

# The Chemical and Biochemical Reactions of Compounds with Sulpha, Ammonia, and Organic Compounds From Water in Aerobic and Anaerobic Conditions

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**Abstract** - The current investigation focuses on the chemical and biological interactions between chemicals and sulfa, ammonia, and organic molecules from water under aerobic and anaerobic circumstances. Investigating the chemical and biological interactions of chemicals with sulfa, ammonia, and organic molecules is the primary goal of this study. In order to extract hydrogen sulfide from groundwater, techniques and materials were used. Hence, the process was used to describe a physical phenomenon in which gas molecules exchange along the gas-liquid boundary between the liquid and gaseous phases. Anaerobic processes dominated the nitrogen cycle, as shown by the analysis of the data on the spatiotemporal dynamics of the nitrogen forms and concentrations in the low-sulfide, ferro-manganese meromictic subarctic lake.

The predominant form of mineral nitrogen shifts when the Red/Ox conditions change. The predominant mineral form of nitrogen switches between oxidized (NO<sub>3</sub>) and reduced (NH<sub>4</sub>). This phenomenon may be a result of the waterbody's iron-manganese kind of Meromixia. Manganese oxide (MnO<sub>2</sub>) functions as an oxidizing agent in the anaerobic oxidation of ammonium with the generation of nitrates under conditions of high manganese and ammonium concentrations. The biogeochemical nitrogen cycle offers such a chance, and the study's findings are more thorough research of these linkages should provide the required information on how the ecosystem functions. More research is needed in this field, especially for the assessment of the gas nitrogen cycle components like N<sub>2</sub> and N<sub>2</sub>O concentration. In this context, among other mechanisms, NO may be particularly significant.

**Keywords:** Chemical, Biochemical, Reactions of Compounds, Sulpha, Ammonia, Organic Compounds.

## Introduction

Nitrate contamination of ground and surface waters has become an increasingly serious problem in the U.S. As an

alternative to remove nitrate, the biological autotrophic denitrification process has been receiving more attention recently.

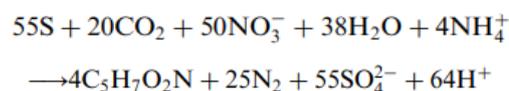
Two major advantages compared to biological heterotrophic processes:

- 1) No need for an external organic carbon source (methanol or ethanol) which lowers the cost and risk of the process.
- 2) Less sludge production, which minimizes the handling of sludge.

Studies on autotrophic denitrification processes have been divided into two major directions: Hydrogen-based and sulfur-based autotrophic denitrification.

Because it is difficult to handle hydrogen gas and generating hydrogen (e.g. from methanol) is expensive, recently much more attention has been on sulfur-based autotrophic denitrification.

Sulfur-based autotrophic denitrification processes utilize autotrophic denitrifiers, such as *Thiobacillus denitrificans* and *Thiomicrospira denitrificans*, to reduce nitrate or nitrite to nitrogen gas. Equation 1 is a stoichiometric equation, which shows an example of sulfur-based autotrophic denitrification.



Energy for autotrophic denitrifying microorganisms is derived from inorganic oxidation ± reduction reactions with elements such as hydrogen or various reduced-sulfur compounds (H<sub>2</sub>S, S, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>) as the electron donor. Autotrophic denitrifiers utilize inorganic carbon compounds (e.g. CO<sub>2</sub>, HCO<sub>3</sub><sup>2-</sup>) as their carbon source therefore, no organic carbon is needed as in heterotrophic denitrification.

The nitrogen from nitrate is reduced to nitrogen gas. Hydrogen ions are produced, meaning alkalinity is consumed by the reaction.

Some studies, made an innovative process using sulfur: limestone autotrophic denitrification for treatment of nitrate-contaminated surface water or wastewater was proposed and the feasibility of this SLAD process was evaluated using lab-scale batch reactors operating under both aerobic and anaerobic conditions. Based on the results of this study, the following conclusions can be made.

1. Autotrophic denitrification occurred in the batch reactors spiked with sulfur: limestone under either aerobic or anaerobic conditions at both high and low initial nitrate concentrations. Within one month, the population of autotrophic denitrifiers and the performance in the batch reactors with sediment and sulfur: limestone could reach the same level as similar reactors with an initial inoculation of autotrophic denitrifiers. Different sediments resulted in similar results, indicating that autotrophic denitrifiers exist widely in natural sediments.
2. Nitrate removal efficiency, sulfate production and biomass accumulation were usually higher under aerobic conditions than under anaerobic conditions.
3. Limestone was necessary to control the pH in SLAD batch reactors. The optimum sulfur: limestone ratio was 3:1 (v/v) in SLAD batch reactors. The extent and rate of nitrate removal depended on the alkalinity within SLAD batch reactors.

4. Bacterial counts indicated that both autotrophic denitrifiers and non denitrifying bacteria such as *T. thiooxidans* were involved in the SLAD process.
5. The sulfur-based autotrophic denitrification may be a replacement for heterotrophic denitrification in pond systems such as constructed wetlands or stabilization ponds due to the fact that no organic carbon source is needed in the SLAD process and autotrophic denitrifiers exist widely in natural sediments or soil.

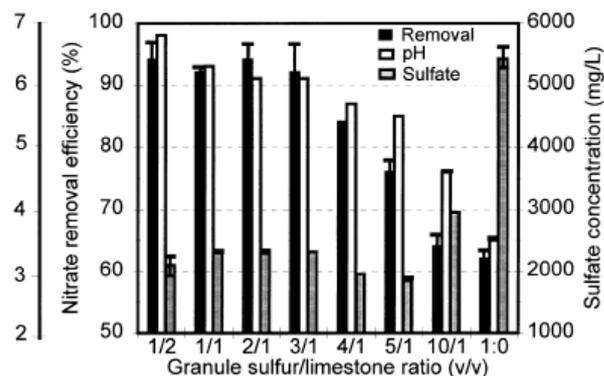


Figure 1: Effect of sulfur/limestone ratios on nitrate-nitrogen removal efficiency, pH and sulfate production. Data presented are average value of five replicates with the sample standard deviation. Bars on symbols indicate sample standard deviations, where absent, bars fall within symbols

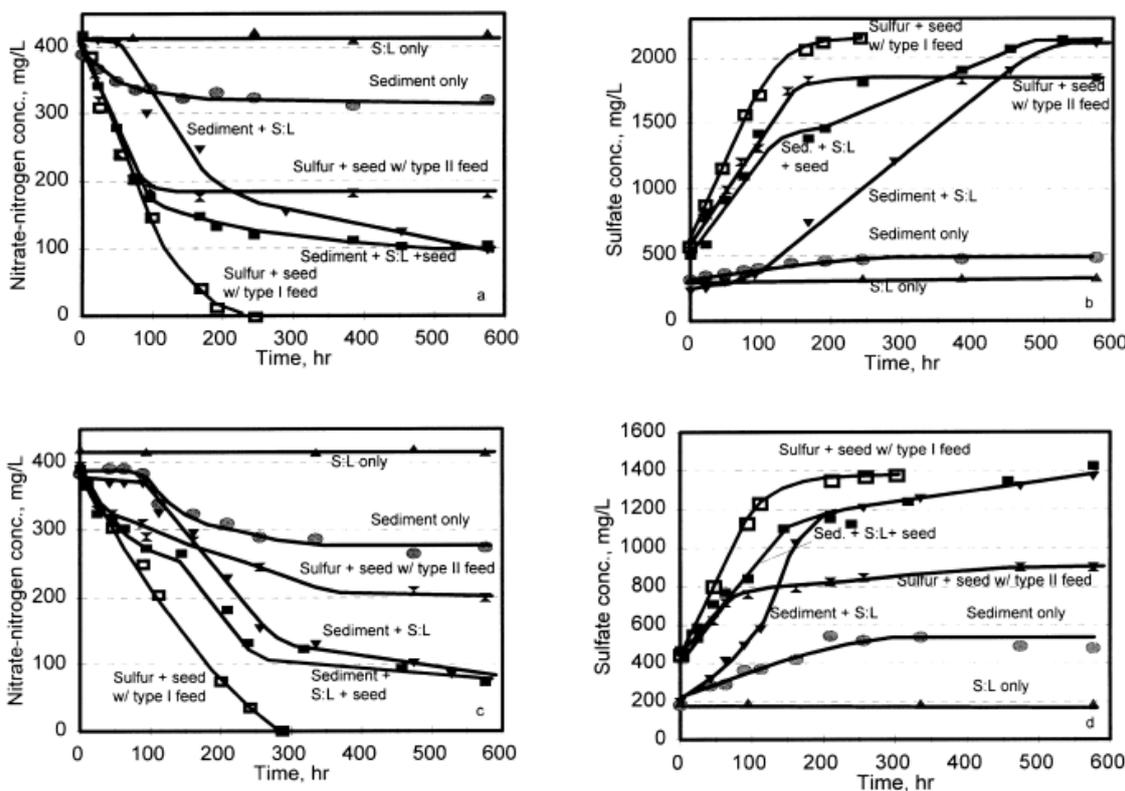


Figure 2: Time courses of nitrate±nitrogen and sulfate concentrations in batch reactors with high initial nitrate concentrations

Nitrate ± nitrogen sulfate concentrations in reactors under anaerobic conditions.

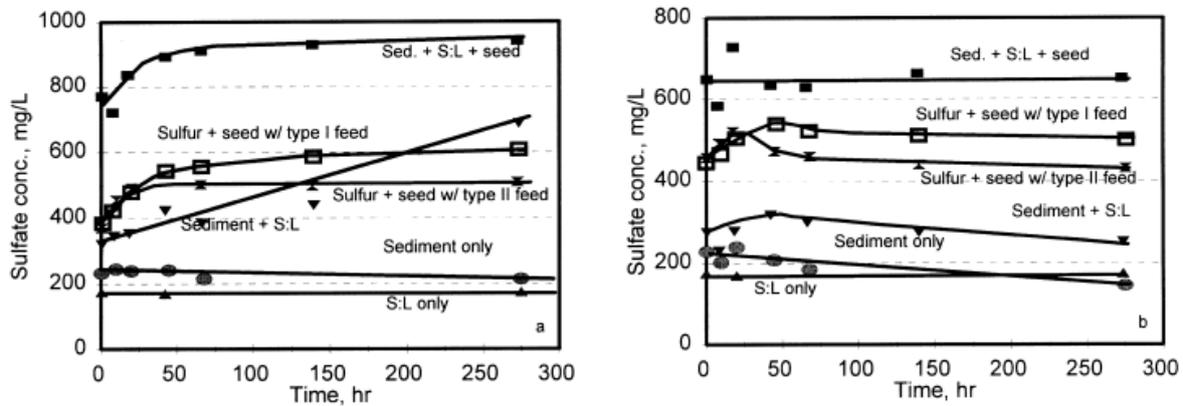


Figure 3: Time courses of sulfate concentrations in batch reactors with low initial nitrate concentrations under (a) aerobic conditions and (b) anaerobic conditions

### Distribution of Dissolved Nitrogen Compounds in the Water Column of a Meromictic Subarctic Lake

Lake Svetloe is located in the northern part of the boreal zone of European Russia (N 65°04.980, E 41°06.260), 65 km NNE of Arkhangelsk, and its watershed is not subjected to any direct anthropogenic influence. The maximum depth of the lake is 39 m.

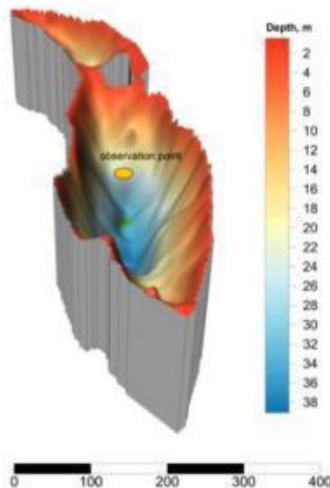


Figure 4: 3D model and bathymetric scheme of Lake Svetloe (scale bar in meters)

### Meromictic Subarctic Lake

Two pronounced relief depressions conditionally divide the lake into two parts with maximum depths of 39 and 20 m. In accordance with the meromictic status, three layers in the water column of the lake can be distinguished:

1. Mixolimnion (from 0 to 20 m), subject to convective mixing throughout the year and exhibiting aerobic conditions;
2. Chemocline, which is a transitional zone at a depth of 20–24 m, where microaerophilic conditions are formed;

in this zone, oxygen is produced by cyanobacteria and is actively consumed by other microorganisms.

3. Monimolimnion (from 25 m to the bottom), which is an anaerobic layer.
4. Lake Svetloe is characterized by a predominance of autochthonous dissolved organic matter with a low content of dissolved organic carbon (83.3 to 333.3  $\mu\text{M}$  and high water transparency (12 to 16 m Secchi depth). The water in the chemocline of Lake Svetloe has a faint pink color of varying intensity, due to the development of phototrophic communities inhabiting the boundary of the aerobic and anaerobic zones.

Studies of phototrophic bacteria in the communities of the chemocline zone have demonstrated that the dominant bacteria are oxygenic phototrophic cyanobacteria of the genus *Synechococcus* (maximum development at a depth of 23 m), which have positive chemotaxis to nitrogen sources and are capable of fixing molecular nitrogen .

### Meromictic Subarctic Lake: Sampling and Analyses

Sampling was carried out from 2010 to 2016 and included 30 survey campaigns during all hydrological seasons. Sampling was carried out over the entire water column from the surface to the bottom, with a step of 1 to 6 m. Water samples were taken at the deepest point of the lake approximately in the middle of the water body (N 65°4.9750, E 41°6.4970) from a PVC boat from May to October, and from the ice in winter (November to April) using a pre-cleaned polycarbonate horizontal water sampler (Aquatic Research Co, ID, New York, NY, USA).

A water sample for measurements of nitrite, nitrate, and total nitrogen was collected with a water sampler, to the tap of which a PVC outlet tube was attached. First, the bottle was rinsed 2–3 times with water from the sampler. Then the outlet tube of the sampler was lowered to the bottom of the bottle and began to fill it with water, passing several volumes of

water, that is, until the water that was in contact with the air in the bottle was entirely displaced. As such, most of the water sample was not in direct contact with the atmosphere. Then the polypropylene containers were closed with screw caps with an inner cone with slight compression of the bottle itself. This technique minimized the possibility of having residual air in the vial. It should be noted that when examining the water samples in the laboratory after transportation, we did not observe the precipitation of Fe (III) hydroxide, which would inevitably form during the oxidation of Fe (II) in a neutral to slightly alkaline medium. Chemical analysis of water samples was carried out on the day of sampling.

A water sample for the determination of N-NH<sub>4</sub> was taken in a separate glass container in the same way as for other forms of nitrogen described above. Fixation of N-NH<sub>4</sub> with reagents was carried out immediately after filling the bottle with water. In addition, at the beginning of the study of Lake Svetloe, we carried out a parallel determination of the content of N-NO<sub>2</sub> and N-NO<sub>3</sub> directly on the lake shore, and afterwards, the samples were delivered to the laboratory. The results of parallel measurements were reproducible within the uncertainty of analyses. The nitrogen forms' (N-NO<sub>2</sub>, N-NO<sub>3</sub>, N-NH<sub>4</sub>, TN) determinations were based on colorimetric assays. The indophenol blue method was used to measure ammonium (N-NH<sub>4</sub>), with a relative error of up to 12% and a detection limit of 1 μM. A spectrophotometric method employing sulfanilamide and N-(1-naphthyl) ethylenediamine dihydrochloride was used for the analysis of nitrite (N-NO<sub>2</sub>), with a relative error of up to 18% and a detection limit of 0.03 μM.

A spectrophotometric method employing sodium salicylate was chosen for the determination of nitrate (N-NO<sub>3</sub>), with a relative error of up to 18% and a detection limit of 7 μM. The total dissolved organic nitrogen (Norg) was evaluated from the difference between the total dissolved nitrogen (TN, persulfate oxidation, relative).

## Methods and materials used to remove hydrogen sulphide from groundwater

### Methods of removing H<sub>2</sub>S from water

#### Aeration (gas transfer)

Hydrogen sulphide can be removed by aeration (gas transfer) above the carbon filters, by cascade aeration, and in concentrations lower than 1-2 mg/L by spraying; in the same process, oxygen is simultaneously added to the water. The aeration aggregates used to remove H<sub>2</sub>S from Hanover's feed water are an example. The processes that take place in enclosed spaces, especially under pressure (which allow the processing of larger amounts of oxygen, as the pressure gets

higher) are far superior to aeration in open spaces (Wells, 1954).

H<sub>2</sub>S is much easier to remove from acidic waters. It is therefore advisable to acidify alkaline waters before applying simple aeration to them in order to remove H<sub>2</sub>S. After aeration at low pH, pH corrections will need to be applied to them in order to avoid aggressiveness. Chlorination after aeration prevents the removal of sulphur. (Höll, 1972)

H<sub>2</sub>S from groundwater is often removed at the same time as iron and manganese are removed and disappears almost completely after degassing operations (spray aeration, percolation through various materials (sand, coal, plastic pipes, etc.) in open air). In such situations, massive growths of bacteria characteristic of sulphur and iron occur. Sulphur bacteria (the most representative, *Beggipton alba*, form a chalky white deposit on the walls of degassers (McKinney, 1962). Beneath this deposit, oily black layers of putrid sludge rich in iron sulphide appear.

The treatment mechanism in the aeration process is primarily the oxidation of H<sub>2</sub>S, resulting in water and free sulphur. In some cases, free sulphur may interfere with other treatment processes. H<sub>2</sub>S can be removed much more efficiently by aerating the water, initially with a high concentration of CO<sub>2</sub>. Under these conditions, H<sub>2</sub>S removal is more favoured (Quasim, 2000), (Scott, 1971), (AWWA, 1990).

#### Gas transfer

The process is a physical phenomenon by which gas molecules are exchanged between the liquid and gaseous phases at the gas-liquid interface. This change leads to an increase in gas concentration in the liquid phase as long as this phase is not saturated with that gas under certain conditions, such as pressure, temperature, and a decrease in gas concentration when the liquid phase is supersaturated (when desorption, precipitation or stripping of that gas occurs). In most cases, in the process of gas transfer, the gaseous phase is represented by air, and the liquid phase by water (and its constituents). This gas transfer is caused by bringing air into contact with water, i.e. by aeration. The purpose of aeration and gas transfer covers a wide range of technological operations. The introduction of oxygen into a body of water by aeration and the desorption of gases dissolved in water are processes based on almost natural phenomena:

- The release of oxygen produced from the growth of algae (night-time respiration) to values above the value of concentrations at saturation;
- The release of odour and taste producing substances - volatile substances whose concentration in the air is low

enough to maintain a significant concentration in the water;

- The release of methane, hydrogen sulphide at water surfaces or sediment deposits, under anaerobic conditions;

While the aeration and gas transfer processes mentioned above play an important role in the natural stabilization of water pollutants, another important part of these types of technological operations applies to:

- Introduction of oxygen in groundwater for the oxidation of iron and manganese in order to remove them;
- Introduction of oxygen in wastewater, as part of the biological treatment processes.

The aeration techniques mentioned above also apply to the release of gases dissolved in water, which deteriorate the water quality in terms of corrosion problems of water distribution networks or tanks, as well as problems of odour or taste of water. Specific operations of this type are as follows:

- Removal of carbon dioxide for chemical stabilization of water (adjustment or control of the calcium carbonate balance with respect to calcium.
- $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{HCO}_3)_2$
- Removal of  $\text{H}_2\text{S}$  in order to eliminate the taste and odour of water and in order to improve the corrosion of metals or the disintegration of concrete;
- Removal of methane in order to prevent fires and explosions;
- Removal of ammonia.

A final category of technological operations for water treatment based on gas transfer is that in which the water is not exposed to air, but to a pure gas or to air mixed with another gas, or to an air-gas mixture at pressures and temperatures other than normal atmospheric temperatures. For example:

- Introduction of carbon dioxide for the chemical stabilization of water after super saturation with  $\text{CaCO}_3$  following softening by treatment with  $\text{Cu}(\text{OH})_2$ ;
- Introduction of carbon dioxide for neutralization;
- Introduction of ozone or chlorine for the disinfection or destruction of substances that cause the odour and taste of water or for the chemical oxidation of certain substances.

## Methods and materials used for the removal of ammonium ion from water sources

### Sources of nitrogen compounds in natural waters and their effects

Typical concentrations of organic nitrogen in water sources range from a few hundred micrograms per litre to over 20 mg/L in wastewater, (APHA, AWWA, WPLF).

Total oxidized nitrogen is the sum of nitrogen  $-\text{NO}_2^-$  and nitrogen  $-\text{NO}_3^-$ . Nitrates are generally found in traces in surface waters, but sometimes reach high values (over 50mg/L) in some groundwater. In concentrations exceeding 50 mg/L, in drinking water, nitrates can cause methemoglobinemia, also called “blue babies” because it occurs to infants.

Consequently, the maximum allowable limit of nitrates concentration in drinking water is of 50 mg  $\text{NO}_3^-$ /L, i.e. 10 mg  $\text{NNO}_3$ . Table 1 shows the values of maximum allowable concentrations (MAC) of nitrogen compounds in surface water and groundwater, drinking water, bathing water and fish farming water to support fish fauna, according to Romanian and European regulations.

Nitrates are found in low concentrations in raw urban wastewater (treatment plant influents), but in treated wastewater they can reach values of concentrations up to 30 mg  $\text{NNO}_3^-$ /L, (APHA, AWWA, WPCF). Nitrates are the essential factor for the photosynthetic activity of autotrophic organisms and are, therefore, considered as a limiting factor for eutrophication in the New Water Directive.

Nitrites are the intermediate phase of the oxidation of ammonium  $\text{NH}_4^+$  to  $\text{NO}_3^-$ , but also of the reduction of  $\text{NO}_3^-$ . These oxidation and reduction reactions may originate from industrial water supply systems from their application as corrosion inhibitors.

Nitrates are, in fact, the aetiological agent of methemoglobinemia.

Table 1: Maximum allowable concentrations (MACs) of NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and KJELDANL nitrogen in water

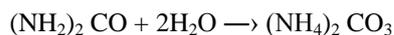
Water Category		NH <sub>3</sub> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NO <sub>2</sub> <sup>-</sup> (mg/L)	N-kjeldal (mg/L)
Raw Surface Water CD 75/440/EEC GD 180/2002	A1	-	25/50 (E)	NS	NS	1*
	A2	-	NS/50 (E)	NS	NS	2*
	A3	-	NS/50(E)	NS	NS	3*
Raw groundwater 2006/118/EEC/ GD 53/2009	CD	-	-	50	-	-
Drinking Water CD 80/778/EEC L. 458/2002 L. 311/2004		NS	0.05 (G) 0.5 (MAC)	25 (G) 50	0.1* 0.5 (L 458)	1*
Bathing Water CD 76/160/ EEC GD 459 / 2002		-	NS* 0.05 (HG 459)	NS* 50 (E)		
Water to support fish fauna 78/759/ EEC GD 202/2002	CD	≤ 0,005	≤ 1	NS	≤ 0.01 (S) ≤ 0.03 (C)	-

\*- values entered in the Directives without being specified in the Romanian regulatory documents.

NS- not specified values; E-Exceptional values; G-guideline values; S-Salmonides; C-Cyprinides\*

Nitrous acid formed from nitrites in acidic solutions can react with secondary amines (RR' NH), forming nitrosamines (RR'N-NO) which are considered carcinogenic (APHA, AWWA, WPCF). This phenomenon has been one of the subjects of the current research.

NH<sub>4</sub><sup>+</sup> ammonium is present in natural surface waters and wastewater. NH<sub>4</sub><sup>+</sup> concentrations of groundwater are low because it is absorbed by soil particles and clays and does not spread easily through infiltration. NH<sub>4</sub><sup>+</sup> results from the deamination reactions of nitrogen-containing organic compounds and from the hydrolysis reaction of urea:



In feed water treatment technologies, -NH<sub>4</sub><sup>+</sup> ammonium is dosed in water to form bound residual chlorine (NH<sub>2</sub>Cl, NHCl<sub>2</sub>) which has a prolonged bactericidal effect compared to free residual chlorine (NaCl si OCl<sup>-</sup>). Wastewater may have concentrations above 30 mg N-NH<sub>4</sub><sup>+</sup> /l. The presence of ammonium (NH<sub>4</sub><sup>+</sup>- N) in water causes high levels of chlorine required in the disinfection operation, which leads to the formation of trihalomethanes or other organochlorine

substances that have been proved to be carcinogenic, (EC. Official Journal of the European Communities, 1998).

#### Methods for the removal of NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> from water

##### Desorption by stripping in columns filled with various contact materials

This method is applied, in particular, in wastewater treatment, after passing through the biological stage. The technological process consists in correcting the pH value to convert NH<sub>4</sub><sup>+</sup> ions into volatile NH<sub>3</sub> molecules, as described in section 2.1 (equations 13 and 14). The equilibrium constant depends, to a large extent, on the temperature. Figure 4 shows that at pH = 10 the presence of ammonia molecules in water, at 0°C is 50% (50%, being NH<sub>4</sub><sup>+</sup>), at 20°C, NH<sub>3</sub> is 80% (20%, being NH<sub>4</sub><sup>+</sup>), and at a temperature of 40°C, NH<sub>3</sub> is 95% (5%, being NH<sub>4</sub><sup>+</sup>). Therefore, almost total removal of -NH<sub>4</sub><sup>+</sup> ammonium is possible at pH values of the order of 10.8-11.5. The pH correction is achieved by dosing lime.

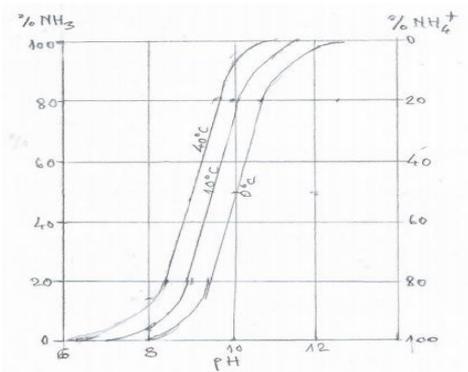


Figure 4: Effects of pH and water temperature on the distribution of ammonia and ammonium (Pöpel, 1954)

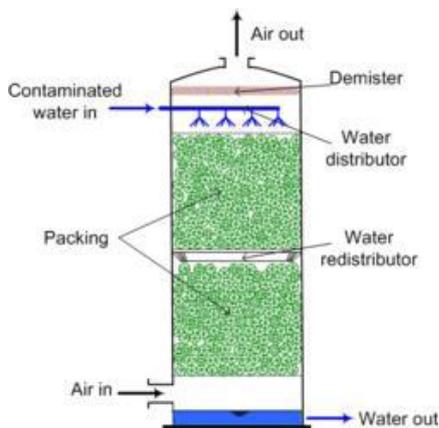


Figure 5: Operating diagram of a stripping column

It should be stressed out that ammonia stripping decreases significantly as the temperature decreases because:

- 1) The conversion of  $\text{NH}_4^+$  to  $\text{NH}_3$  is incomplete at low water temperatures (see Figure 3.1);
- 2) The diffusion velocity and the interface area between air and water decreases;

The value of the ammonium saturation concentration increases, determining the reduction of the driving force of the transfer.

In order to maintain the efficiency of ammonium removal at lower water temperatures, it is possible to increase the air flow/water flow ratio, or to decrease the hydraulic loading of the horizontal section of the column.

The operating diagram of a stripping column is shown in Figure 5.

The table below presents an extract from the results of the experiments performed for stripping ammonia from wastewater, at a temperature of 20°C, knowing that the pH value = 11, (Pöpel, 1954). From the data presented it results the influence of the hydraulic loading and of the  $Q_{\text{air}}/Q_{\text{water}}$  ratio on the percentage of removal of ammonium -N. The column packing consisted of sandalwood fragments.

Table 2: The results of the experiments for the removal of ammonia by stripping in columns packed with sandalwood fragments (Pöpel, 1954)

Ammonium removal percentage	H column = 6*60 m		H column = 7*90 m	
	Hydraulic loading (mm/s)	Q air/ Q water	Hydraulic loading (mm/s)	Q air/ Q water
80	2.5	1700	2.7	1500
85	2.2	1800	2.4	1600
90	1.7	2100	2.0	1900
95	-	-	1.4	3000
98	-	-	0.5	6000

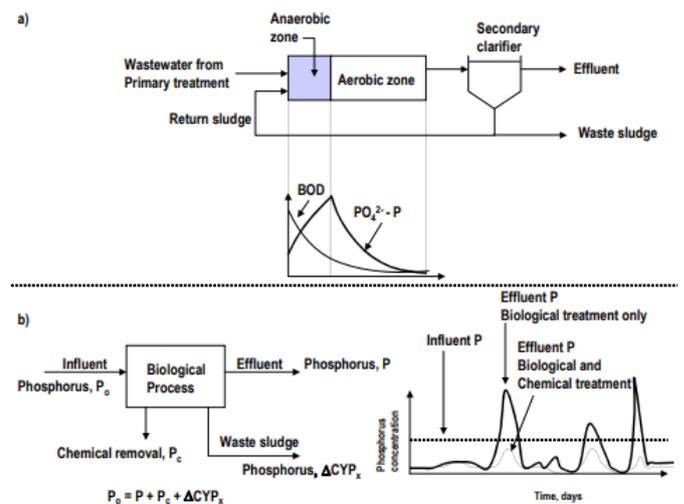
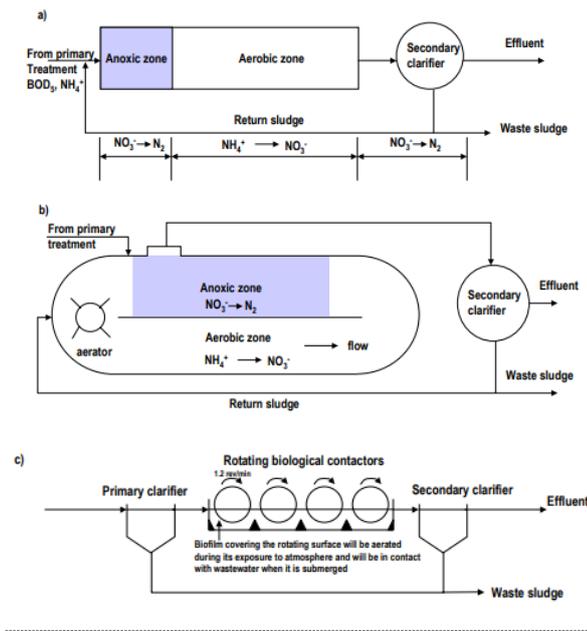
The operating problems that arise are:

- Decreased ammonium removal efficiency due to low temperatures (in winter), up to 50-60%. At temperatures of 0°C the removal efficiency decreases to 30%; the appearance of freezing, which involves stopping the operation. In order to avoid freezing, the air flow is reversed and therefore defrosting is carried out by contact with warm wastewater;
- Reducing the efficiency of ammonium removal due to calcium carbonate deposits on the contact material. Soft

deposits can be removed by backwashing. Hard deposits can be removed by treatment with dilute acid solutions in combination with organic dispersing agents.

### Biological Nitrogen Removal

Organic nitrogen present in the wastewater is hydrolyzed and converted to ammonia nitrogen ( $\text{NH}_4^+$  -N) under aerobic conditions and  $\text{NH}_4^+$  -N is oxidized to nitrite-nitrogen ( $\text{NO}_2^-$  -N) by Nitrosomonas and thereafter to nitrate-nitrogen ( $\text{NO}_3^-$  -N) by Nitrobacter.



a) Phosphorus removal using anaerobic and aerobic zones in a secondary treatment system.  
b) Phosphorus removal by chemical and biological treatment.

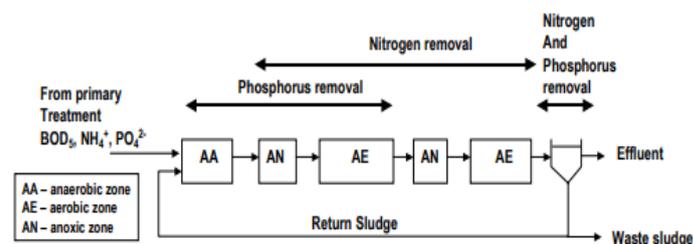
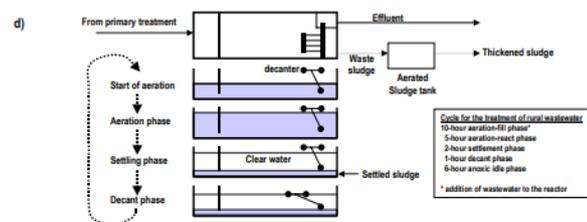
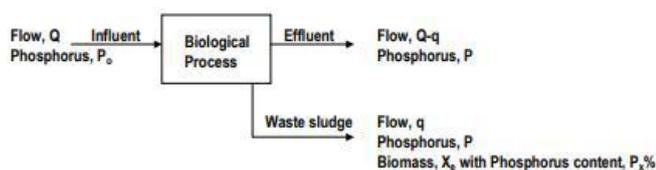


Figure 6: Biological nutrient removal (BNR) process

- a) Nitrogen removal using anoxic and aerobic zones in a secondary treatment system.
- b) Oxidation ditch used for the removal of organic matters and nitrogen.
- c) Rotating biological contactors used for the removal of organic matters and nitrogen.
- d) Fill and draw method used in the sequencing batch reactor for the removal of organic matter and nitrogen.



Phosphorus balance:  
 $QP_o = (Q-q)P + q(P + X_p P_x) = QP + qX_p P_x$   
 $Q(P_o - P) = qX_p P_x$

Carbon (or BOD<sub>5</sub>) balance:  
 $QC_o = (Q-q)C + qX_c C_c + C_{gas}$   
 $Q(C_o - C) = qX_c/Y$ , where Y = sludge produced/ carbon (or organic matter) utilised

$[Q(P_o - P)]/[Q(C_o - C)] = \Delta P/\Delta C = YP_x$   
 $\Delta P = (Y \Delta C) P_x$

Phosphorus removed = sludge produced x phosphorus content in the sludge

$Q, q$  -  $[L]^3[T]^{-1}$   
 $P_o, P, C_o, C, X_c$  -  $[M][L]^{-3}$   
 $C_{gas}$  -  $[M][T]^{-1}$

Figure 5: Material balance for organic matters and phosphorus around a biological process unit

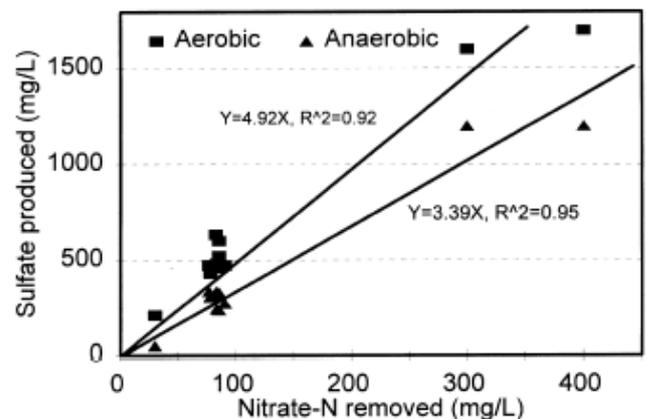


Figure 7: Relationship between nitrate±nitrogen reduced and sulfate produced in SLAD batch reactors under either aerobic or anaerobic conditions

### Conclusion

- Analysis of the data on the spatio-temporal dynamics of the nitrogen forms and concentrations in the low-sulphide, ferro-manganese meromictic subarctic lake demonstrated the predominance of anaerobic processes in the nitrogen cycle. When the Red/Ox conditions

change, the dominant form of mineral nitrogen changes from oxidized ( $\text{NO}_3$ ) to reduced ( $\text{NH}_4$ ).

- The  $\text{N-NO}_3$  form always predominated in the mixolimnion of Lake Svetloe, and seasonal fluctuations in the nitrogen concentration were associated with phytoplankton consumption.
- Below the depth of 22 m,  $\text{N-NH}_4$  predominated, whereas the concentration of  $\text{N-NO}_2$  never exceeded 4% of the sum of inorganic forms of nitrogen. In the horizons of the chemocline and monimolimnion, there was a close relationship between the biogeochemical cycles of methane and nitrogen. This is indirectly confirmed by the local minimum of the nitrate concentration in the chemocline, where the methanotrophic bacteria could use  $\text{N-NH}_4$  or  $\text{N-NO}_3$  for methane oxidation. A peculiar feature of the nitrogen cycle in Lake Svetloe is high concentrations of nitrate in the anaerobic waters of monimolimnion.
- This phenomenon is possibly a consequence of the iron-manganese type of meromixia of the waterbody. Under conditions of high concentrations of manganese and ammonium, anaerobic oxidation of ammonium with the formation of nitrates could occur, where  $\text{MnO}_2$  acts as an oxidizing agent.

This process is described in the literature for other meromictic bodies. The functioning of the nitrogen cycle in the meromictic Lake Svetloe reflects the climatic features of the subarctic (long glacial season), geochemical factors of the catchment (low DOC content and high transparency), the type of meromixia of the lake (high concentrations of Fe and Mn), and the features of the carbon cycle (methanogenesis/methane oxidation).

Further, a more comprehensive analysis of these relationships should provide the necessary information on the functioning of the ecosystem, and the biogeochemical nitrogen cycle provides such an opportunity. Further work is required in this direction, in particular, the assessment of the content of gas components of the nitrogen cycle such as  $\text{N}_2$  and  $\text{N}_2\text{O}$ . In this regard,  $\text{NO}$  might be especially important among other processes as it is closely related to denitrification.

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