DEGRADATION OF NITROGEN COMPOUNDS FROM HEAVILY LOADED WASTEWATER OF PIG MANURE BY THE ROOT-ZONE METHOD

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SUMMARY**:** Wastewater treatment plants based on the root-zone method have been widely and successfully used for over 3 decades to treat heavily loaded and toxic wastewater. In the past totally unexpected results occurred especially concerning the degradation of nitrogen compounds from wastewater. The mechanisms dealing with these degradation processes have remained unclear until now. The following presentation shows the results from a wastewater treatment plant working with the root-zone method which treats heavily loaded manure from a pig farm of 700 mother sows. Emphasis has been given to the dynamic of the nitrogen compounds degradation processes, which has been presented as a "Black Box" model.

1. INTRODUCTION

About 60 % of the organic matter in pig manure coming from intensive stock farming of pigs consists of solids of an extremely fine texture. This makes their separation into a liquid and solid phase very difficult. For this reason such a separation can be achieved in large volume lagoons, where, due to the long residence time of the manure, sedimentation together with partial degradation of the organic matter take place. The pig manure of the pig farm under consideration in this paper is treated by such a sedimentation lagoon.

The total hydraulic day flow contains 100 m^3/d and the dimensions of the lagoon are 300 m in length, 10 m in width and 3 m in depth. The lagoon overflow presents remaining loads of wastewater parameters which range as follows: 2.100 – 3.100 mg/l COD, 500 – 900 mg/l BOD_5, 1.050 – 1.500 mg/l TKN and 100 – 180 mg/l NO_3-N. Much more problematic than the heavy loads of this organic matter is the degradation especially in the range 4:1 for the parameters COD:BOD_5.

Although this wastewater is very problematic, successful results concerning its treatment have occurred in a treatment plant working with the root-zone method (Kickuth, 1984). The plant was designed and built in June 2004 by RHIZOTECHNIKI based in Athens.

2. MATERIALS AND METHODS

The installation for treating the pig manure working according to the root-zone method is a natural wastewater treatment facility. The treatment plant consists of an active soil bed with a surface of 1.300 m^2, which is planted with specialized hybrids of Phragmites australis. The average depth of the soil bed is 0,45 m. The daily volume of hydraulic load is 30 m^3/d, which arrives from the overflow of the adjacent sedimentation lagoon. The infiltration of liquid takes place through the soil bed as a combination of horizontal and vertical flow. The outputs of the soil bed flow into an artificial pond with a wide variety of water plants especially designed for these outflows.

The installation of the root-zone system has been sealed by a special membrane to prevent wastewater escaping into the underground aquifer. The facility was built in June 2004 and became operational immediately. During the first months of functioning operational controls were carried out and necessary improvements were made. Today the plant is operating at its optimum. Very positive from the beginning was the response and strong resilience of the particular genotype of the plant Phragmites australis used for these heavily loaded wastewater.

3. RESULTS AND DISCUSSION

3.1 Results of chemical analysis

For the evaluation of nitrogen compounds degradation, the results of chemical analysis of three samples taken on 07.9.2004, 20.11.2004 and 02.06.2005 from the inlet and outlet ditches have been taken into account. The wastewater parameter results are shown in Table 1.

Table 1 - Results of chemical analysis of the wastewater treatment plant treating pig manure by the root-zone method

Parameter	Input results (mg/l)			Output results (mg/l)			Efficiency %		
	09/04	11/04	06/05	09/04	11/04	06/05	09/04	11/04	06/05
BOD_5	640	542	875	140	80	385	78,1	85,3	56
COD	2260	2105	3090	933	531	1700	58,7	74,8	45
S.S.	561	-	1286	97	-	680	82,5	-	47,1
TKN	1044	1240	1421	430	455	572	58,8	63,3	60
NO_3-N	100	114	181	49,3	56,8	95,8	50,6	50,2	47,1
NH_4-N	512	1104	1386	429	398	567	16,2	64	59

No chemical analysis has been made for the estimation of nitrite nitrogen (NO_2-N) concentration, because its value is considered as negligible, since this certainly is an intermediate product in the decomposition of nitrogen compounds.

Much more interesting in this case are the remains of organic nitrogen compounds. Such compounds are many in this type of wastewater, which through hydrolysis convert into ammoniac nitrogen (NH_4-N). That is why these compounds in the output effluent are detected in small quantities.

3.2 Estimation of nitrogen compounds

In order to evaluate the concentrations of the other forms of nitrogen compounds required for the completion of the nitrogen estimation, arithmetic calculations have been made on the basis of the parameter values shown in Table 1.
These calculations are as follows:

- Organic nitrogen ($N_{organic}$) = TKN – (NH_4-N)
- Total Nitrogen (N_{total}) = TKN + (NO_3-N)
- NH_4-N (hypothetically nitrificated) = TKN – (NH_4-N) output
- NO_3-N (total) = (NO_3-N) input + (NO_3-N) output

Table 2 – Arithmetical results of nitrogen compounds

Date	Dimension	$N_{organic}$	N_{total}	NH_4-N (hypothetically nitrificated)	NO_3-N (total)
07/09/2004	mg/l	532	1144	615	715
20/11/2004	mg/l	136	1354	842	956
02/06/2005	mg/l	35	1602	854	1035

The TKN values give information about the sum of the concentrations of ammonia and organic nitrogen together contained in the mixture of pig wastewater.

To make an assessment of efficiency of this establishment in nitrification based on the results available, it is necessary to take into account the values of organic nitrogen compounds, i.e. the ammonia production.

Based on the results shown in Table 1, if the values of the ammoniac nitrogen (NH_4-N) in the output remains, is deducted from TKN values, shows the amount of the ammoniac nitrogen that must have been nitrificated. In Table 2 these values have been calculated according to the results of Table 1 and they are equal to the values of intermediate nitrate nitrogen compounds (Table 2). They are 615 mg/l, 842 mg/l and 854 mg/l of hypothetical nitrificated NH_4-N respectively.

By adding the above values to the values of nitrate nitrogen input results shown in Table 1, we take the total sum of the nitrate nitrogen compounds (Table 2), which are 715 mg/l, 956 mg/l and 1035 mg/l NO_3-N respectively. Of course these nitrate nitrogen values are theoretical, since a wastewater treatment plant operating with the root-zone system cannot have such high levels of output nitrate nitrogen values. The reason for this is the fact that nitrification and denitrification take place simultaneously in the aerobic and the anaerobic parts of the root zone respectively, that exist one next to the other in the soil matrix (Kickuth, 1984). The low output nitrate nitrogen values shown in Table 1 prove this assumption.

3.3 Degradation processes in nitrogen compounds

The fact that high levels of nitrate occur in the effluent already at the inlet ditch of the wastewater treatment plant is very surprising. The effluent is coming out of the overflow of the sedimentation lagoon. The high pollution load of pig manure on easily degradable organic compounds, as evidenced by the values of the parameter of BOD_5, refer at this stage much more to an oxidative reaction of carbon compounds but not to nitrification. Normally in wastewater the oxidation of ammoniac nitrogen compounds into nitrate must take place at a later stage after the carbon compounds have reached an advanced degradation level. What may be happening here is a total consumption of nitrate through a nitrate oxidation of the carbon organic compounds (Kramer 1990).

The pig manure stays in the sedimentation lagoon for about 30 days. The free surface area of the lagoon is about 3.000 m^2, so that with a specific daily oxygen input of around 3 g/m^2, it is likely to bring about 9 kgO_2/d. This means that these daily quantities of oxygen could be used for the oxidation of both carbon and/or nitrogen compounds entirely or partially.

The remarkably high degradation of ammonia compounds also takes place through the oxidative process in the root-zone area. The incorporation of nitrogen in plant tissue or through the plant which reaches values of 200 kgN/ha·a as well as the decomposition of microbial biomass in the soil, are considered as negligible in this case. For this reason they are not taking into account in the estimation of the quantities of nitrogen compounds (Kickuth, 1977).

In the sample of 20.11.2004 the highest COD degradation occurs and reaches 75 % efficiency (Table 1). At this point the question inevitably arises, if for this massive COD degradation there are enough amounts of nitrate available, to make possible this high COD degradation yield and whether this occurs exclusively through the combustion of nitrate compounds.

As shown in Table 1, the daily COD degradation in the sample of 20.11.2004 contains reduction from 2.105 mg/l at the entrance of the facility to 531 mg/l in the output of the plant. This means a daily COD degradation of 1.574 mg/l.

The equation of the nitrate oxidation is expressed as follows:

$$2\,NO_3^- + 2\,H + 10\,(H) \rightarrow N_2 + 6\,H_2O$$

This gives an equivalent gain of oxidation of 2,9 gO_2/gNO_3 (Kramer, 1990).

In the case under consideration, according to the above equation, the nitrate demands for nitrate COD degradation would be for the three samples around 458 mg/l, 543 mg/l and 479 mg/l NO_3^- respectively (Figures 1, 2 and 3). At the same time the results in Table 1 show the concentration of ammoniac nitrogen (NH_4-N) which has been hypothetically nitrificated. These nitrogen amounts must not be less than 615 mg/l, 842 mg/l and 854 mg/l respectively. At the same time they should be equal to the potential nitrate nitrogen concentrations, which must have been used for the complete oxidative COD degradation. After the COD degradation there are remaining quantities of 157 mg/l, 299 mg/l and 375 mg/l NO_3^- respectively, which must have been removed or degraded through another reaction process which so far remains unknown.

The present research based its calculations on the work of Kramer (1990) that considered that for the degradation of nitrogen compounds from wastewater other biochemical processes could also be involved. For example, the combined reaction of the nitrite nitrogen, which is an intermediate secondary product of nitrification, with the remaining quantities of ammonia compounds (Kramer, 1990), the so called VAN SLYKE reaction. According to this reaction the denitrification takes place through a short route without containing any reductive equivalents. The equations of the VAN SLYKE reaction are expressed as follows:

$$(NH_4)NO_2 \rightarrow NH_2NO + H_2O$$

$$NH_2NO \rightarrow N_2 + H_2O$$

Nitrosamine

Until now there is no evidence of such a type of wastewater nitrification, apart from the fact that the nitrite nitrogen is present in the oxidative treatment of wastewater at the output of all facilities, mainly in cases where there is insufficient oxygen supply. Serious suppositions for a denitrification process following this short route in the present research facility are based on the estimation of the concentration values according to the results of chemical analyses. The values of the parameters leave no room for any other conclusion than to suppose that large quantities of nitrogen split and disappear from the system through denitrification following the VAN SLYKE reaction.

To show the results a “black box” model has been chosen, in order to present the mix of values for COD and derivatives of nitrogen (Figures 1, 2, 3, 4, 5 and 6). For each sample date the results are presented in two figures in order to show the correlation in concentration values of nitrogen and COD, according to the results of chemical analyses. The “black box” model was considered the best way to show the combination and explanation of the results. The only arbitrary assumption in this model is the assumption that the removal of nitrogen comes first. This has been attributed to COD oxidation of nitrate compounds, followed by nitrogen removal through the VAN SLYKE reaction (Figures 1, 2 and 3).

If nitrification is separated from carbon oxidation then the presentation of the results takes the form as shown in figures 4, 5 and 6. This means that we look at what is already known that wastewater degradation begins with the oxidation of carbon compounds as the normal route through oxygen oxidation. Then it appears necessarily an even greater denitrification result by means of the VAN SLYKE reaction. Undoubtedly the VAN SLYKE reaction takes place.

It is very important to point out that the pig manure ratio between carbon and nitrogen is completely different from wastewater of household origin. Here the ratio C:N is around 2:1, while in the household effluent this is approximately 10:1. It is therefore clear that the oversupply of ammonia compounds, which must be degradated, offers the most favourable conditions to induce the VAN SLYKE reaction.

The impact of this assumption in Figures 1, 2, 3, 4, 5 and 6 is that practically all the nitrogen degradation must have taken place through denitrification of the VAN SLYKE reaction followed by elementary nitrogen removal from the system to the atmosphere.

Between these two extreme cases shown in the figures, there is no doubt that the VAN SLYKE reaction takes place in large amounts in any case in these processes, so that it can be considered certain that at least 30 % of nitrification occurs through this route.

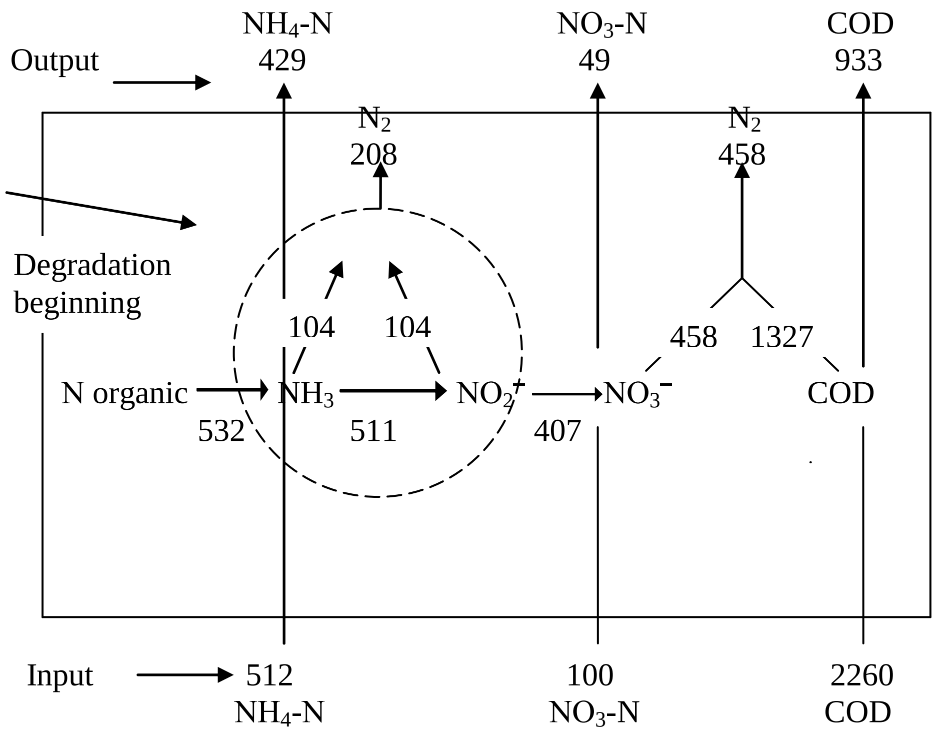

Figure 1. “Black Box” model for the sample of September 2004 with the placement of VAN SLYKE reaction as by pass when COD degradation begins using the nitrate oxygen.

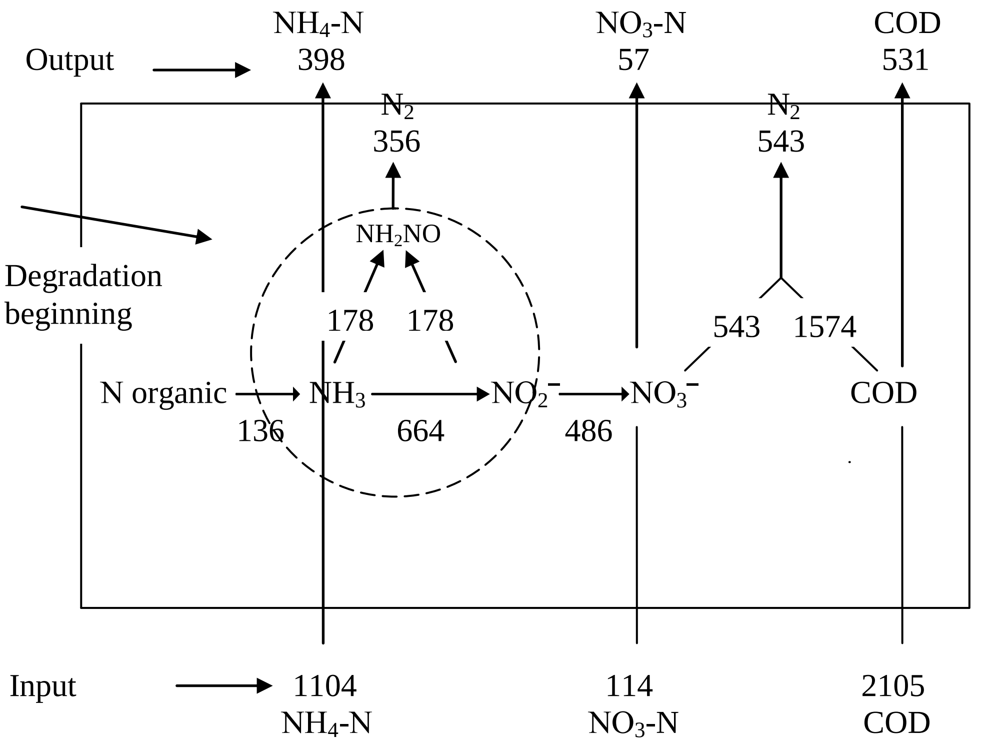

Figure 2. "Black Box" model for the sample of November 2004 with the placement of VAN SLYKE reaction as by pass when COD degradation begins using the nitrate oxygen.

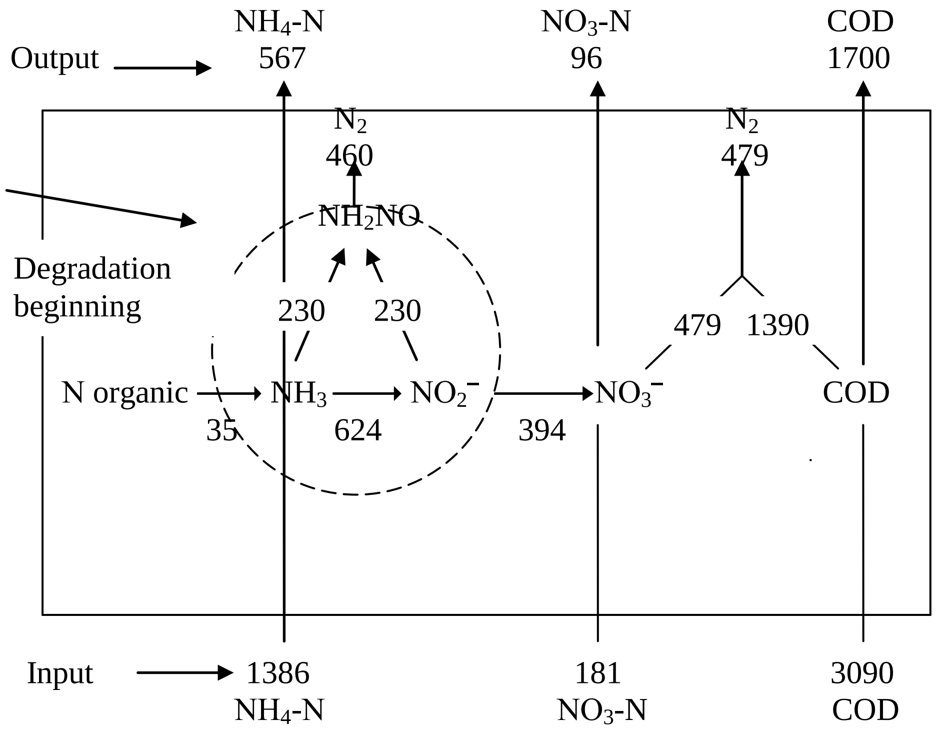

Figure 3. "Black Box" model for the sample of June 2005 with the placement of VAN SLYKE reaction as by pass when COD degradation begins using the nitrate oxygen.

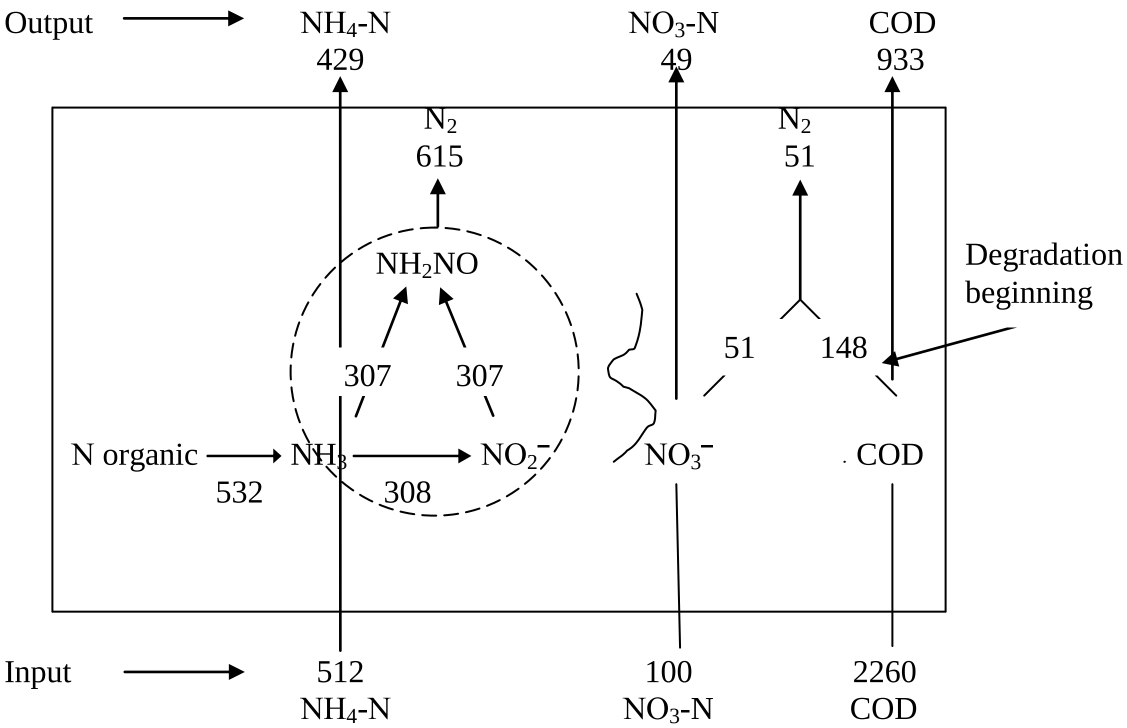

Figure 4. “Black Box” model for the sample of September 2004 with the placement of VAN SLYKE reaction separately from COD degradation.

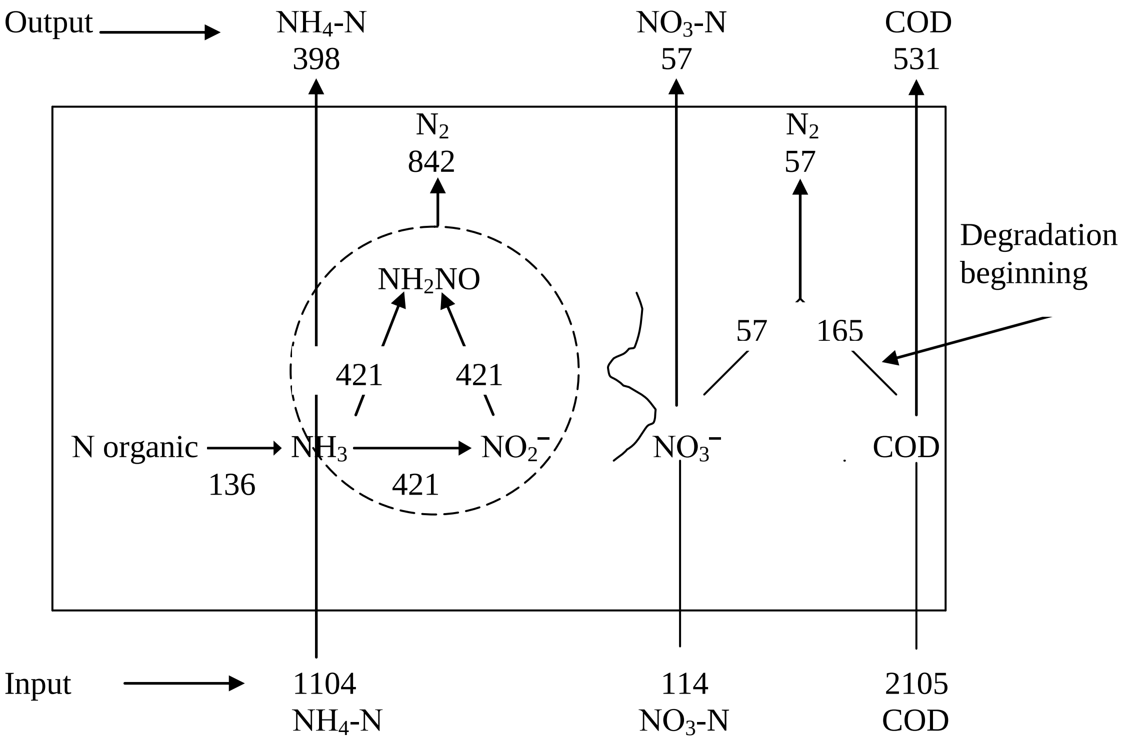

Figure 5. “Black Box” model for the sample of November 2004 with the placement of VAN SLYKE reaction separately from COD degradation.

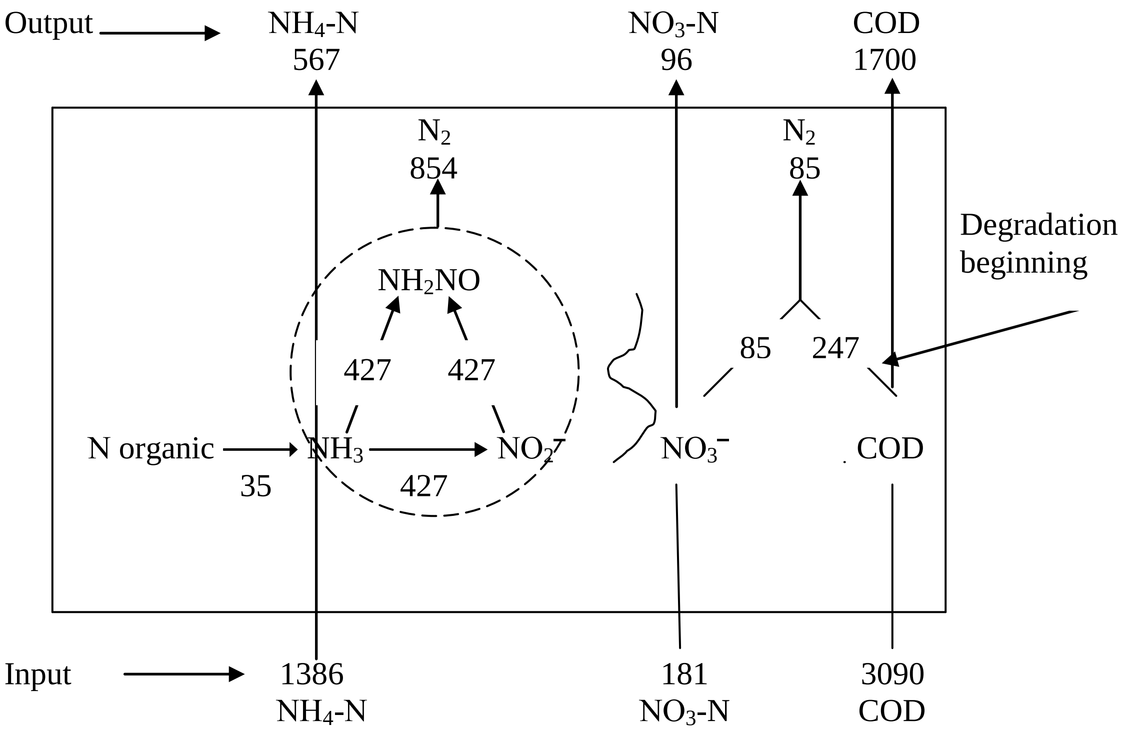

Figure 6. “Black Box” model for the sample of June 2005 with the placement of VAN SLYKE reaction separately from COD degradation.

For the root-zone method is well known that there is an inseparable relationship between nitrification and denitrification, which results -unlike other wastewater treatment techniques- in the absence of nitrite nitrogen as a final product. The degradation process goes even further than the technical aeration methods. Thus, in the root-zone method, the nitrite nitrogen reacts with the carbon compounds of the wastewater and through the shortcut path for the VAN SLYKE reaction gets converted into elementary nitrogen, as in the root zone plant under consideration.

The figures 1, 2, 3, 4, 5 and 6 show that the most extreme cases occur with the contribution of two sources of nitrogen. The actual conditions are between these two extremes. It must be stressed that in all cases investigated so far the VAN SLYKE reaction participates significantly in the production of elementary nitrogen (N_2). This conclusion is new to the up to date knowledge about the processes in biological wastewater treatment. It should, however, for the time being be considered that this applies to wastewater with extremely high nitrogen loads.

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Παρουσίαση στο συνέδριο:

1st International Conference on "Hazardous Waste Management"
Οκτώβριος 2008 στα Χανιά

Πρόκειται για μία εγκατάσταση που λειτουργεί με τη Μέθοδο του Ριζικού Συστήματος για τον καθαρισμό λυμάτων χοιροτροφείου στην Βόρεια Ελλάδα.

Η έρευνα έδειξε την ταυτόχρονη αποικοδόμηση των ανθρακούχων και αζωτούχων ενώσεων στα λύματα του χοιροτροφείου μέσα στην εγκατάσταση του Ριζικού Συστήματος. Αυτό το φαινόμενο εκτός του ότι είναι άγνωστο μέχρι τώρα, έχει τεράστιες τεχνικές συνέπειες, όπως:

- Προστασία των φυσικών αποδεκτών από αζωτούχες ενώσεις
- Ταυτόχρονη δευτεροβάθμια και τριτοβάθμια επεξεργασία λυμάτων υψηλού ρυπαντικού φορτίου
- Εξοικονόμηση απαιτούμενης έκτασης εγκατάστασης
- Εξοικονόμηση κόστους επένδυσης
- Αειφορία στη λειτουργία των εγκαταστάσεων