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Project Summary

Nitrogen and Phosphorus Reactions in Overland Flow of Wastewater

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Biochemical transformations of labelled ammonium-nitrogen resulting from the overland flow treatment of simulated wastewater were studied in small scale test models established with vegetated soils. The results of overland flow experiments indicated the existence of aerobic-anaerobic zones in the soil mass to facilitate nitrification-denitrification processes and enhance nitrogen losses to the atmosphere. The incomplete nitrification of ammonium nitrogen in the simulated wastewater applied to overland flow models suggests that nitrification reactions may be limiting the proportion of nitrate-nitrogen available for denitrification reactions. The loss of applied ammonium-nitrogen attributed to denitrification reactions in the overland flow experiments ranged from 3 to 35%. In the growth chamber studies where alternate aerobic-anaerobic conditions were maintained with controlled soil moisture, loss was as high as 59%. The rate of nitrogen loss in the nitrate treatments was about twice that in the ammonium treatments. The plant uptake of nitrogen in the overland flow and growth chamber studies accounted for 23 to 62% of applied ammonium-nitrogen. About 5% of applied ammonium was lost through ammonia volatilization in the studies.

The mechanisms of phosphorus sorption and desorption were investigated under both laboratory and overland flow conditions. The results of laboratory studies indicated that initial flooding of aerated soil for about three weeks was accompanied by a large increase in phosphorus sorption capacity and decrease in phosphorus mobility. Longer periods of flooding, however, caused a marked decrease in phosphorus sorption capacity and a corresponding increase in phosphorus mobility and leaching losses in acid soils. Calcium phosphate precipitation under alkaline soil conditions increased phosphorus sorption capacity of soils. The results of the overland flow experiment also demonstrated that the efficiency of phosphorus removal from municipal wastewater was greatly enhanced by lime addition to the soil compared to nonlimed flooded soil.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The implementation of Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) has been a driving force in the development of land application as a major management alternative for the effective treatment of municipal wastewater. This has resulted in a renewed interest in studying the various processes involved in the removal of pollutants in various land treatment systems. Most municipal wastewaters contain significant concentrations of nutrients, primarily nitrogen and phosphorus. Both nitrogen and phosphorus can be serious pollutants if discharged to surface waters. Overland flow, also called grass filtration, has been shown to be an effective land treatment system for removal of nitrogen from municipal wastewater while phosphorus removal efficiency has been found to vary over a wide range. The United States Environmental Protection Agency (EPA) had undertaken a comprehensive research program dealing with loading rates for different soil types, frequency of application for maximum nutrient removal, mechanisms involved in transformations, retention, and movement in the soil, and management practices for controlling nitrogen and phosphorus behavior in an overland flow treatment system. The present investigation, funded by EPA, was focused on the mechanisms of various nitrogen and phosphorus removal processes in an overland flow treatment model.

The specific objectives of this research investigation were:

1. To investigate the distribution of applied simulated wastewater in the various components of overland flow treatment system.
2. To evaluate the role of nitrification-denitrification reactions, ammonia volatilization, plant uptake and immobilization in nitrogen removal in small scale overland flow treatment systems.
3. To measure the effects of controlled oxidation-reduction conditions and pH changes on phosphorus sorption and mobility in a soil suspension.
4. To determine the effects of pre-reduced soil conditoins and lime application on the efficiency of soil-plant system in the removal of phosphorus in an overland flow treatment model.

Conclusions

Several controlled laboratory and small scale overland flow experiments were conducted to determine the mechanisms of nitrogen and phosphorus removal processes from simulated wastewater during overland application. Crowley, Olivier, Mhoon and Granada soils and rye grass, Bermuda grass and rice plants were used in the various experiments. Overland flow test models, 30 centimeters (cm) width, 152 cm length and 13 cm depth, were used to study the distribution of applied water into various system components (Figure 1). The results were fitted into a mathematical model to predict the behavior of water movement under field conditions.

Similar overland flow test models were used to investigate the fate of applied labelled nitrogen in an established soil-plant system. Measurements of gaseous nitrogen losses were made in the sealed overland flow test models (Figure 2) and growth chamber studies (Figure 3).

The mechanisms of phosphorus sorption and desorption were investigated under both laboratory and simulated overland flow conditions. Laboratory studies were conducted to determine the effects of changes in redox potential, pH, and the duration of anaerobiosis and re-oxidation on phos-

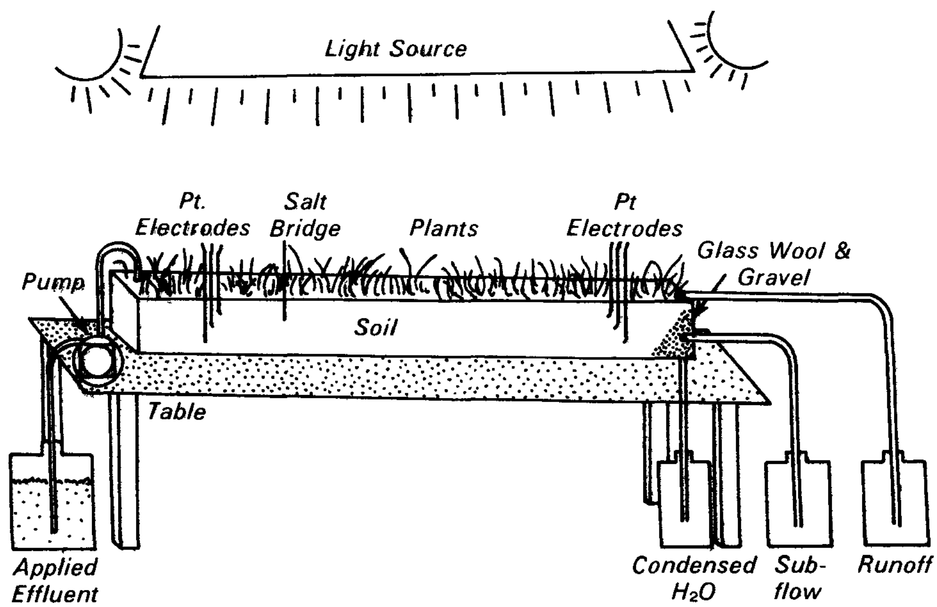


Figure 1. *Longitudinal section of the overland flow wastewater treatment model.*

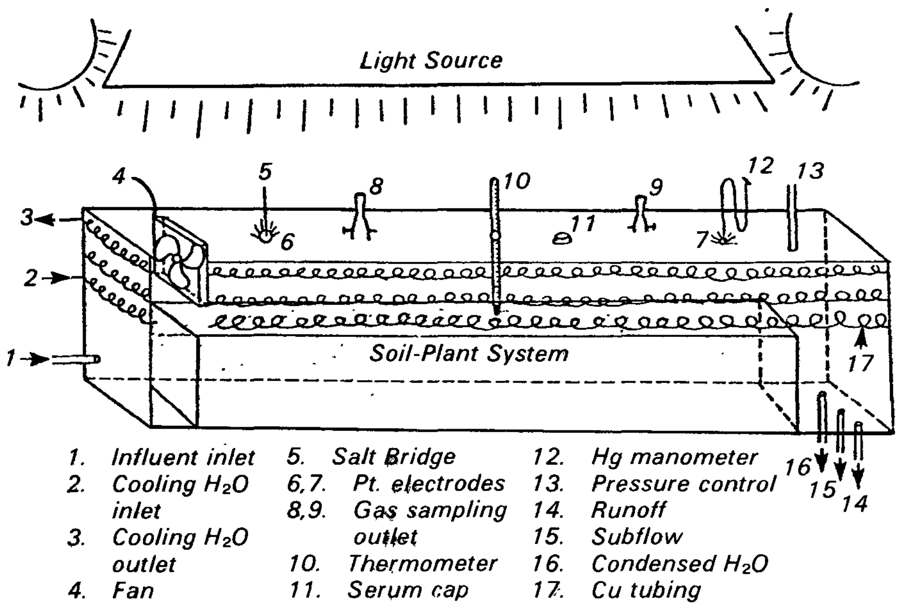
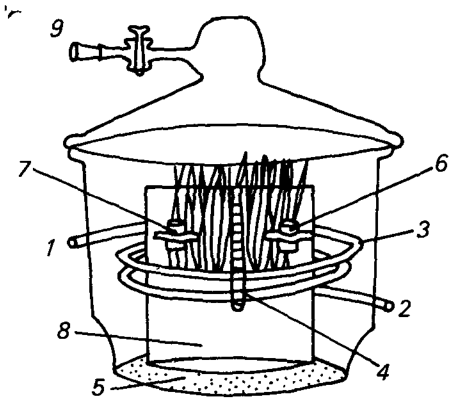


Figure 2. *A schematic diagram of the sealed overland flow treatment model used in the nitrogen transformation's study.*



1. *Cooling H_2O inlet*
2. *Cooling H_2O outlet*
3. *Copper tubing*
4. *Thermometer*
5. *NH_3 trap*
6. *CO_2 trap*
7. *H_2S trap*
8. *Plexiglass container with soil and plants*
9. *Gas sampling and pressure monitoring outlet*

Figure 3. *A schematic diagram of the sealed dessicator assembly used for the determination of gaseous nitrogen losses in a soil-plant system.*

phorus sorption and mobility in soil suspensions. An overland flow experiment was performed to determine the influence of prereduced soil conditions and pH amendment on the removal of phosphorus-32 applied in simulated wastewater.

The results of controlled laboratory and small scale overland flow experiments with simulated wastewater containing nitrogen and phosphorus that may be significant in the land application of municipal wastewater are as follows:

Water Movement

The recovery of simulated wastewater in the runoff fraction in the small scale overland flow experiments ranged from 50 to 60% of applied water. The fraction of applied water collected in the subflow was 9 to 23%. The effect of varying slope from 1.1 to 4.4% on the flow rate of simulated wastewater was not significant in the small scale overland flow model with growing plants as indicated in Figure 4.

The phenomenon of water movement in the overland flow model as a function of slope was computed by a set of equations representing nonsteady flow model. The data plotted in Figure 5 indicate that the computed rate of total water recovered agreed well with experimental data, but the computed rate of subflow did not. This discrepancy could be attributed to the difficulty in the experimental determination of the relative proportional of runoff and subflow. It is possible that some physical processes that may influence water movment in the system were overlooked.

The results of these computations and the comparison with the experimental data suggest that the water movement in the system was primarily

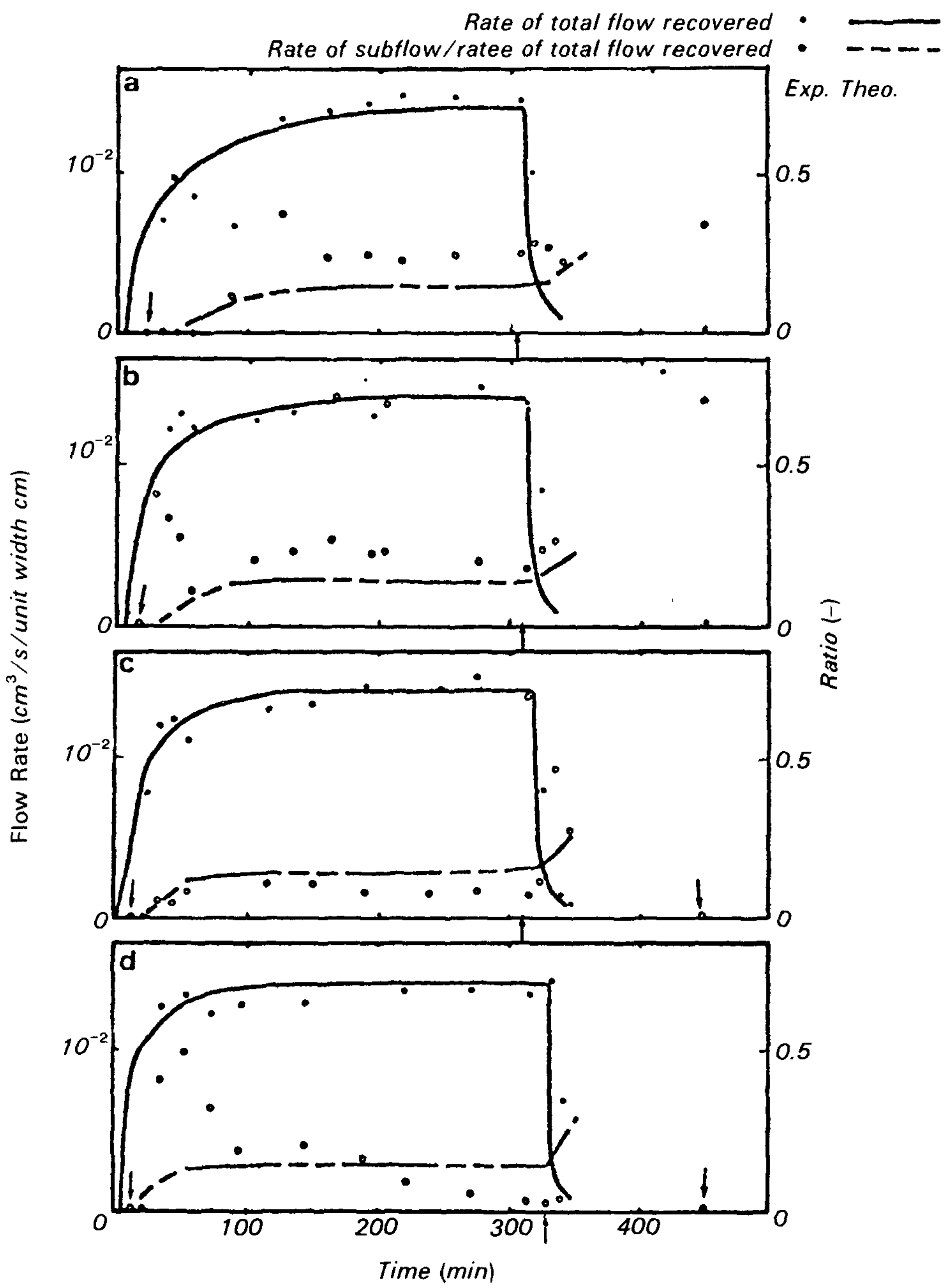


Figure 4. *Comparison between the experimental data and the results of computations (a) 1.1% slope; (b) 2.2% slope; (c) 3.3% slope; (d) 4.4% slope.*

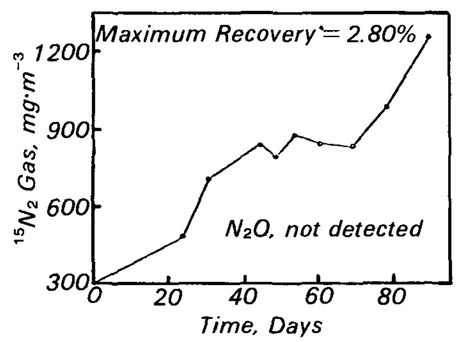


Figure 5. *Gaseous nitrogen-15 production as a function of time in a sealed overland flow Olivier soil-Bermuda grass system.*

controlled by the application rate, the friction slope, the slope angle, the hydraulic characteristics of soils, and the evapotranspiration. The computer simulation of non-steady flow satisfactorily predicts the rate of total water recovered. An understanding of the physical processes may be an important first step to obtain quantitative information on the mechanisms of chemical and biological processes in the overland flow treatment system of wastewater containing pollutants.

Nitrogen Reactions

The contribution of various biochemical tranformations in the removal of wastewater nitrogen in an overland flow treatment system were investigated in several laboratory and overland flow experiments. The results of these studies which may be significant in the land application of municipal waste water are summarized as follows:

1. The redox potential values of surface soil in various overland flow experiments remained well oxidized, indicating the existence of favorable conditions for the nitrification of ammonium-nitrogen added to simulated wastewater. In the subsurface soil, redox potential values ranged from well oxidized to very reduced. These aerobic-anerobic zones in the soil mass facilitate nitrification-denitrification processes and enhance nitrogen losses to the atmosphere.

2. Low soil pH in the range of 5.1 to 6.0 and the lack of easily available energy source resulted in negligible losses of applied ammonium-nitrogen through nitrification-denitrification reactions. Unfavorably low pH is known to inhibit the growth of both nitrifying and denitrifying organisms resulting in reduced gaseous nitrogen loss. Absence of a readily available carbon source results in reduced activity of denitrifying microorganisms.

3. The loss of ammonium-nitrogen through ammonia volatilization reaction in the overland flow experiments and sealed growth chamber studies accounted for about 5% of the total nitrogen added. The pH of soils used in various ammonia volatilization studies ranged from 6.4 to 7.6. This explains the relatively small losses of applied ammonium-nitrogen through ammonia volatilization reactions. Published literature suggests that in more alkaline soil conditions ammonia volatilization losses would be appreciable.

4. Incomplete nitrification of added ammonium-nitrogen was occurring in the overland flow experiments conducted on Mhoon and Olivier soils and in the growth chamber studies with Grenada soil simulating overland flow environment. These results suggest that nitrification reactions may be limiting the proportion of nitrate-nitrogen available for denitrification reactions.

5. The movement of ammonium-nitrogen in the simulated wastewater applied to the overland flow model was restricted to the upper end of the slope. Most of the residual ammonium-nitrogen recovered at the end of overland flow experiments was present in the top few centimeters of soil mass. More nitrate-nitrogen had moved downslope and in the subsurface soil compared to ammonium-nitrogen.

6. The loss of applied ammonium-nitrogen attributed to denitrification reactions in the overland flow experiments ranged from 2.8 to 35.4%. In the growth chamber studies where alternate oxidized and reduced soil conditions were attained with controlled soil water content, loss of applied ammonium-nitrogen was as high as 59%. The recovery of nitrogen-15 gas with time as a result of denitrification reaction in a sealed overland flow system is given in Figure 5.

7. The plant uptake of nitrogen in the overland flow and growth chamber studies accounted for 23 to 62% of applied ammonium-nitrogen and resulted in the maximum removal of wastewater nitrogen compared to other chemical and biochemical processes. Also, preferential uptake by rye grass plants of ammonium-nitrogen over nitrate-nitrogen was demonstrated in the studies.

8. The results of overland flow experiments and growth chamber studies demonstrated that the rate of nitrogen loss in the nitrate-nitrogen treatments was about twice as much as in the ammonium-nitrogen treatments.

The results of the experiments suggest that the gaseous loss of applied nitrogen can be maximized during land application of wastewater if conditions favorable for simultaneous nitrification-denitrification reactions are attained through careful manipulation of soil-plant systems. Some of the important factors that control these reactions are redox potential, pH, readily available carbon source, and large population of appropriate microbes. Any overland flow treatment facilities aimed at maximizing nitrogen loss must optimize these variables. Plant uptake of wastewater nitrogen during overland flow application accounts for a large fraction of nitrogen removed.

The role of various physical chemical, biochemical and biological processes in the overall distribution of nitrogen with the overland flow treatment of wastewater and in the eventual reductions of groundwater and stream contamination is illustrated in Figure 6.

Phosphorus Reactions

Laboratory Studies

The results of these studies can be applied, strictly, only to acid soils containing significant quantities (more than 1000 ppm) of reductible or oxalate-extractable iron. The results for the pH 8 treatment may be applied, with modification to alkaline soils, taking into account the fact that reduction of an alkaline soil will cause a decrease in pH whereas these results are for an acid soil whose pH has been raised artificially to 8.0. The results of this study may be interpreted to draw the following conclusions:

1. At least three days of flooding are probably required before significant reduction and changes in phosphorus sorption and mobility occur.

Applicable to Acid Soils

2. For about 18 days after reduction has occurred, phosphorus sorption capacity will be significantly higher and phosphorus mobility will be lower than in an aerated soil.
3. After about 20 days of continuous flooding, there will be a very large

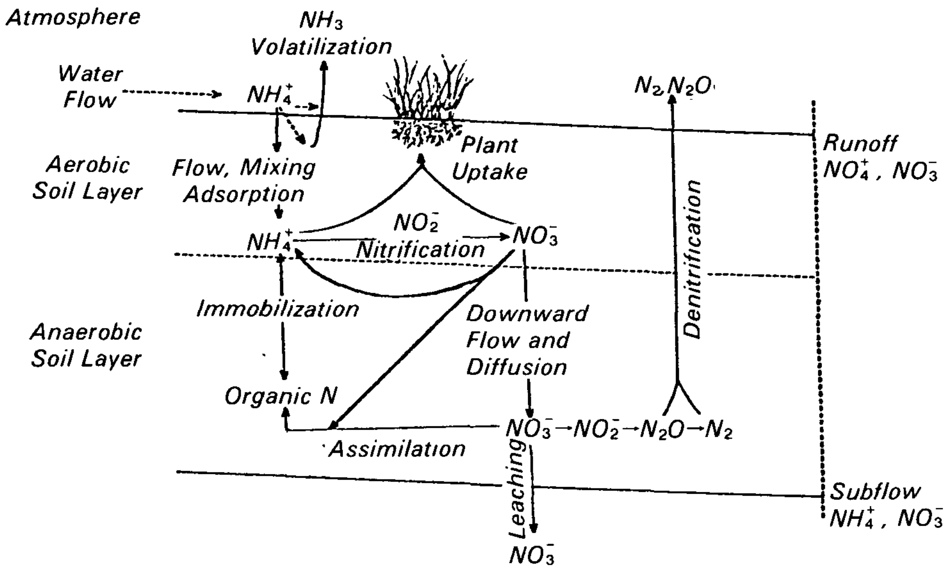


Figure 6. *A schematic diagram of various nitrogen removal processes occurring in an overland flow treatment of wastewater.*

increase in sorption capacity and decrease in leaching losses from wastewater additions containing more than 5 ug phosphorus/ml. However, from more dilute wastewater there may be a slight increase in leaching losses compared with those from aerated soil.

4. Longer periods of flooding (more than 40 days) will cause a gradual decrease in phosphorus sorption capacity and a corresponding increase in phosphorus mobility and leaching losses.
5. Re-oxidation for periods up to 30 days will cause a marked decrease in phosphorus sorption capacity, and leaching losses from previously applied wastewater will be moderately greater than from wastewater applied to aerated soil.

Applicable to Non-Acid Soils

6. Phosphorus sorption capacity will be increased immediately by the addition of calcium in the wastewater, causing an increase in calcium phosphate precipitation.
7. With increasing reduction, pH will fall to near neutral causing a decrease in the negative charge of the iron oxide surfaces and an increase in the solubility of calcium phosphates. Consequently, phosphorus sorption by calcium phosphate precipitation will decrease but the bonding energy of the iron oxide surfaces will increase. The net effect of these changes would be some increase in sorption capacity and a larger increase in buffer capacity so that leaching losses would be smaller than from an aerated soil.
8. Re-oxidation would reverse the changes in pH and buffer capacity so that the phosphorus sorption capacity and leaching losses would be similar to those of an aerated soil.

Overland Flow Studies

The results of the overland flow experiment conducted on Crowley silt loam-rye grass sytem established at 1.2% slope demostrate that the efficiency of phosphorus removal from municipal wastewater would be greatly enhanced by the addition of lime (calcium carbonate) to the soil. The prereduction of soil-plant system for extended period of time may also result in more phosphorus removal than less-reduced, non-limed soil. A mass balance of applied Phosphorus-32 recovered at the end of the overland flow experiment is given in Table 1.

The phosphorus sorption isotherms conducted in the laboratory on the pretreated soils and the sorption parameters computation by the Langmuir two-surface equation demonstrated that the efficiency of phosphorus removal in the overland flow experiment was related to the phosphorus sorption capacity of various treatments. A slightly higher desorption of phosphorus sorbed in the overland fow as well as laboratory studies in the limed treatments was due to the lower phosphorus bonding energy in this treatment. Phosphorus sorbed under alkaline conditions was more available to growing plants than in the unamended treatments. The results of this study suggest that phosphorus sorption is a kinetic process and that the leaching losses of phosphorus retained by the soil mass during overland flow application would be smaller due to the longer reaction time as compared to the desorption potential determined in the laboratory.

Recommendations

Nitrogen

The results of nitrogen studies suggest that the gaseous loss of nitrogen should be maximized to improve the efficiency of nitrogen removal in the overland flow treatment system. Important parameters such as pH, easily-available energy source, and application schedule should be carefully manipulated to maximize simultaneous nitrification-denitrification reactions. Whenever economically feasible, lime additions may be made with the wastewater to enhance ammonia volatilization losses of applied ammonium nitrogen. More research should be conducted on the selection of plant species having affinity for greater nitrogen accumulation and which can be harvested often to maximize nitrogen removal.

Table 1. *Mass Balance of Applied Phosphorus-32 Recovered at the End of Overland Experiment in Crowley Soil-Rye Grass System*

System component	*Treatments*		
	untreated	*prereduced*	*limed*
		^{32}P recovered, %	
^{32}P added	*100*	*100*	*100*
Runoff plus subflow	*34.65*	*18.25*	*3.21*
Plant uptake	*14.37*	*11.32*	*18.45*
Remaining in soil	*50.98*	*70.43*	*78.34*

Phosphorus

Because of the importance of soil pH and reducible iron content in phosphorus reactions further research of this type should be carried out on a range of soils varying in pH and reducible iron content. Short-term kinetic studies of phosphorus sorption are important because adsorption and precipitation are fast reactions. However, the kinetics of anaerobic changes, such as pH and iron chemistry, which affect subsequent phosphorus sorption and mobility, require further study. Long term kinetic studies of phosphorus sorption due to occlusion in hydrous oxide crystals and organic incorporation also require further research. Experimental evidence suggests that re-oxidation of soils can reverse the beneficial effects of reduction on phosphorus sorption capacity and mobility. Further longer term studies should be conducted to optimize management strategies for the duration of wastewater application and re-aeration intervals. Field studies should be conducted to determine the rates of lime applications to maximize phosphorus precipitation during overland flow applications.

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***Bert E. Bledsoe** is the EPA Project Officer (see below).*
The complete report, entitled "Nitrogen and Phosphorus Reactions in Overland Flow of Wastewater," (Order No. PB 81-239 311; Cost: $15.50, subject to change) will be available only from:
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