nitrogen cycles, to understand the global effects of our nitrogen emissions,
- the regional and local nitrogen cycles and budgets,
- the sources of nitrogen emission and their relative quantitative importance
- the typical effects of elevated nitrogen concentrations in aquatic ecosystems

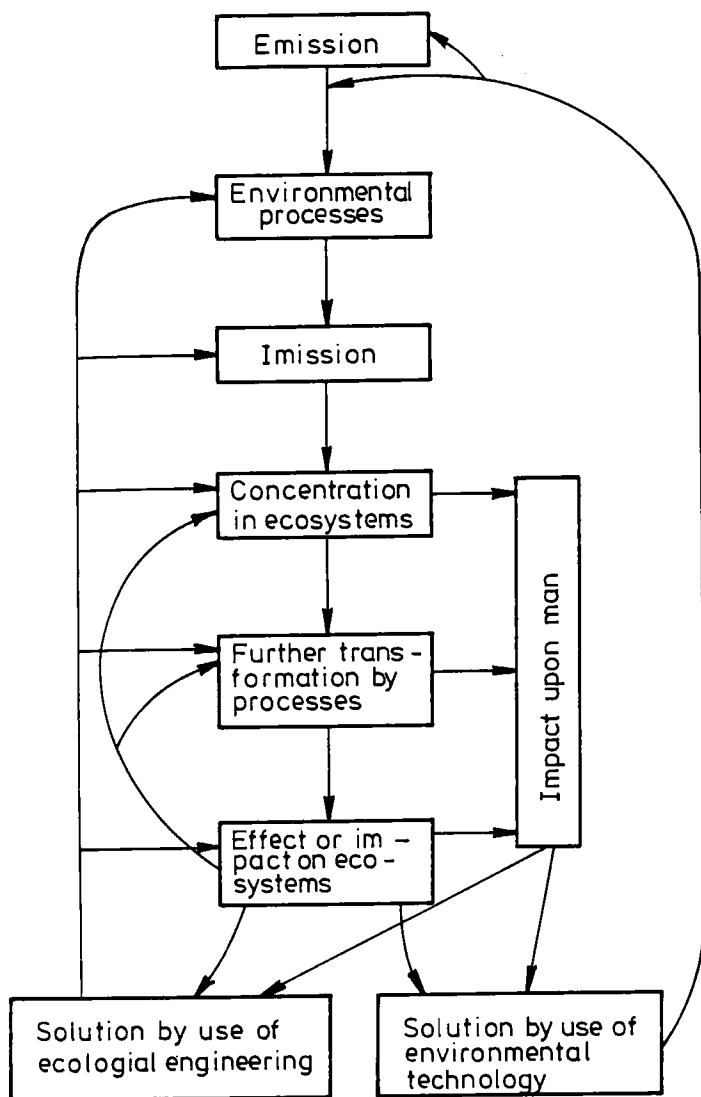


Figure 1.1. The flow chart illustrates a procedure which can be used to get from emission to the solution of the problem.

tems and in portable water. This includes a brief presentation of the toxicity of nitrogen compounds.

1.2. The Nitrogen Cycle

Figure 1.2 illustrates the global nitrogen cycle. The amount of nitrogen in the various pools and the transfer flows are mainly based upon the figures from Bolin and Cook (1983). As seen from Fig. 1.2 many of the numbers are indicated as ranges due to uncertainty in the estimation. The figures have steadily been adjusted due to new measurements and new knowledge gained during the last two decades. Further changes of our knowledge about the nitrogen cycle can be expected in the coming years.

The cycle is not in balance due to human activity. The production of nitrogen fertilizer the conversion of gaseous nitrogen as dinitrogen (N_2) into ammonia and nitrate, which are deposited in the lithosphere. The major part is washed out to the hydrosphere, where no major global change of the concentration of nitrogen is observed, but where the nitrogen together with phosphorus may cause eutrophication on a local or regional scale; see also Section 1.4.

Another unbalance in the nitrogen cycle is the transfer of nitrogen by combustion from the lithosphere to the atmosphere. These fluxes would influence the atmospheric concentrations of inorganic nitrogen radically, if the inorganic nitrogen was not deposited in the hydrosphere and lithosphere. It implies that also from this source there is a net, diffuse input of nitrogen to the lithosphere and hydrosphere, contributing to the eutrophication of aquatic ecosystems on a local or regional scale.

Figure 1.3 shows another important nitrogen cycle, namely in soil and ground water. All nitrogen compounds and in particular nitrate show an increasing concentration in the root-zone, due to the increasing nitrogen input to the lithosphere from dry and wet deposition and from industrial fixation; see also Fig. 1.2. A part of this nitrate will leach to the groundwater and an elevated nitrate concentration in this potable water source is observed as a result of the above mentioned unbalance in the nitrogen cycle. As the time needed for the nitrate to reach the ground water table is several decades, the final results of the increasing nitrogen pollution during the last 25 years have not yet been reflected in the nitrate

concentration of ground water. Elevated nitrate concentrations are already a threat to the ground water quality in many industrialized countries due to the increased

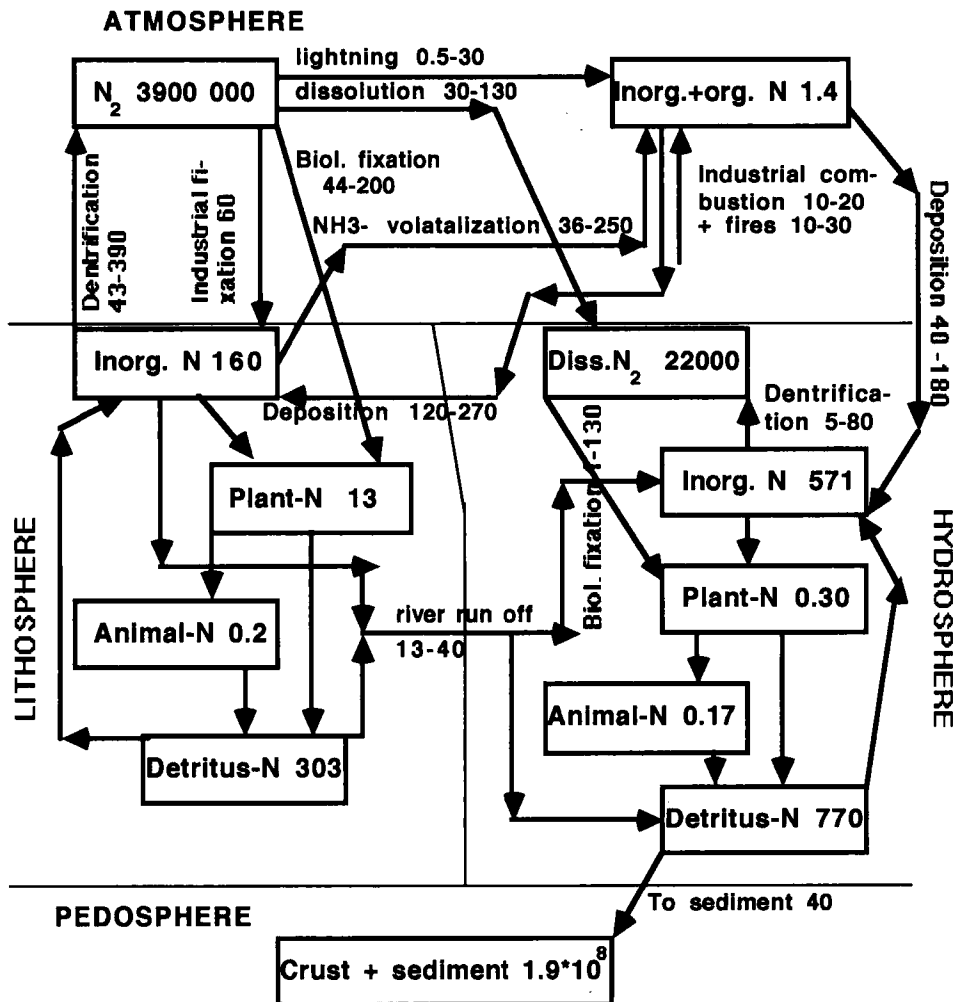


Figure 1.2. The global nitrogen cycle is shown. Values in compartments are in Pg N, while the fluxes are in Tg N / yr.

nitrogen consumption and pollution over the last 30-40 years, but we can expect that the problem will increase very rapidly in the coming years due to the above mentioned time lag.

Figure 1.4 gives the nitrogen cycle in many aquatic ecosystems. The increasing inflow of nitrate and ammonium to the aquatic ecosystems due to the in-

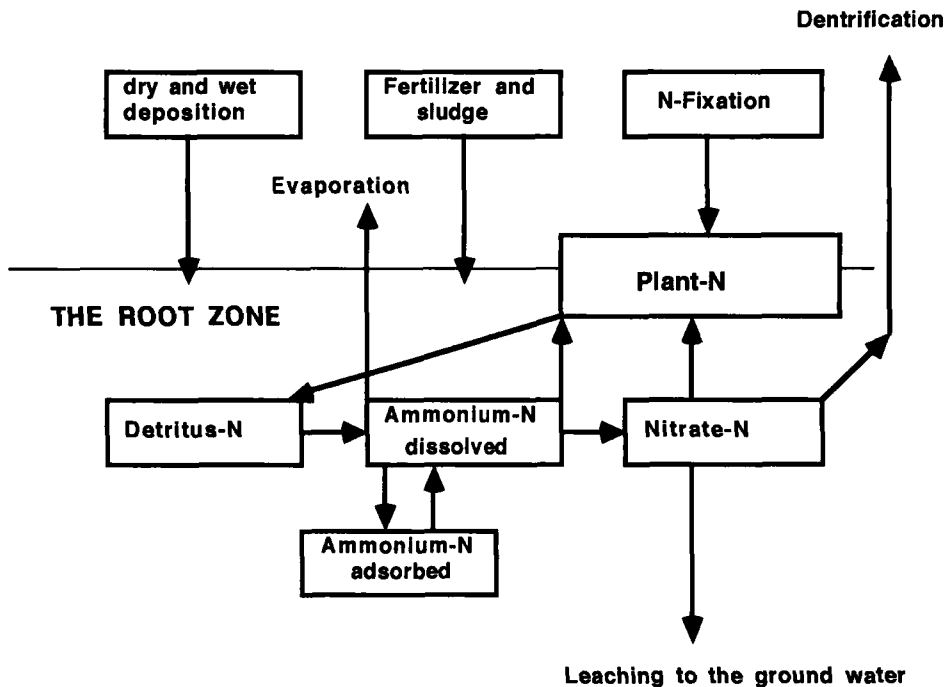


Figure 1.3. The nitrogen cycle in soil and ground water. Note that the processes causing the global unbalance are included in the figure: the industrial production of fertilizers and the wet and dry deposition. These two processes are causing the nitrate pollution of the ground water sources.

creased production of fertilizers and the increase in nitrogenous emission from human activities in general to the atmosphere and further on to the lithosphere and atmosphere, accelerate directly the growth of plants. This process, named *eutrophication*, may cause several other problems as will be touched upon in the next sections, dealing with the sources and effects of nitrogen pollution.

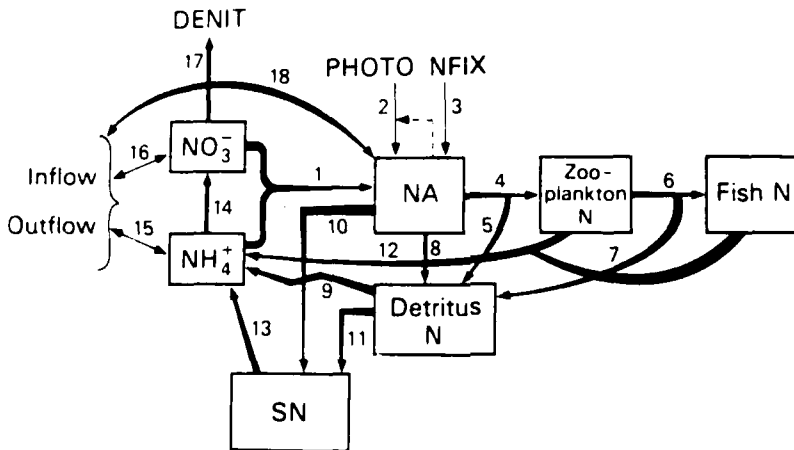


Figure 1.4. The nitrogen cycle in an aquatic ecosystem. The processes are: 1) uptake of inorganic nitrogen by algae (and plants), 2) photosynthesis, 3) nitrogen fixation, 4) grazing, 6) predation 5) and 7) loss of undigested matter 8) mortality, 9) mineralization, 10) and 11) settling, 12) excretion of ammonia, 13) release of ammonium from sediment, 14) nitrification, 15) 16) and 18) input / output, and 17) denitrification.

1.3. Sources of Nitrogen Pollution

The abatement of nitrogen pollution must be based upon a knowledge of the quantities of nitrogen from the various sources. Mass balances must be set up for ecosystems and for entire regions. Table 1.1 gives an example. The estimated nitrogen loadings for the San Francisco Bay Basin (from "California ", 1974) are shown. The mass balance shows clearly that major problems are rooted in the discharge of waste water and nitrogen from dairies and feedlots. The abatement should therefore concentrate primarily on these sources of nitrogen emissions.

Table 1.2 gives the nitrogen balance for Denmark, which is a country characterized by intensive agriculture and many food processing industries. The balance shows that a comprehensive reduction of the nitrogen emission requires that the non-point sources are included in the abatement scheme. It is, however, in most cases more difficult to find good solutions to the reduction of nitrogen emission from non-point sources than from point sources. Some of the

ecotechnological methods briefly touched upon in part B may be applied effectively to reduce these sources, but a wide spectrum of methods, which include planning and legislation, is needed in practical environmental management to achieve an acceptable result.

It would be going too far in this context to present these methods in detail in this context, but it should be mentioned that the following components have been included in the management of nitrogen pollution in Denmark:

1. Legislation concerning manure application schemes and storage capacity for surplus manure.
2. Use of wetlands close to sensible aquatic ecosystems.
3. Legislation on the needs for green fields during the winter season.
4. Encouragement of limited use of fertilizers. Were this not be successful, the imposition of a tax on the use of fertilizers will be considered.
5. Financial support for erection of biogas-plants for treatment of manure and other animal wastes.

Table 1.1.

Estimated nitrogen loadings for the San Francisco Bay Basin*)

Nitrogen source	t per year	Percent of total
Municipal waste water	26 000	49
Industrial waste water	16 000	30
Dry deposition	590	1.1
Wet deposition	390	0.8
Urban run-off	1 400	2.7
Non-urban run-off	1 900	3.6
Nitrogen from irrigated agricultural land	900	1.7
Nitrogen from dairies and feedlots	6 000	11.1
Total	53 000	100

*) Source "California", 1974.

The methods for nitrogen removal presented in Parts B and C are aimed at the reduction of nitrogen in the effluents from industries and municipalities, i.e., the point sources. The few ecotechnological methods, mentioned in Part B can be used for both point sources and non-point sources. These methods are defined as the application of ecologically sound engineering methods for restoration of ecosystems. They are included in this volume, as they are based on the same principles as the other methods, presented in Part B. All the methods presented otherwise can be considered as environmental technological methods.

Table 1.2.

Nitrogen loadings for Denmark *)

Source	1000 t N / yr.	
Municipal Waste water	24.1	
Villages, summer houses without sewage systems	2.9	
Industries	5.3	
Run-off	0.8	
Fertilizers	115-130	
Animal waste, manure	45-109	
Dry and wet deposition	12-30	
Biological nitrogen fixation	10-28	
Removed by harvest		115-130
Denitrification		25-43
Run-off, agriculture (difference)	42-124	
Total loadings of nitrogen	75-157	

*) Sources: SJVF (1985) and Miljøstyrelsen (1984).

1.4. The Effect of Nitrogen Discharge

The effects of nitrogen discharge will be mentioned briefly in this section to be able to relate the methods of nitrogen removal with the expected effects of their application.

The four major effects are:

1. Fertilization (eutrophication) of aquatic ecosystems
2. Oxygen depletion in aquatic ecosystems.
3. Toxicity to aquatic life.
4. Contamination of ground water by nitrate and its effect on the public health.

The word **eutrophic** generally means "nutrient rich." Naumann introduced in 1919 the concepts of oligotrophy and eutrophy. He distinguished between oligotrophic lakes containing little planktonic algae and eutrophic lakes containing much phytoplankton.

The eutrophication of lakes in Europe and North America has grown rapidly during the last few decades due to the increased urbanization and the increased discharge of nutrients per capita.

The production of fertilizers has grown exponentially in this century as demonstrated in Fig. 1.5, and the concentration of nutrients in many lakes reflects the same exponential growth, (Ambühl, 1969).

The word eutrophication is used increasingly in the sense of the artificial addition of nutrients, mainly nitrogen and phosphorus, to water. Eutrophication is generally considered to be undesirable, although it is not always so.

The green color of eutrophic lakes makes swimming and boating less safe due to increased turbidity. Furthermore, from an aesthetic point of view the chlorophyll concentration should not exceed 100 mg m^{-3} . However, the most critical effect from an ecological viewpoint is the reduced oxygen content of the hypolimnion, caused by the decomposition of dead algae. Eutrophic lakes might show high oxygen concentrations at the surface during the summer, but low oxygen concentrations in the hypolimnion, which may cause fishkill.

On the other hand an increased nutrient concentration may be profitable for shallow ponds used for commercial fishing, as the algae directly or indirectly form food for the fish population.

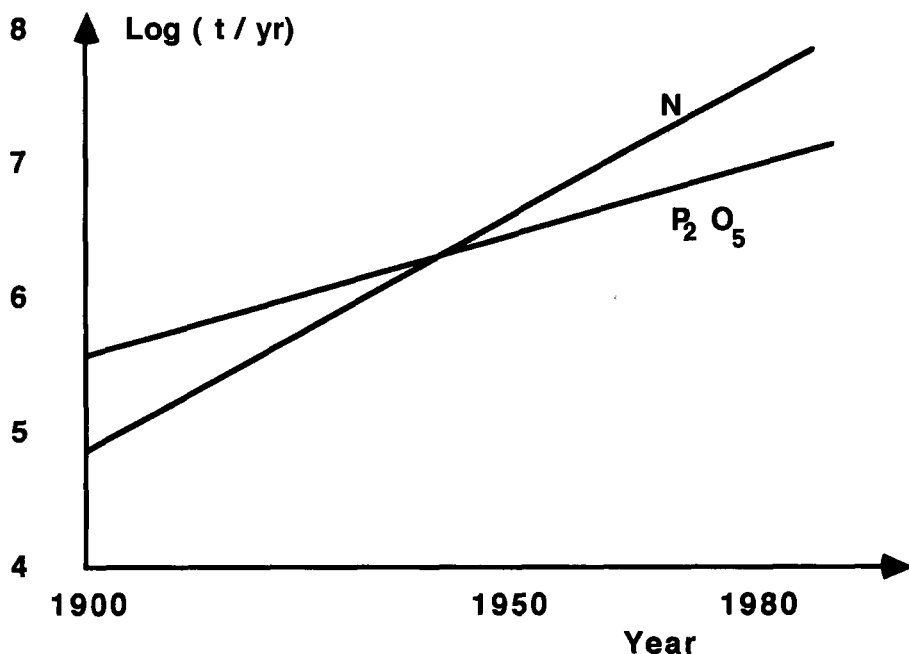


Figure 1.5. The production of fertilizers (t yr^{-1}), as demonstrated for N and P_2O_5 , has grown exponentially (the y-axis is logarithmic).

About 16-20 elements are necessary for the growth of freshwater plants, as shown in Table 1.3, where the relative quantities of essential elements in plant tissue are shown.

The present concern about eutrophication relates to the rapidly increasing amounts of phosphorus and nitrogen, which are normally present at relatively low concentrations. Of these two elements phosphorus is often considered the major cause of eutrophication, as it was formerly the growth-limiting factor for algae in the majority of lakes but, as demonstrated in Fig. 1.5, its usage has greatly increased during the last decades. Nitrogen is a limiting factor in a number of East African lakes as a result of the nitrogen depletion of soils by intensive erosion in the past. Nitrogen may, however, become limiting to growth in lakes and in coastal zones as a result of the tremendous increase in the phosphorus concentration caused by discharge of waste water, which contains relatively more phosphorus than nitrogen. While algae use 4-10 times more nitrogen than phosphorus, waste water generally contains only 3 times as much nitrogen as phosphorus.

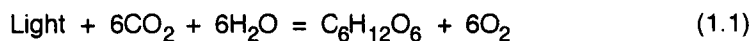
Table 1.3.**Average fresh-water plant composition on wet basis**

Element	Plant content (percentage)
Oxygen	80.5
Hydrogen	9.7
Carbon	6.5
Silicon	1.3
Nitrogen	0.7
Calcium	0.4
Potassium	0.3
Phosphorus	0.08
Magnesium	0.07
Sulfur	0.06
Chlorine	0.06
Sodium	0.04
Iron	0.02
Boron	0.001
Manganese	0.0007
Zinc	0.0003
Copper	0.0001
Molybdenum	0.00005
Cobalt	0.000002

Nitrogen accumulates in lakes to a lesser extent than phosphorus and a considerable amount of nitrogen is lost by denitrification (nitrate to gaseous N_2).

The growth of phytoplankton is the key process in eutrophication and it is therefore of great importance to understand the interacting processes regulating its growth.

Primary production has been measured in great detail in many large lakes. This process represents the synthesis of organic matter, and can be summarized as follows:



This equation is necessarily a simplification of the complex metabolic pathway of photosynthesis, which is dependent on sunlight, temperature and the concentration of nutrients. The composition of phytoplankton is not constant (note that Table 1.5 only gives an average concentration), but reflects to a certain extent the chemical composition of the water. If, for example, the phosphorus concentration is high, the phytoplankton will take up relatively more phosphorus - termed the luxury uptake.

The sequence of events leading to eutrophication often occurs as follows. Oligotrophic waters often have a N:P ratio of more than or equal to 10, which means that phosphorus is less abundant relative to the needs of phytoplankton than nitrogen. If sewage is discharged into the lake the ratio will decrease since, the N:P ratio for municipal waste water is about 3:1. Consequently, nitrogen will be less abundant than phosphorus relative to the needs of phytoplankton. Municipal waste water contains typically $30 \text{ mg l}^{-1} \text{ N}$ and $10 \text{ mg l}^{-1} \text{ P}$. In this situation, however, the best remedy for the excessive algal growth is not necessarily to remove nitrogen from the sewage, because the mass balance might show that nitrogen-fixing algae would produce an uncontrollable input of nitrogen into the lake.

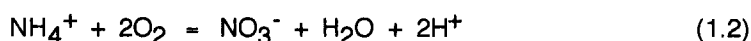
It is necessary to set up a mass balance for the nutrients. This will often reveal that the input of nitrogen from nitrogen-fixing blue green algae, dry and wet deposition and tributaries is already contributing too much to the mass balance for any effect to be produced by nitrogen removal from the sewage. On the other hand the mass balance may reveal that most of the phosphorus input (often more than 95%) comes from the sewage, and so demonstrates that it is better management to remove phosphorus from the sewage rather than nitrogen. It is, therefore not a matter of which nutrient is limiting, but which nutrient can most easily be made to limit the algal growth.

These considerations have implied that the eutrophication process can be controlled by a reduction in the nutrient budget. For this purpose a number of eutrophication models have been developed, which take a number of processes into account. For details, see Jørgensen (1976), Jørgensen et al., (1978), Jørgensen et al., (1986) and Jørgensen (1988).

Generally however, it is possible to conclude that reduction of the

eutrophication in aquatic ecosystems requires a solution which is tailored to the particular case. Some will require reduction in the phosphorus inputs, some in the nitrogen inputs and some will require reductions in inputs of both nutrients. Nitrogen reductions seem to be most important for the eutrophication control in lakes and marine environment during the summer time, while spring run-off often transfers large amounts of nitrogen to the aquatic environment, making it difficult to control nitrogen as the limiting factor.

Maintenance of a high **oxygen concentration** in aquatic ecosystems is crucial for survival of the higher life forms in aquatic ecosystems. At least 5 mg / l is needed for many fish species. At 20-21 °C this corresponds to 5/9 = 56% saturation. The oxygen concentration is influenced by several factors, of which the most important are the decomposition of organic matter, and the nitrification of ammonia (ammonium) according to the following process:



Ammonia is formed by decomposition of organic matter. Proteins and other nitrogenous organic matter are decomposed to simpler organic molecules such as amino acids, which again are decomposed to ammonia. Urea and uric acid, the waste products from animals, are also broken down to ammonia. Nitrifying microorganisms can use ammonia as an energy source, as the oxidation of ammonia is an energy-producing process. This decomposition chain is illustrated in Fig. 1.6, where it can be seen that the free energy (chemical energy) is decreased throughout the chain.

The nitrification process can be described by the following first order kinetic expression:

$$\frac{dN}{dt} = -K_n * t \quad (1.3)$$

$$\ln \frac{N_t}{N_o} = -K_n * t \quad (1.4)$$

or

$$N_t = N_0 * e^{-K_n * t} \quad (1.5)$$

where

N_t = concentration of ammonium at time = t

N_0 = concentration of ammonium at time = 0

K_n = rate constant, nitrification

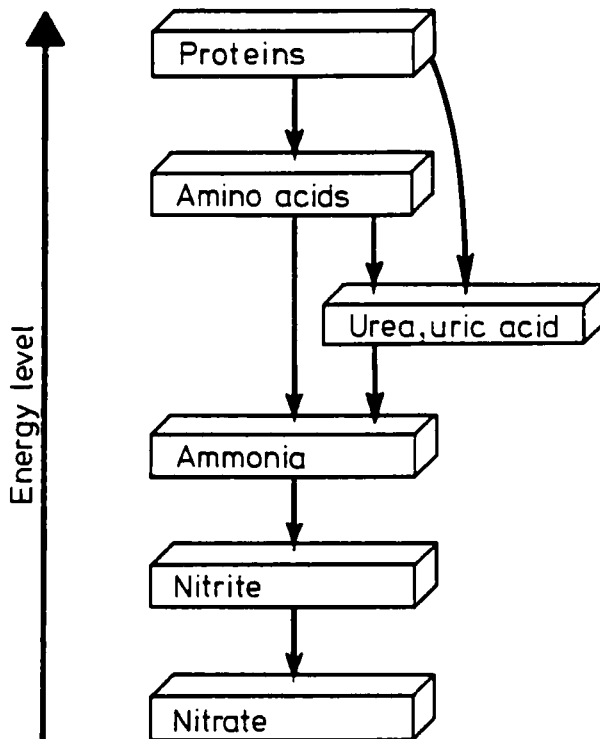


Figure 1.6. Decomposition chain: from protein to nitrate.

N_t and N_0 may here be expressed by the oxygen consumption corresponding to the ammonium concentration. Values for K_N and N_0 are given for some characteristic cases in Table 1.4. K_n is dependent on the temperature as illustrated in the following expression:

$$K_n \text{ at } T = (K_n \text{ at } 20^\circ\text{C}) * K_T^{(T-20)} \quad (1.6)$$

where T = the temperature ($^\circ\text{C}$), K_T = a constant in the interval 1.06-1.08.

Table 1. 4.

Characteristic values, K_n , and N_0 (20°C)

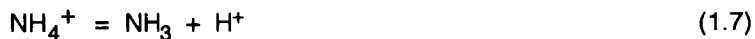
	K_n (1 / 24h)	N_0
Municipal waste water	0.15-0.25	80-130
Mechanical-treated municipal waste water	0.10-0.25	70-120
Biological-treated municipal waste water	0.05-0.20	60-120
Potable water	0.05	0-1
River water	0.05-0.10	0-2

The relation between ammonium concentration and oxygen consumption according to (1.2) may be calculated as $(2 * 32)/14 = 4.6 \text{ mg O}_2 \text{ per mg NH}_4^+ - \text{N}$, but due to bacterial assimilation of ammonia this ratio is reduced to $4.3 \text{ mg O}_2 \text{ per mg NH}_4^+ - \text{N}$ in practice.

It is easy to see from the values of ammonium nitrogen or total nitrogen in municipal waste water that the oxygen consumption for nitrification is significant. If a total nitrogen concentration of 28 mg N / l is presumed, the oxygen consumption for nitrification becomes 128 mg / l , which may be compared with the BOD5 of municipal waste water on about $200 - 250 \text{ mg / l}$. The growth of nitrifying microorganisms is, however, relatively slow, which implies that the nitrification is not completed in aquatic ecosystems with short retention times. Ecological models (Jørgensen, 1988 and Jørgensen and Johnsen, 1989) can be used to characterize the role of the oxygen depletion caused by nitrification and therefore the

consequences for the aquatic life of nitrifying ammonium in waste water before discharge. The conclusion will, however, generally be that nitrification of municipal waste water is required for all discharge into inland water ecosystems. Many industrialized countries have therefore introduced an effluent standard for ammonium and organic nitrogen concentrations.

While nutrients are necessary for plant growth, they may produce a deterioration in life conditions for other forms of life. **Ammonia is extremely toxic to fish**, while ammonium, the ionized form is harmless. As the relation between ammonium and ammonia is dependent on pH: (see also Section 7.1)



$$\text{pH} = \text{pK} + \log \{ [\text{NH}_3] / [\text{NH}_4^+] \} \quad (1.8)$$

where $\text{pK} = -\log K$ and K = equilibrium constant for process (1.7).

The pH value as well as the total concentration of ammonium and ammonia is thus important. This is demonstrated in Table 1.5. This implies that the situation is very critical in many hypereutrophic lakes during the summer, when photosynthesis is most pronounced, as the pH increases when the acidic component CO_2 is removed or reduced by this process. The annual variations of pH in a hypereutrophic lake are shown in Fig. 1.7. pK is about 9.24 - 9.30 in distilled water at 18 - 25°C, but increases with increasing salinity. It implies that the concentrations shown in Table 1.5 are higher in sea water.

It is a clear conclusion from these considerations that ammonium discharge into aquatic ecosystems, in particular inland waters, is not desirable and that municipal waste water therefore must be nitrified before discharge.

The public health hazard is associated with nitrate in groundwater, which occurs due to leaching of nitrate; see Fig. 1.3. Nitrate in drinking water is associated with methemoglobinemia, which affects infants less than three months, because of their lack of an enzyme capable of oxidizing nitrite.

Table 1.5

Concentrations of ammonium nitrogen (ammonium + ammonia), in mg per.l, which contains an unionized ammonia concentration of 0.025 mg

NH₃ / l at various pH and temperatures

° C	pH = 7.0	pH = 7.5	pH = 8.0	pH = 8.5	pH = 9.0	pH = 9.5
5	19.6	6.3	2	0.65	0.22	0.088
10	12.4	4.3	1.37	0.45	0.16	0.068
15	9.4	5.9	0.93	0.31	0.12	0.054
20	6.3	2	0.65	0.22	0.088	0.045
25	4.4	1.43	0.47	0.17	0.069	0.039
30	3.1	1	0.33	0.12	0.056	0.035

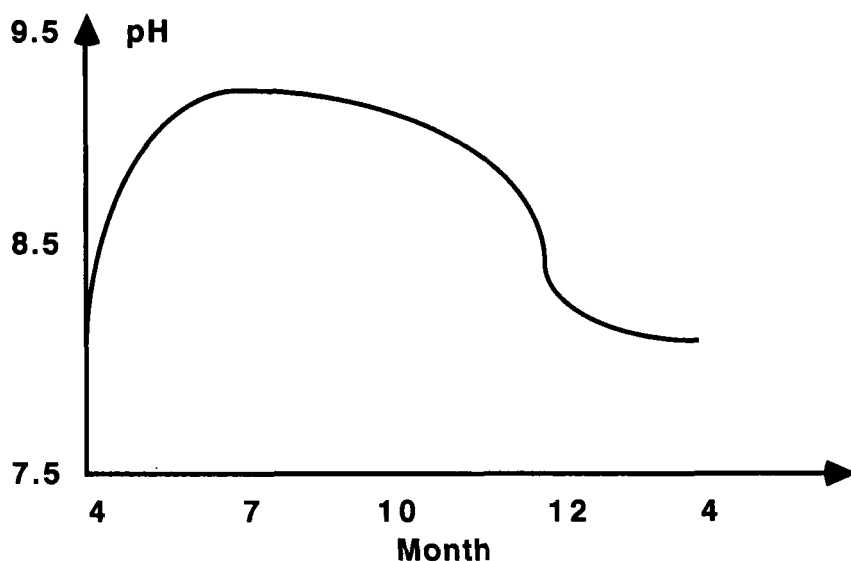


Figure 1.7. The seasonal variation in pH in a hypereutrophic lake (Lake Glumsø, Denmark).

When water with a high concentration of nitrate is used in preparing infant formulas, nitrate is reduced to nitrite in the stomach after ingestion. The nitrites react with hemoglobin in the blood to form methemoglobin, which is incapable of carrying oxygen in comparison to hemoglobin. The result is suffocation accompanied by bluish tinge to the skin, which explains the use of the term "blue babies" in conjunction with methemoglobinemia.

From 1945-1975 about 2000 cases of methemoglobinemia were reported in the U.S. and Europe with a mortality rate of 7-8%. Because of the difficulties in diagnosing the disease and because no reporting is required, the actual incidence may be many times higher (Kaufman, 1974).

WHO and most countries have set up standards for nitrate in drinking water. Typical standards are: U.S. 10 mg nitrate- N / l and in most European countries 30 - 100 mg nitrate / l.

1.5 Treatment Processes for the Removal of Nitrogen

In the past several years a number of processes have been developed with the specific purpose of transforming nitrogen compounds for removing nitrogen from waste water.

The processes considered in this book are presented as follows; in part B, the biological removal methods, nitrification and denitrification; and in part C, the physical and chemical methods, Stripping, Break-point Chlorination, Ion Exchange, Membrane Processes and Precipitation.

In determining which method is most suitable for a particular application, the following aspects must be considered:

- 1) Form and concentration of the nitrogen compounds in the process influent.
- 2) The required effluent quality of the waste water.
- 3) Other treatment processes to be applied for the removal of other compounds.
- 4) The construction and running costs for the process.
- 5) The reliability of the process.
- 6) The flexibility of the process.

As an short introduction to parts B and C of this text book, the following section will, present a brief description of the various nitrogen removal processes described. The process characteristics, compound selectivity, and normal range of efficiency are presented.

1.6 The Major Processes in the Removal of Nitrogen

The major processes considered in the removal of nitrogen in this text are: Biological nitrification and denitrification (Part B) and Stripping, Break-Point Chlorination, Ion Exchange, Membrane Processes and Precipitation (Part C). These processes are technically and economically the most suitable at the present time.

Biological nitrification and denitrification

The principal effect of the nitrification process is to transform ammonia-nitrogen into nitrate by the use of nitrifying bacteria under aerobic conditions. Denitrification converts nitrate to nitrogen gas by use of denitrifying bacteria, under anoxic conditions. The efficiency of the nitrification process depends on the extent to which organic nitrogen is transformed into ammonia-nitrogen. Chapters 3 and 4 present, in detail, the different factors governing the nitrification and denitrification processes. Nitrification can be carried out in conjunction with secondary treatment (combined oxidation of organic material and nitrification) or as a tertiary treatment (separate stage nitrification) see Chapters 5 and 6. In both cases, either attached-growth reactors or suspended-growth processes can be used. Denitrification can also be carried out in either attached or suspended growth reactors. For the denitrification process to be carried out, a carbon source and an anoxic environment are required. Chapter 5 explains the biofilm theory used in the attached-growth technology and shows the application of some of the most frequently used attached-growth processes: trickling filter, rotating biological contactor and submerged filters. The application of the submerged filter is mainly described as a case study on the use of clinoptilolite as a submerged biobed, for the *simultaneous* nitrification and denitrification processes. Chapter 6 shows the practical use of the activated sludge process.

The overall removal efficiency in a nitrification and denitrification plant ranges from 70 to 95 per cent for tertiary treatment, and down to 10-20 per cent for secondary treatment. The costs of attached-growth biological removal plants are moderate compared with activated sludge plants.

Air stripping

The stripping process (Chapter 7) is used to remove volatile gases such as hydrogen sulfide, hydrogen cyanide and ammonia by blowing air through the waste water. The process is, therefore, to be considered as a transfer of a compound from a liquid phase to a gas phase. The basic principle of this process of nitrogen removal is illustrated in Figure 7.1.

The rate at which ammonia can be removed by air stripping is highly dependent on pH, because the exchange between the two forms, ammonium which is the ion form, and ammonia, which is a highly water soluble gas, is an acid base reaction. High efficiency in ammonia removal requires adjustment of the pH to about 11.0 prior to the stripping process.

The principal problems associated with ammonia stripping are its inefficiency in cold weather, required shut down during freezing conditions, and the formation of calcium carbonate in the air stripping tower.

The best practical results are achieved by the use of countercurrent packed towers (Ødegaard 1988). As the amount of air needed is roughly independent of the ammonia concentration, the cost per kg of ammonia removed is much lower at high ammonia concentrations. Stripping is, therefore, most attractive for industrial waste water with a high concentration of ammonium.

Break-Point Chlorination

Breakpoint chlorination is accomplished by addition of chlorine to the waste stream in an amount sufficient to oxidize ammonia-nitrogen into nitrogen gas (see Chapter 8). In practice, approximately 9-10 mg/l of chlorine is required for every 1 mg/l of ammonia-nitrogen. In addition, the acidity produced by the process (equation 8.2) must be neutralized. The chemicals add greatly to the total dissolved solids and result in substantial operating expenses.

The method has, however, two advantages:

- 1) By using sufficient chlorine it is possible to obtain effluents reduced in ammonia concentration to near zero.
- 2) The low spatial requirement makes it particularly suitable for certain applications, including addition to an existing facility, where nitrogen removal is required, but space is limited. Nitrite and nitrate are not removed by this method, which is a major disadvantage.

Ion Exchange

Ion exchange is a process in which ions on the surface of a solid are exchanged for ions of a similar charge in a solution with which the solid is in contact (Chapter 9). When all the exchange sites have been replaced, the resin must be regenerated.

Both natural solids, such as the natural clay mineral *clinoptilolite*, and synthetic ion exchange, can be used in the removal of ammonium ions.

pH control is crucial in the ion exchange process, as the form of the ion exchanger is dependent on the pH, see equations (9.1) to (9.3), unless the ion exchanger is a strong acid or base, and also because the form of the ions to be taken up is dependent on pH. The optimum ammonium exchange by clinoptilolite occurs within an influent pH range of 4 to 8. If the pH drops below this range, hydrogen ions begin to compete with ammonium for the available ion exchange capacity. As the pH increases above 8, a shift in the ammonia-ammonium equilibrium toward ammonia begins. Consequently, any operation outside the pH range 4 to 8 results in a decrease in the exchange capacity. Neither ammonia, nitrate or nitrite or organic nitrogen can be bound to clinoptilolite.

Ion Exchange is very effective in removing ammonium from waste water, but is, however, not a very attractive treatment method for removal of *high ammonium* concentrations. This is because the regeneration becomes more frequent. The operational costs, therefore, become high due to the elution frequency. Using clinoptilolite clay as matrix in a submerged bio-bed as presented in Chapter 5, diminishes this problem because the micro-organisms (nitrifying bacteria) regenerate the ion exchanger. A combination of ion-exchange and nitrification seems, therefore, to be attractive, as presented in Chapter 5.

Membrane Processes

Membrane separation, electrodialysis, reverse osmosis, ultrafiltration and other such processes play an increasingly important role in the treatment of waste water (Chapter 10).

A *membrane* is defined as a phase that can act as a barrier between other phases. It can be a solid, a solvent-swollen gel, or even a liquid.

Osmosis is defined as the spontaneous transport of a solvent from a diluted solution to a concentrated solution across a semi-permeable membrane. At a certain

pressure, the so-called osmotic pressure, equilibrium is reached. The osmotic pressure varies with the concentration and the temperature, and depends on the properties of the solution.

Nitrogen compounds treated in such systems are mainly in the form of ammonium or nitrate. Electrodialysis can be expected to remove about 40 per cent of these forms; in reverse osmosis, 80 per cent.

Today the application of membrane techniques is still limited, but waste water engineers and scientists in the field of membrane processes expect a rapid growth in the use of these technologies in the very near future.

Precipitation

Precipitation, in a strictly chemical sense, is the transition of a substance from the dissolved state to the non-dissolved state by the addition of other reagents that lead to the formation of precipitates.

Most nitrogen compounds are, unfortunately, readily dissolved in water, which implies that precipitation cannot be used as an easy solution to the problem of nitrogen removal. Nitrogen removal by the use of precipitation may, however, be carried out by the two processes shown as equations (11.33) and (11.34) in Chapter 11. The nitrogen needs to be in form of either proteins or ammonium.

The application of precipitation in the removal of nitrogen requires a three-step plant. Addition of chemicals is the first step. The second step is flocculation and as the third step follows some sort of separation process to separate the suspended matter (precipitate) from the clear water phase.

1.7 Summary

Table 1.6 summarizes the effect, advantages and disadvantages of the various processes presented in this volume for the removal of nitrogen from waste water. The effect that each process has on each of the three major forms of nitrogen, organic nitrogen, ammonium and nitrate are shown. Average removal percentages which can be expected from the different processes are also indicated.

Table 1.7 shows an estimation of costs for the different processes compared with the efficiency. The processes are divided into three categories; expensive, moderate and low cost processes, because it is difficult to estimate exact figures. Also, the efficiency is divided into low, medium and high content of nitrogen in the influent

waste water.

The overall removal in a particular treatment plant will depend on the types of unit processes employed and their relation to each other.

In general, the reliability of a given treatment process is higher for the physico-chemical treatment processes than for the biological treatment processes.

On the other hand, costs are generally higher for the physico-chemical methods than for the biological methods. It is, therefore, important to find a balance between costs and reliability for the process, used for each of the types of waste water. This can only be found by conducting pilot-plant studies of the specific waste water before deciding which application is to be used.

Table 1.6 The effect, advantages and disadvantages of various treatment processes on nitrogen compounds

Treatment process	Effect on nitrogen form			Removal of total nitrogen entering process %	Process Advantages	Process Disadvantages	Reference Chapter
	Organic N	NH ₃ /NH ₄ ⁺	NO ₃ ⁻				
Biological treatment Processes							
Attached-growth processes							
- Nitrification (separate stage)	Limited effect	→NO ₃ ⁻	No effect	70-90	Good protection against most toxicants. Stable operation. Stability not linked to secondary clarifier as organisms are attached to media.	Greater number of unit processes required than for combined carbon oxidation and nitrification.	5
Nitrification (combined oxidation and nitrification)	Limited effect	→NO ₃ ⁻	No effect	5-20	Combined treatment of carbon and ammonia in a single stage not linked to a secondary clarifier as biomass attached to media.	No protection against toxicants. Only moderate stability of operation. Cold weather operation impracticable in most cases.	5

Table 1.6 (continued)

Treatment process	Effect on nitrogen form			Removal of total nitrogen entering	Process Advantages	Process Disadvantages	Reference Chapter
	Organic N	$\text{NH}_3/\text{NH}_4^+$	NO_3 process %				
Denitrification using methanol following a nitrification stage.	No effect	No effect	80-90% removal	70-95	Denitrification rapid; demonstrated stability of operation; stability not linked to clarifier as organisms on media. High degree of nitrogen removal possible.	Methanol required. Greater number of unit processes required for nitrification/denitrification than in combined systems.	5
Simultaneous nitrification and denitrification (SND).	No effect	$\rightarrow \text{NO}_3^-$	$\rightarrow \text{N}_2$	60-80	Conversion of ammonium to gaseous nitrogen. Rapid nitrogen removal compared with suspended cultures. Low space required for application.	Still only possible on pilot plant scale. Fluctuation in stability. Very sensitive to high BOD_5 in influent.	5

Table 1.6 (continued)

<i>Treatment process</i>	<i>Effect on nitrogen form</i>			<i>Removal of total nitrogen entering process %</i>	<i>Process advantages</i>	<i>Process disadvantages</i>	<i>Reference Chapter</i>
	<i>Organic N</i>	<i>NH₃/NH₄⁺</i>	<i>NO₃⁻</i>				
Combined carbon oxidation nitrification/denitrification in suspended-growth reactor using endogenous carbon source.	No effect	No effect	80-90% removal	5-20	No methanol required; lesser number of unit processes required; better control of filamentous organisms in activated-sludge process possible; single basin can be used; adaptable to sequencing batch reactor; process can be adapted to include biological phosphorus removal.	Denitrification occurs at very slow rates; longer detention time and much larger structures required than methanol-based system; stability of operation linked to clarifier for biomass return; difficult to optimize nitrification and denitrification separately; biomass requires sufficient dissolved-oxygen level for nitrification to occur; less nitrogen removal than methanol based system.	6
Combined carbon oxidation nitrification/denitrification in suspended-growth reactor using waste water carbon source.	No effect	No effect	80-90% removal	5-20	No methanol required; lesser number of unit processes required; better control of filamentous organisms in activated-sludge process possible; single basin can be used; adaptable to sequencing batch reactor; process can be adapted to include biological phosphorus removal.	Denitrification occurs at slow rates, longer detention time and larger structures required than methanol-based system; stability of operation linked to clarifier for biomass return; difficult to optimize nitrification and denitrification separately; biomass requires sufficient dissolved-oxygen level for nitrification to occur; less nitrogen removal than methanol-based system.	6

Table 1.6 (continued)

<i>Treatment process</i>	<i>Effect on nitrogen form</i>			<i>Removal of total nitrogen entering process %</i>	<i>Process advantages</i>	<i>Process disadvantages</i>	<i>Reference Chapter</i>
	<i>Organic N</i>	<i>NH₃/NH₄⁺</i>	<i>NO₃⁻</i>				
Suspended-growth denitrifiers using methanol following a nitrification stage.	No effect	No effect	80-90% removal	70-95	Denitrification rapid; small structures required; demonstrated stability of operation; few limitations in treatment sequence options; excess methanol oxidation step can be easily incorporated; each process in system can be separately optimized; high degree of nitrogen removal possible.	Methanol required; stability of operation linked to clarifier for biomass return; greater number of unit processes required for nitrification/denitrification than in combined systems.	6
Bacterial assimilation	No effect	40-70% removal	Slight	30-70			3

Tabel 1.6 (continued)

<i>Treatment process</i>	<i>Effect on nitrogen form</i>			<i>Removal of total nitrogen entering process %</i>	<i>Process Advantages</i>	<i>Process Disadvantages</i>	<i>Reference Chapter</i>
	<i>Organic N</i>	<i>NH₃/NH₄⁺</i>	<i>NO₃⁻</i>				
Denitrification using methanol following a nitrification stage.	No effect	No effect	80-90% removal	70-95	Denitrification rapid; demonstrated stability of operation; stability not linked to clarifier as organisms on media. High degree of nitrogen removal possible.	Methanol required. Greater number of unit processes required for nitrification/denitrification than in combined systems.	5
Simultaneous nitrification and denitrification (SND).	No effect	→NO ₃ ⁻	→N ₂	60-80	Conversion of ammonium to gaseous nitrogen. Rapid nitrogen removal compared with suspended cultures. Low space required for application.	Still only possible on pilot plant scale. Fluctuation in stability. Very sensitive of high BOD ₅ in influent.	5

Table 1.6 (continued)

Treatment process	Effect on nitrogen form			Removal of total nitrogen entering process %	Process advantages	Process disadvantages	Reference Chapter
	Organic N	$\text{NH}_3/\text{NH}_4^+$	NO_3^-				
Suspended growth processes							
-Nitrification (separate stage)	Limited effect	$\rightarrow \text{NO}_3^-$	No effect	70-90	Good protection against most toxicants. Stable operation. Low effluent ammonia possible.	Sludge inventory requires careful control when BOD_5/TKN ratio is low. Stability of operation linked to operation of secondary clarifier for biomass return.	6
-Nitrification (combined oxidation and nitrification).	Limited effect	$\rightarrow \text{NO}_3^-$	No effect	5-20	Combined treatment of carbon and ammonia in a single stage. Inventory control of mixed-liquor due to high BOD_5/TKN ratio.	No protection against toxicants. Only moderate stability linked to operation of secondary clarifier for biomass return. Large reactors required in cold weather.	6

Table 1.6 (continued)

Treatment process	Effect on nitrogen form			Removal of total nitrogen entering process %	Process advantages	Process disadvantage	Reference Chapter
	Organic N	NH ₃ NH ₄ ⁺	NO ₃ ⁻				
Physical and chemical treatment processes.							
Air stripping (Air)	No effect	60-95% removal	No effect	50-90	Process can be controlled for selected ammonia removals. Most applicable if required seasonally in combination with lime system for phosphorus removal. Process may be able to meet total nitrogen standards. Not sensitive to toxic substances.	Process is sensitive to temperature. Ammonia solubility increases with lower temperatures. Air requirements also vary. Fogging and icing occur in cold weather. Ammonia reaction with sulphur dioxide may cause air pollution problems. Process usually requires lime for pH control, thereby increasing treatment cost and lime-related operating and maintenance problems. Carbonate scaling of packing and piping. Potential noise and aesthetic problems.	7

Table 1.6 (continued)

<i>Treatment process</i>	<i>Effect on nitrogen form</i>			<i>Removal of total nitrogen entering process %</i>	<i>Process advantages</i>	<i>Process disadvantages</i>	<i>Reference Chapter</i>
	<i>Organic N</i>	<i>NH₃/NH₄⁺</i>	<i>NO₃⁻</i>				
Break-point chlorination	Uncertain	90-100% removal	No effect	80-95	With proper control, all ammonia nitrogen can be oxidized. Process can be used following other nitrogen removal processes for fine tuning of nitrogen removal. Concurrent effluent disinfection. Limited space requirement. Not sensitive to toxic substances and temperature. Low capital costs. Adaptable to existing facility.	May produce high chlorine residuals that are toxic to aquatic organisms. Wastewater contains a variety of chlorine-demanding substances which increase cost of treatment. Process is sensitive to pH, which affects dosage requirements. Trihalomethane formation may impact quality of water supplies. Addition of chlorine raises effluent TDS. Process may not be able to meet total nitrogen standards. Requires careful control of pH to avoid formation of nitrogen trichloride gas. Requires highly skilled operator.	8

Table 1.6 (continued)

Treatment process	Effect on nitrogen form			Removal of total nitrogen entering process %	Process advantages	Process disadvantages	Reference Chapter
	Organic N	$\text{NH}_3/\text{NH}_4^+$	NO_3^-				
Ion-Exchange							
- Ammonium	Slight, uncertain	80-97% removal	No effect	70-95	Can be used where climatic conditions inhibit biological nitrification and where stringent effluent standards are required. Produces a relatively low TDS effluent. Produces a reclaimable product (aqueous ammonia). Process may be able to meet total nitrogen standards. Ease of product quality control.	Organic matter in effluent from biological treatment can cause resin binding. Pre-treatment by filtration is usually required to prevent the build up of excessive headloss due to suspended solids accumulation. High concentration of other cations will reduce ammonia removal capability. Regeneration recovery may require the addition of another unit process (e.g., gas stripping). High capital and operating costs. Regeneration products must be disposed of. Requires highly skilled operator.	9
- Nitrate	Slight effect	Slight effect	75-90				

Table 1.6 (continued)

Treatment process	Effect on nitrogen form			Removal of total nitrogen entering process %	Process advantages	Process disadvantages	Reference Chapter
	Organic N	NH ₃ /NH ₄ ⁺	NO ₃ ⁻				
Membran processes							
Electrodialysis	100% of suspended organic N removed	30-50% removed	30-50% removed	40-50	High degree of nitrogen removal. Removes all forms of nitrogen.	Chemical precipitation of salts with low solubility on the membrane surface, clogging of the membrane by the residual colloidal organic matter in waste water effluents usually about 10 per cent of the feed volume, is required to wash the membrane continuously.	10

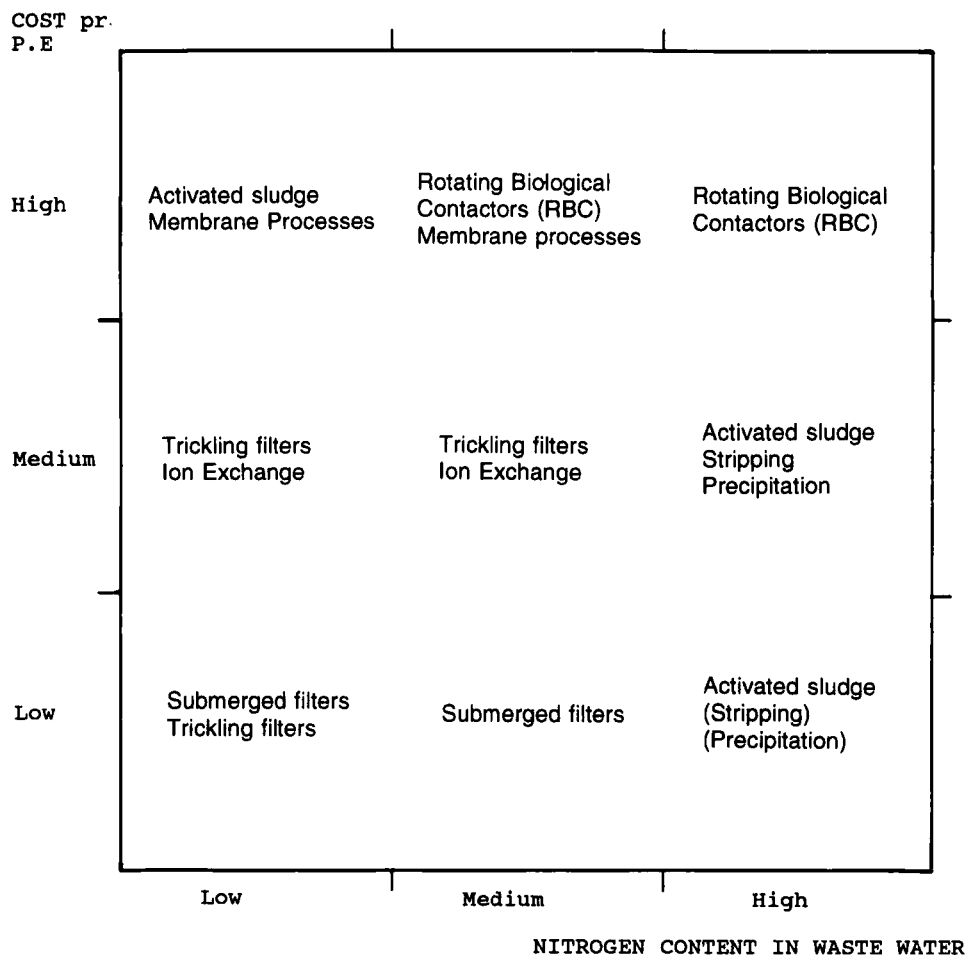
Table 1.6 (continued)

Treatment process	Effect on nitrogen form			Removal of total nitrogen entering process %	Process advantages	Process disadvantages	Reference Chapter
	Organic N	NH₃/NH₄⁺	NO₃⁻				
Reverse Osmosis	60-90% removed	60-90% removed	60-90% removed	80-90	High amount of nitrogen removed. Removes all forms of nitrogen.	Membrane elements in the reverse osmosis unit can be fouled by colloidal matter. Pre-treatment of a secondary effluent by chemical clarification and some sort of filtration is usually necessary. Iron and manganese in influent can provoke decreased scaling potential. Regular cleaning of membrane necessary.	10
Precipitation	50-70% removed	Slight effect	Slight effect	20-30		Results in net increase in total dissolved solids of effluent. Large amount of sludge requiring treatment. Only organic nitrogen can be easily removed.	

Partly adapted from: EPA (1975),
Metcalf and Eddy (1991),
WPCF Nutrient Control Manual (1983),
Weston (1984).

Table 1.7.

The building and running costs of various treatment processes compared with efficiency and reliability of the process. The building and running costs are indicated as expensive, moderate or low.



P.E = Personal Equivalent

1.8 Some Useful Definitions

To understand the concept of biological treatment processes, it will be helpful to know the following definitions.

Aerobic processes are biological treatment processes that occur in the presence of oxygen. *Anaerobic processes* are biological treatment processes that occur in the absence of oxygen.

Anoxic denitrification is the process by which nitrate-nitrogen is converted biologically into nitrogen gas in the absence of oxygen. This process is also known as anaerobic denitrification.

Biological nutrient removal is the term applied to the removal of nitrogen and phosphorus in the biological treatment processes.

Nitrification is the biological process by which ammonia is converted first to nitrite and then to nitrate.

Denitrification is the biological process by which nitrate is converted into nitrogen gas.

Substrate is the term for the organic matter or nutrients that are converted during the biological treatment or that may be limiting in the biological treatment.

Suspended-growth processes are the biological treatment processes in which the microorganisms responsible for the conversion of the organic matter or other constituents in the waste water to gases and cell tissue are maintained in suspension within the liquid.

Attached-growth processes are the biological treatment processes in which the microorganisms responsible for the conversion of the organic matter or other constituents in the waste water to gases and cell tissue are attached to some inert medium such as rocks, slag, or specially designed ceramic or plastic materials. Attached-growth treatment processes are also known as fixed-film processes.

BOD₅ (Biological oxygen demand): The determination of the biochemical oxygen demand (BOD) is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of waste water, effluents, and polluted waters during 5 days. The test measures the oxygen required for the biochemical degradation of organic material and the oxygen used to oxidize inorganic material such as sulphides and iron. It may also be used to oxidize reduced forms of nitrogen unless their oxidation is prevented by an inhibitor. The method consists of placing a sample in a full, airtight bottle and incubating the bottle under specified conditions for a specific time. Dissolved oxygen (DO) is measured initially and after the incubation. The BOD is computed from the difference between initial

and final DO.

COD (chemical oxygen demand): The chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source COD can be related empirically to BOD, organic carbon or organic matter content.

Ammonia (NH_3) is a gas that is very soluble in water. Ammonia is a base.

Ammonia is produced in nature when any nitrogen-containing organic material decomposes in the absence of air.

Ammonia is a colourless gas with an irritating odour. Gaseous ammonia has a vapor pressure of about 10 atmospheres at 25°C, and is readily liquefied, giving a colourless liquid that boils at minus 33°C.

Ammonium is a weak base, ammonia readily accepts protons from acids and hydronium ions, forming salts of the ammonium ion (NH_4^+).

Ammonium-nitrogen or ammonium-N: both terms are used to indicate that the nitrogen is calculated as 1 mole of ammonium-N equal to 14 g of ammonium-N. It convenient to calculate from one nitrogen form to another using this term.

Nitrate: (NO_3^-) Is a substrate for the denitrification process.

Nitrate-N: as for ammonium-N

Nitrite: (NO_2^-) In the gas phase this exists in equilibrium with the colourless dimer N_2O_4 . When it dissolves in water, nitrogen dioxide disproportionates and forms nitric acid. It is a component of the nitrification process.

Nitrite-N: as for ammonium-N