

Use of Shallow Reservoir and Flooded Organic Soil Systems for Waste Water Treatment: Nitrogen and Phosphorus Transformations¹

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ABSTRACT

Use of a shallow reservoir (with a marly clay loam bottom) and flooded organic soil (Histosol) for inorganic N and $\text{PO}_4\text{-P}$ removal from waste water (agricultural drainage effluent) was evaluated under simulated conditions. The results show that the shallow reservoirs and flooded organic soils could be effectively used for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ removal from the waste waters. Aerating the floodwater resulted in rapid removal of $\text{NH}_4\text{-N}$ as a result of nitrification and NH_3 volatilization. Creating an anaerobic condition in the water column resulted in slower removal of $\text{NH}_4\text{-N}$ due to volatilization. Nitrate N removal was more rapid under anoxic water column conditions than with aerobic water column conditions. Rapid nitrification resulted in the initial increase in $\text{NO}_3\text{-N}$ levels in the water column. Aerating the water column with CO_2 free air resulted in rapid losses of $\text{NH}_4\text{-N}$ through volatilization. Aerating the water column with the air containing CO_2 resulted in a greater loss of $\text{NH}_4\text{-N}$ through nitrification than volatilization. A shorter residence time (1-6 days) of waste water over a soil column was required for effective removal of $\text{NH}_4\text{-N}$, and a longer residence time of 12-24 days was required for effective removal of

$\text{NO}_3\text{-N}$ from the water. For reservoir soil, about 70 and 76% of the floodwater P was removed under aerobic and anaerobic water column conditions, respectively. For flooded organic soil, 51% of the aerobic floodwater P was removed after 2 days of incubation, followed by an increase in soluble P concentration of the overlying water. whereas about 64% of the anaerobic floodwater P was removed during a 29-day incubation.

Additional Index Words: ammonium N removal, nitrate N removal, soluble P removal, waterlogged soils, waste water, agricultural drainage effluent, treatment system, aquatic system.

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One of the causes of pollution of lakes and streams is the addition of large quantities of inorganic nutrients, particularly N and P from several nonpoint sources such as land areas receiving fertilizers and organic wastes, agricultural drainage waters, and from point sources such as municipal and industrial effluents. To reduce pollution from these sources, regulatory agencies are suggesting that these waste waters may be treated before being discharged into water bodies. Land application of waste water effluent has become an accepted means for reducing nutrient levels of waste waters. Recently, wetland soils have been used for reducing the nutrient levels of waste water effluents (Fetter et al., 1978; Boyt et al., 1977; Turner et al., 1976; Tilton and Kadlec, 1979). Use of shallow reservoirs and flooded fields was also being considered as a possible means of reducing the nutrient levels of waste waters (K. R. Reddy, 1980. Unpublished results, Univ. of Florida.).

When waste water is pumped into these reservoirs and flooded fields or wetlands, inorganic N in these effluents may be removed as a result of NH_3 volatilization and nitrification-denitrification reactions (Bouldin et al., 1974; Engler and Patrick, 1974; Mikkelsen et al., 1978; Patrick and Reddy, 1976; Reddy et al., 1976; Reddy et al., 1980; and Vlek and Crasswell, 1979). Depending on the physico-chemical nature of the waste water, $\text{NH}_4\text{-N}$ can be either volatilized or oxidized to $\text{NO}_3\text{-N}$. Nitrate N, thus formed in the water column, diffuses into the underlying soil column where it undergoes denitrification. Phosphorus removal from the waste water is dependent on the concentration of soluble P in the water, pH and alkalinity, interstitial P concentration of the underlying sediments, and adsorption-desorption characteristics of the sediments. A portion of N and P is also removed by aquatic plants and algae.

To improve the efficiency of the aquatic system for inorganic N and P removal from the waste waters, it is important to quantify the physiochemical processes involved in the removal of N and P. The objectives of the present investigations were: (i) to evaluate the relative rates of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$ removal from aerobic and anaerobic water columns with an underlying soil column; (ii) to determine the effect of residence time of the waste water above a soil column on inorganic N and $\text{PO}_4\text{-P}$ removal; (iii) to determine the significance of nitrification and NH_3 volatilization in the water column; and (iv) to evaluate the P adsorption-desorption characteristics of the anaerobic reservoir sediments and flooded organic soils.

MATERIALS AND METHODS

Waste water (agricultural drainage effluent) used in this study was obtained from drainage canals surrounding organic soils (Lithic Medisapristis, euic hyperthermic) planted to vegetable crops located in Zellwood (near Lake Apopka), Florida. Undisturbed soil columns were obtained from the existing field reservoirs and flooded fields located in the same area by driving a PVC pipe using a sledge hammer. The reservoir consisted of a calcareous marl layer while the flooded field bottom consisted of the organic soil. Selected characteristics of the waste water and soil columns are presented in Tables 1 and 2. In all experiments, NH_4Cl and KNO_3 were used as N sources for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, respectively. All experiments were conducted in the dark at 28°C . A description of the individual experiments is given as follows.

Table 1—Selected characteristics of the agricultural waste water used in the study.

Parameter	Concentration
	$\mu\text{g/ml}$
Total P	0.66
Total ortho-P	0.49
Dissolved ortho-P	0.29
Nitrate N	0.85
Ammonium N	0.51
Total Kjeldahl N	7.20
Total alkalinity (as CaCO_3)	240
Chemical oxygen demand	150
Ca	60.1
pH	7.4
Conductivity, $\mu\text{mhos/cm}$	550

1. *Inorganic N and $\text{PO}_4\text{-P}$ Removal Under Aerobic and Anaerobic Floodwater Systems*—Intact soil columns were obtained by driving a polyvinyl chloride (PVC) pipe (12.7 cm. o.d.) 15 cm deep into the reservoir bottom and up to 30 cm deep into flooded field bottoms. Soil columns were brought to the laboratory where the bottoms were sealed to a PVC plate using silicone glue. The columns were then placed in a shallow pan containing melted paraffin wax to insure sealing (Fig. 1).

Each soil column was preincubated with 20 cm of floodwater for a period of 10 days. At the end of preincubation, the floodwater was replaced with (i) waste water with no additional nutrients added; and (ii) waste water amended with $10\ \mu\text{g N/ml}$ each of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $5\ \mu\text{g P/ml}$ as KH_2PO_4 . The depth of the water column was 15 cm for the flooded organic soil column and 30 cm for the reservoir soil column. Each treatment was replicated three times. In the treatment where $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ were added, for one replication, labeled $^{15}\text{NH}_4\text{-N}$ along with nonlabeled $\text{NO}_3\text{-N}$ were added to the water column, and for another replication, labeled $^{15}\text{NO}_3\text{-N}$ along with nonlabeled $\text{NH}_4\text{-N}$ were added to the water column. For the third replication, the water column was treated with nonlabeled $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$. Ammonium sulfate enriched with 10.02 atom % ^{15}N excess was used as $\text{NH}_4\text{-N}$ source and KNO_3 enriched with 10.34 atom % ^{15}N excess was used as $\text{NO}_3\text{-N}$ source. One set of the columns was bubbled with air at a flow rate of 30 ml/min to create an aerobic water column, and another set of the columns was bubbled with N_2 at a flow rate of 30 ml/min to create an anaerobic water column. After 0, 2, 5, 9, and 29 days of incubation, 40 ml of water were removed and analyzed for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$. For the soil columns with 15 cm of floodwater, a 40-ml water sample was removed by inserting a pipette about 7 cm deep into the water. For the soil columns with 30 cm of floodwater, a 10-ml water sample was removed by inserting a syringe needle through a serum cap fitted at 10-cm-depth intervals (Fig. 1). Four samples obtained for each column were combined together, filtered through 0.45- μm filter paper, and analyzed for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$. During the incubation period, dissolved O_2 , pH, and Eh of the floodwater were also measured.

2. *Effect of Residence Time of the Waste Water on Inorganic N and $\text{PO}_4\text{-P}$ Loss*—Soil columns were obtained by driving a PVC pipe (5 cm, o.d.) to a depth of 30 and 15 cm into flooded organic soils and reservoirs, respectively. All soil columns were equilibrated with the waste water for a period of 10 days. At the end of preincubation, water was replaced with the waste water amended with $5\ \mu\text{g N/ml}$ each of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, and $3\ \mu\text{g P/ml}$ as KH_2PO_4 . Water depths of 15 and 30 cm were maintained for flooded organic soil and reservoir soil, respectively. Overlying water was replaced with fresh enriched water at intervals of 1, 2, 4, 6, 12, and 24 days, over a 24-day period. This resulted in the waste water replacement of a total of 24, 12, 6, 4, 2, and 1 times for the treatments where water was replaced for every 1, 2, 4, 6, 12, and 24 days, respectively. Each treatment was replicated three times. All water samples were filtered through 0.45- μm filter paper and were analyzed before and after the replacement of the waste water for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{PO}_4\text{-P}$.

3. *Ammonium N Transformations in the Waste Water Column.*

This study was designed to evaluate the significance of nitrification and NH_3 volatilization in the removal of $\text{NH}_4\text{-N}$ from the waste water.

Table 2—Selected properties of the soil columns used in the study.

Parameter	Units	Soil columns	
		Reservoir soil	Flooded organic soil
Water soluble $\text{NH}_4\text{-N}$	$\mu\text{g/g}$	31.5	9.4
Exchangeable $\text{NH}_4\text{-N}$	$\mu\text{g/g}$	27.7	39.1
Total $\text{NH}_4\text{-N}$	$\mu\text{g/g}$	59.2	48.5
Total Kjeldahl N	%	0.61	3.5
Total organic C	%	6.67	45.1
Water soluble P	$\mu\text{g/g}$	0.25	19.1
Double acid extractable P	$\mu\text{g/g}$	0.49	41.8
EPC	$\mu\text{g/ml}$	0.05	2.25
P-adsorbed at 500 $\mu\text{g P/g}$, added	$\mu\text{g/g}$	273	162.0
P-desorbed at 500 $\mu\text{g P/g}$, added	$\mu\text{g/g}$	200	454.0
pH	—	6.8	6.7
Bulk density	g/cm^3	1.1	0.4
Soil column length	cm	15	30.0
Depth of water column	cm	30	15.0

Intact soil columns were obtained from the field reservoirs by driving a 5-cm (o.d.) PVC pipe to a depth of 15 cm. The bottom and top of each PVC column were fitted with rubber stoppers. Soil columns were equilibrated with a floodwater of 20 cm for a period of 10 days. At the end of preincubation, floodwater was replaced with the waste water (water column depth = 30 cm) containing 25 $\mu\text{g NH}_4\text{-N/ml}$. The rubber stopper at the top of the PVC column was provided with an inlet and outlet tubing. Inlet tubing was connected to the cylinder containing air, and the outlet tubing was connected to the test tubes containing 0.1N H_2SO_4 . The water column was continuously bubbled with air at a flow rate of 30 ml/min. In an additional treatment, 500 ml of waste water were added to an erlenmeyer flask and incubated at the same temperature under the conditions described above. Each treatment was replicated three times. Ammonia evolved under both the systems was trapped in 0.1N H_2SO_4 . A 25 ml aliquot of water was removed at 1, 2, 4, 8, 16, and 24 days after incubation and analyzed for both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$.

In a companion study, 500 ml of waste water was transferred to an erlenmeyer flask and treated with two levels of $\text{NH}_4\text{-N}$, i.e., 25 and 50 $\mu\text{g N/ml}$ (three replications). Air (with and without CO_2) was bubbled through the water at a flow rate of 30 ml/min for a period of 9 days. Ammonia evolved during the incubation was trapped in 0.1N H_2SO_4 and analyzed for $\text{NH}_4\text{-N}$. The pH and $\text{NH}_4\text{-N}$ of the water was determined at the end of 9 days.

4. Phosphorus Adsorption-Desorption Reactions of the Flooded Organic and Reservoir Soils—Soil samples (0–15 cm) from the flooded organic soil and reservoir bottom were used to evaluate the P adsorption-desorption characteristics of these anaerobic soils. Five grams (oven-dry basis) of wet soil were transferred into duplicate wide mouth centrifuge tubes and equilibrated with 25 ml of waste water for a period of 10 days under N_2 (oxygen-free) atmosphere. At the end of preincubation, duplicate tubes were amended with 0, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, and 50.0 $\mu\text{g P/ml}$ as KH_2PO_4 and 3 drops of toluene. The tubes were then purged with N_2 and were equilibrated under continuous shaking for a period of 24 hours in the dark at 28°C. At the end of the equilibration period, soil solutions were centrifuged and the supernatant liquid was filtered through 0.2- μm filter paper.

The fraction of freshly adsorbed P was desorbed by shaking the residual soil material with 0.0015M CaCl_2 (an equivalent Ca^{2+} concentration of the waste water) for 1 hour at a soil to solution ratio of 1:5. The soil suspension was centrifuged, filtered through 0.2- μm filter paper, and analyzed for ortho-P. The desorption step was repeated three more times. For each extraction, N_2 atmosphere was created in the centrifuge tube.

Analytical Methods

Ammonium N and $\text{NO}_3\text{-N}$ in the water samples were determined by steam distillation (Bremner, 1965). Redox potential and pH of the water and soil were measured using a Corning pH meter. Dissolved oxygen was measured with a YSI oxygen meter. Labeled N content of the water samples was analyzed using 21-614 (DuPont) isotope ratio

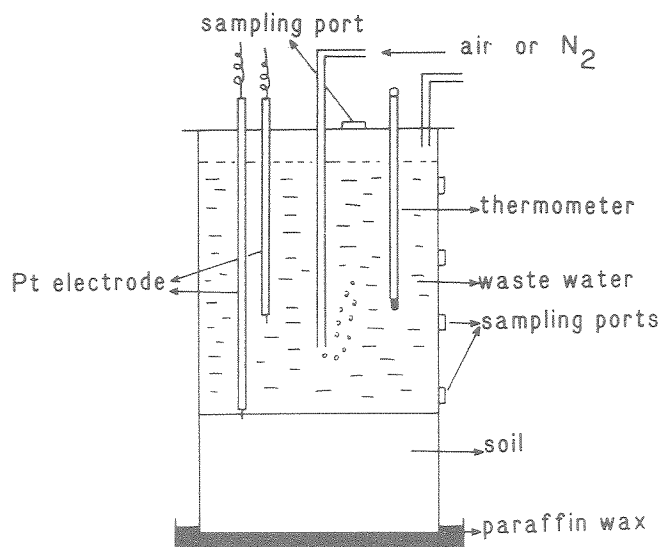


Fig. 1—Schematic representation of the experimental setup used in the study.

mass spectrometer. Ortho-P was determined using a single reagent method (Murphy and Riley, 1962). Total P was determined by persulfate digestion followed by the ascorbic acid reduction method (APHA, 1971).

Total soil N was determined by the digestion in a block digester, followed by steam distillation. A portion of the wet reservoir soil and flooded organic soil were mixed separately with deionized water to obtain a soil water ratio of 1:4, and filtered through Whatman no. 42 filter paper after shaking for 30 min. Another portion of the wet soil sample was extracted with 2M KCl and analyzed for $\text{NH}_4\text{-N}$. Ammonium N in the water and KCl extractions were determined using steam distillation (Bremner, 1965). Exchangeable $\text{NH}_4\text{-N}$ was calculated from the difference between KCl extractable $\text{NH}_4\text{-N}$ and water soluble $\text{NH}_4\text{-N}$.

A portion of wet soil was shaken with deionized water at a 1:4 ratio for 30 min and filtered through 0.2- μm filter paper. Another portion of the wet soil was shaken for 30 min with 0.05N HCl + 0.025N H_2SO_4 in a soil to an extracting solution ratio of 1:5 and filtered through 0.2- μm filter paper. Water and dilute acid extractable P were determined using the single reagent method (Murphy and Riley, 1962).

RESULTS AND DISCUSSION

Nitrogen Transformations

INORGANIC N REMOVAL FROM THE WASTE WATER UNDER AEROBIC AND ANAEROBIC SYSTEMS

1. Redox Potential (E_h), pH, and Dissolved Oxygen—The E_h of the aerobic water column was in the range of 420–480 mV, while the E_h of anaerobic water declined from about 495 mV at the start to 240 mV after 29 days. The E_h values of underlying soil columns were approximately –250 mV for all treatments. The pH of the aerobic water column held constant at about 8.4 while anaerobic water pH increased to 8.9 early in the incubation, and then decreased to a pH of 7.4 at the end. The dissolved O_2 was about 7.5 $\mu\text{g/ml}$ in the aerobic water and <0.1 $\mu\text{g/ml}$ in the anaerobic water.

2. Ammonium N Loss in the Water Column—When inorganic N was added (Fig. 2) to the water, $\text{NH}_4\text{-N}$ concentration of the aerobic water column was decreased to <0.5 $\mu\text{g/ml}$ for both soils. Where no addi-

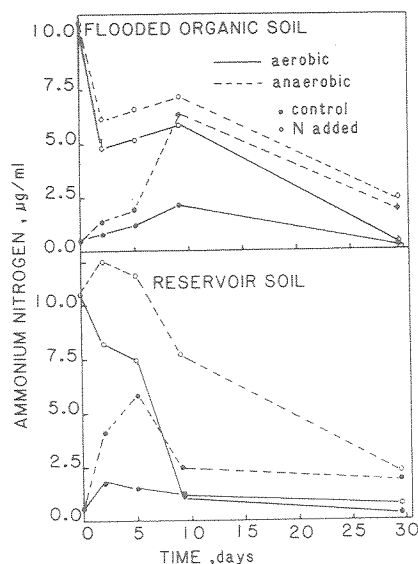


Fig. 2—Ammonium N removal rates from the water column with an underlying organic soil (L.S.D. 0.05 = 1.37 µg N/ml) and reservoir soil (L.S.D. 0.05 = 1.40 µg N/ml).

tional N was added, the $\text{NH}_4\text{-N}$ levels increased to 2.0 µg/ml for both soils early in the incubation, followed by a rapid decrease later. Increase in $\text{NH}_4\text{-N}$ concentration of the water was the result of mineralization of organic N in the soil followed by diffusion of $\text{NH}_4\text{-N}$ into the overlying water. For the soils with an overlying anaerobic water, $\text{NH}_4\text{-N}$ levels of the water decreased to about 2.5 µg N/ml. Labeled N data also showed a rapid decrease in $^{15}\text{NH}_4\text{-N}$ concentration of the aerobic water columns (99% of added N loss) as compared to anaerobic water columns (83% of added N loss) for both soil types.

Loss of $\text{NH}_4\text{-N}$ in the aerobic water was due to nitrification and NH_3 volatilization and loss of $\text{NH}_4\text{-N}$ in the anaerobic water was due to the NH_3 volatilization process. Under aerobic system, aerating the water column provided an inorganic C supply to the nitrifiers. The pH of the water column was in the range of 7.4–8.6, which

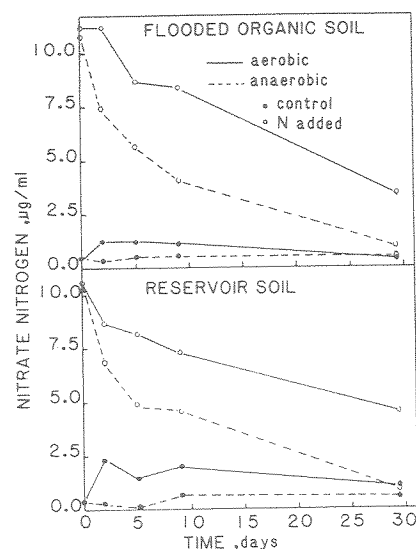


Fig. 3—Nitrate N removal rates from the water column with an underlying organic soil (L.S.D. 0.05 = 2.12 µg N/ml) and reservoir soil (L.S.D. 0.05 = 2.68 µg N/ml).

is the optimum pH range for the maximum activity of the nitrifying organisms. Use of labeled $^{15}\text{NH}_4\text{-N}$ indicated appreciable amounts of $^{15}\text{NO}_3\text{-N}$ formation in the aerobic water for both soil types. In the anaerobic water column, the pH of the water reached a maximum of 8.9, thus resulting in significant losses of $\text{NH}_4\text{-N}$ through volatilization.

3. Nitrate N Loss in the Water Column—Under aerobic conditions, $\text{NO}_3\text{-N}$ concentration of the water decreased by 58 and 71% in 29 days for reservoir and flooded organic soils, respectively (Fig. 3). Under anaerobic conditions, 94% of the $\text{NO}_3\text{-N}$ was lost in 29 days, for both soils. However, labeled $^{15}\text{NO}_3\text{-N}$ data indicate 100% of added $^{15}\text{NO}_3\text{-N}$ removal for both aerobic and anaerobic water column conditions. Increase in the $\text{NO}_3\text{-N}$ concentration of the water was due to the nitrification of $\text{NH}_4\text{-N}$ that was released from the underlying soil.

Table 3—Effect of residence time on N and P removal from the waste water (expressed on an average value for the number of times waste water replaced).

Residence time days	No. of times waste water replaced	Ammonium		Nitrate N		Inorganic N		Ortho-P	
		Co†	Cf‡	Co	Cf	Co	Cf	Co	Cf
Flooded organic soil									
1	24	5.2	1.1a	5.7	8.5a	10.9	9.6a†	3.2	2.5a§
2	12	5.4	1.4a	5.4	7.0a	10.8	8.4b	3.2	2.5a
4	6	5.1	0.7b	5.4	7.5a	10.5	8.2b	3.6	2.5a
6	4	5.6	0.4b	5.5	7.8a	11.1	8.2b	3.9	2.5a
12	2	5.9	0.5b	6.2	3.7b	12.1	4.2c	4.0	3.3b
24	1	5.5	0.4b	6.1	2.1c	11.6	2.5d	4.0	3.0b
Reservoir soil									
1	24	5.3	2.5a	5.6	7.4c	10.9	9.9a	3.1	2.4a
2	12	5.3	2.0a	5.1	8.1c	10.4	10.1a	3.0	2.4a
4	6	5.4	1.5ab	5.5	8.4bc	10.9	9.9a	3.2	2.2a
6	4	4.5	1.2b	6.9	9.8ab	11.4	11.0a	3.2	2.3a
12	2	5.7	0.9b	6.1	5.2d	11.8	6.1b	3.4	2.1a
24	1	5.1	0.1c	6.7	3.1e	11.8	3.2c	3.4	1.2b

† Co = initial concentration of the waste water.

‡ Cf = final concentration of the waste water.

§ Values following with the same letter are not significant at 0.05 level of probability.

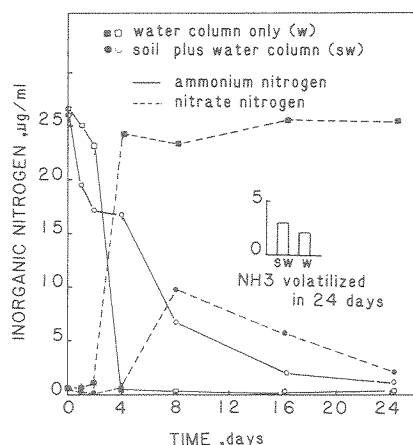


Fig. 4—Relative rates of nitrification and NH_3 volatilization in the water column with and without an underlying soil (L.S.D. 0.05 for $\text{NO}_3\text{-N} = 3.96 \mu\text{g N/ml}$ and $\text{NH}_4\text{-N} = 4.40 \mu\text{g N/ml}$).

EFFECT OF RESIDENCE TIME OF WASTE WATER ON INORGANIC N LOSS

Under both the soil systems, an increase in the residence time of the water column increased the inorganic N loss (Table 3). For the residence times of 1–24 days, reduction in the $\text{NH}_4\text{-N}$ concentration of the floodwater was 74–93% and 53–98% for the organic soil and reservoir soil, respectively. A rapid decrease in $\text{NH}_4\text{-N}$ resulted in an increase in the $\text{NO}_3\text{-N}$ concentration of the water. Nitrate N levels of the water with an underlying organic soil column increased by 49, 30, 39, and 41% for the residence time of 1, 2, 4, and 6 days, respectively. However, for the residence time of 12 and 24 days, reduction in $\text{NO}_3\text{-N}$ concentration was 40 and 66%, respectively. Similarly, for the reservoir soil columns, the $\text{NO}_3\text{-N}$ concentration of the water also increased by 32, 58, 56, and 42% for the residence time of 1, 2, 4, and 6 days, respectively. The $\text{NO}_3\text{-N}$ concentration of the water column was decreased by 15 and 54% for the residence time of 12 and 24 days, respectively.

For both soil systems, nitrification in the overlying water was rapid resulting in the accumulation of $\text{NO}_3\text{-N}$ in the water during the shorter residence time (1–6 days). Denitrification under these conditions was dependent on the diffusion of $\text{NO}_3\text{-N}$ from the water column to the underlying soil. This overall diffusion-controlled denitrification was slower compared to the

nitrification. The total reduction in inorganic N concentration of the water column with an underlying organic soil, as a result of nitrification-denitrification and NH_3 volatilization, was 12–78% for the residence times of 1–24 days. For the reservoir soil columns, the inorganic N concentration of the water decreased by 9–73% for the residence times of 1–24 days. The discrepancies in inorganic N reduction at shorter residence time periods were probably due to varying levels of $\text{NH}_4\text{-N}$ released from the bottom sediments.

AMMONIUM N TRANSFORMATIONS IN THE WATER

In the water with no underlying soil layer, $\text{NH}_4\text{-N}$ decreased rapidly to a negligible concentration within 4 days (Fig. 4). In the water with an underlying reservoir soil column, the $\text{NH}_4\text{-N}$ concentration of the water decreased at a relatively slower rate compared to the water with no underlying soil (Fig. 4). A decrease in the $\text{NH}_4\text{-N}$ concentration of the water was followed by an increase in the $\text{NO}_3\text{-N}$ concentration, which reached a maximum level of $9.5 \mu\text{g/ml}$ after an 8-day incubation. Only part of the $\text{NH}_4\text{-N}$ lost was recovered as $\text{NO}_3\text{-N}$ and the remaining $\text{NH}_4\text{-N}$ was lost from the system. Loss of $\text{NH}_4\text{-N}$ through volatilization amounted to 7.4 and 10.5% of initial $\text{NH}_4\text{-N}$ for the water with and without soil columns, respectively.

Nitrification of $\text{NH}_4\text{-N}$ in the water column is dependent on the availability of inorganic C (Alexander, 1965). Data presented in Table 4 indicate the significance of CO_2 on the nitrification process. When the overlying water was bubbled with air (containing CO_2), nitrification functioned at a maximum rate, resulting in the accumulation of $\text{NO}_3\text{-N}$. In the treatment where water was bubbled with CO_2 free air, NH_3 volatilization was more active, resulting in the evolution of NH_3 . Increased pH and a limited inorganic C supply in the water decreased the nitrifying activity, thus increasing the NH_3 volatilization process.

In flooded fields, shallow ponds, and reservoirs, dissolved CO_2 from the water is consumed by algal cells during photosynthesis, thus releasing O_2 into the system. This can result in increased pH, and favor NH_3 volatilization losses (Bouldin et al., 1974; Mikkelsen et al., 1978). However, in the same system where dissolved CO_2 and bicarbonates predominate, the pH of the water can be buffered around 8.5 and if adequate nitrifying populations are present in the water, $\text{NH}_4\text{-N}$ can be rapidly converted to $\text{NO}_3\text{-N}$.

Major processes functioning in these treatment systems in reducing the inorganic N levels of the waste waters are nitrification of $\text{NH}_4\text{-N}$, NH_3 volatilization. Nitrification and NH_3 volatilization are effectively functioning in the water and denitrification was functioning in the underlying soil column. Nitrate removal from the water was dependent on the diffusion of $\text{NO}_3\text{-N}$ from the water column into the underlying anaerobic soil layer. The underlying soil columns were anaerobic ($E_h = -250 \text{ mV}$) and were functioning as an effective sink for $\text{NO}_3\text{-N}$ removal. One of the limiting processes for inorganic N removal from the water column was diffusion of $\text{NO}_3\text{-N}$ from the water column to the underlying soil column, since nitrification and denitrification were functioning at a more rapid rate.

Table 4—Ammonium N transformations in the waste water column, as influenced by CO_2 during 9-day incubation period.

Initial $\text{NH}_4\text{-N}$ conc.	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	$\text{NH}_3\text{-N}$	Total $\text{NH}_4\text{-N}$ recovered
	$\mu\text{g/ml}$			
	Waste water bubbled with air			
25	0.1a	21.4a	2.4a†	23.9a
50	19.2b	27.0b	2.0a	48.2b
	Waste water bubbled with CO_2 free air			
50	3.9a	2.8a	18.1a	24.8a
50	17.2b	3.8a	28.4b	49.4b

† Values following with the same letter are not significant at 0.05 level of probability.

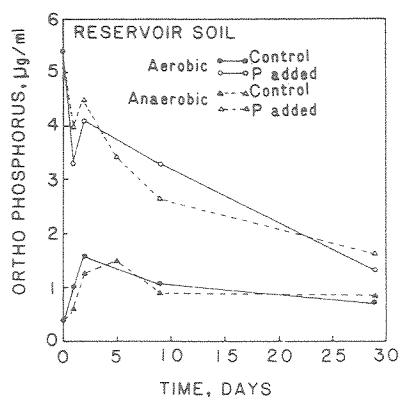


Fig. 5a—Ortho-P removal rate from the waste water with an underlying reservoir soil (L.S.D. 0.05 = 0.95 µg P/ml).

Phosphorus Transformations

PHOSPHORUS REMOVAL FROM THE WASTE WATER UNDER AEROBIC AND ANAEROBIC SYSTEMS

For the reservoir soil, the floodwater P removal rate was the same for both aerobic and anaerobic water columns with about 73% reduction in 29 days (Fig. 5a). Phosphorus removal from the P-enriched aerobic water overlying an organic soil was rapid after a 2-day incubation, with about 51% removal of soluble ortho-P (Fig. 5b). After this period, the soluble ortho-P concentration of the water increased to a final concentration of 5.25 µg P/ml at the end of 29 days. Anaerobic water overlying an organic soil removed about 64% of the floodwater P in 29 days (Fig. 5b). The pH values indicate that HPO_4^{2-} ions of P are predominantly involved in sorption and precipitation reactions.

EFFECT OF RESIDENCE TIME OF WASTE WATER ON P REMOVAL

Data pertaining to the soluble ortho-P removal from the waste water overlying anaerobic soil are shown in Table 3. For reservoir soil, the average reduction in the soluble ortho-P concentration of the water ranged from 20 to 41% for the residence times of 1–12 days, and 65% for the residence time of 24 days. Reduction in soluble ortho-P concentration of the water overlying an organic soil was 18–31% for the residence times of 1–24 days. For reservoir soil, maximum reduction (65%) in the ortho-P concentration of the water was observed with 24-day residence time, whereas for the water overlying organic soil, maximum reduction (36%) was observed with the residence time of 6 days.

ADSORPTION-DESORPTION OF P BY ANAEROBIC RESERVOIR AND ORGANIC SOILS

At all levels of P additions, P removal from soil solutions was higher by reservoir soil than organic soil (Fig. 6). The equilibrium P concentration (EPC) at which no P was gained or lost from the soil solution was 0.05 and 2.25 µg P/ml for anaerobic reservoir and organic soils, respectively. Reservoir soil low in organic matter, high in CaCO_3 concentration, removed more added P from the soil solution than organic soil. The fraction of adsorbed P desorbed with CaCl_2 was lower for reservoir

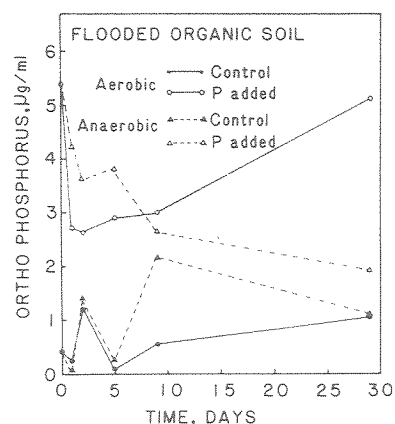


Fig. 5b—Ortho-P removal rate from the waste water with an underlying organic soil (L.S.D. 0.05 = 0.81 µg P/ml).

soil than organic soil (Fig. 6). This indicated that P retained by anaerobic reservoir soil was more tightly held or the compound formed had lower solubilities, thus resulting in the slow release of P into the soil solution. Anaerobic organic soil released nearly the same amount of P into the solution during desorption as that of P added at the start of the equilibration period. This indicated that P retained by anaerobic organic soil was loosely held, thus resulting in a greater release of soluble P into solution.

The results show that the reservoirs (calcareous bottoms with an overlying waste water column) may be effectively used for reducing the soluble P concentration of the waste water. Creating aerobic or anaerobic conditions in the water overlying reservoir soil did not make any difference in the reduction of the soluble P concentration of the water. Flooded organic soil functioned as a source by increasing the soluble P concentration of the overlying aerobic water. Soluble P removal from the anaerobic water overlying an organic soil was probably due to precipitation in the water itself, as a result of high pH conditions. Phosphorus removal from the water was probably a result of precipitation of P with Ca compounds and physical sorption by the underlying soil (Moreno et al., 1960; Stumm and Morgan, 1970; Enfield and Bledsoe, 1975). In shallow aquatic systems, the water pH is dominated by aqueous carbonic acid in the water and influenced to a large extent by the balance between opposing biological processes of respiration and photosynthesis (Mikkelsen et al., 1978). This type of condition in high alkalinity water can result in precipitation of soluble P.

Efficiency of P removal from waste water not only depends on the conditions that exist in the water column, but also depends on the nature of the underlying soil. For example, in this study, the shallow reservoirs with calcareous clay loam bottom functioned effectively in the removal of soluble P from the overlying water. Flooded organic soils do not function as a sink for P removal, because of their poor adsorptive capacity. Low adsorption and high EPC values for organic soil were probably due to the effect of organic anions and lack of iron and aluminum in the soil (Nagarajah et al., 1970). The amount of dissolved inorganic P released into overlying waters of flooded soils,