FLOODPLAIN FILTRATION FOR TREATING MUNICIPAL WASTEWATERS

by

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ABSTRACT

Ph.D. Sobhalatha P Kunjikutty **Bioresource Engineering**

The effectiveness of a cheap, low-tech, environmentally and technically favorable treatment of secondary treated municipal wastewater by contaminant removal through a floodplain-soil filter was evaluated using floodplain-simulating field lysimeters, packed with a sandy soil in 2002 and sand in 2003 and 2004. Secondary treated wastewaters from Vaudreuil (2002 and 2003) and Pincourt (2004) Wastewater Treatment Plants were used as influent. This was applied at rates of 0.06, 0.19, and 0.31 $m^3\ m^{-2}\ d^{-1}$ to vegetated lysimeters, and at a rate of 0.19 $m^3\ m^{-2}\ d^{-1}$ to bare-soil lysimeters.

Removal of NH_4^+-N, NO_3^--N, and COD from the influent was studied in all three years. Irrespective of flow rate or year, the system removed 62~84%, 96~99%, and 6~67% of TKN, NH_4^+-N, and COD, respectively, from the influent. Under 0.19 $m^3\ m^{-2}\ d^{-1}$ flow rate, vegetated systems removed slightly more of these constituents from the influent, than did bare-soil lysimeters. Organic degradation mainly occurred in the top 0.1 m soil depth. Degradation of organic and inorganic influent nitrogen increased NO_3^--N levels in the effluent. Only minimal increases in soil-N levels and N_2O emissions occurred with increasing application rates. The nitrogen mass balance accounted for 85~98% (2003) and 67~96% (2004) of input nitrogen (through leaching, soil retention, and N_2O emissions), the remaining portion being attributable to vegetative effects and volatilization of non-N_2O nitrogenous gases. The under established vegetation on the lysimeters reduced nitrogen leaching through soil, being 6% (2003) and 60% (2004) more effective than bare soil.

Effluent water quality improved with decreasing levels of heavy metals. Compared to influent levels, in vegetated lysimeters, under all flow rates, mean effluent As, Cd, Cu, Ni, Pb, and Zn levels had dropped by 58%, 9%, 3%, 37%, 63%, and 52% in 2003, and by 20%, 63%, 5%, 23%, 18%, 57%, and 79% for As, Cd, Cr, Cu, Ni, Pb, and Zn, in 2004. In both years, similar decreases in heavy metal levels occurred in the bare soil lysimeters. Across all flow rates and influent concentrations, soil heavy metal levels increased. In 2004, even low heavy metal content influent further increased (6~179%) their accumulation in soil. As inputs of heavy metals to the soil increased with the increase in application rates, their associated times to reach maximum permissible limits also decreased.

LEACHN simulation of NO_3^--N in leachate arising from wastewater application, showed lowered levels with increasing flow rates, due to enhanced denitrification in the resulting anoxic upper soil zones. The simulation under continuous wastewater application at different range of nitrogen concentrations (low, medium, high) showed an increase of NO_3^--N levels in the leachate with increasing N-levels. For all flow rates, and under tropical or humid conditions, the effluent NO_3^--N levels remained below permissible limits for the low-N content wastewater applications. Intermittent applications, under all wastewater N-contents and flow rates, reduced NO_3^--N levels in the leachate by 51~89% compared to continuous wastewater application, and permissible limits were not exceeded. Hence, wastewater with high levels of nitrogenous compounds, as occurs in most developing countries, could be treated by land under an intermittent application pattern, allowing a considerable reduction in nitrate pollution.

RESUME

Ph.D. Sobhalatha P Kunjikutty **Génie des bioresources**

Le rejet d'eaux usées non-, partiellement- ou complètement-traités aux eaux non-contaminées a des effets néfastes sur la santé de l'homme, l'environnement, la vie aquatique et la qualité des eaux. Les traitements tertiares sont trop compliqués et coûteux pour être mis en œuvre dans la plupart des pays en voie de développement. Une méthode simple, bon marché, et écologiquement et techniquement favorable de traitement par épandage sur sol de plaine d'inondation fut donc évalué pour sa capacité de nettoyer des eaux usées municipales ayant subi un traitement secondaire.

Comme les paramètres tels la nappe phréatique, l'infiltration, la percolation, etc... ne peuvent être facilement contrôllés sur le terrain d'une plaine d'inondation, l'étude fut entreprise à l'extérieur, dans des lysimètres. Les lysimètres furent construits de tuyau CPV pipe (0.45 m D.I. × 1.0 m en hauteur), équipés d'un tuyau de drainage de 50 mm à la base et de capteurs céramiques pour l'échantillonnage d'eau dans la rhizosphère à des profondeurs de 0.1, 0.2, 0.4, 0.6, and 0.9 m de la surface éventuelle du sol, puis remplis d'un sol sablonneux ou de sable. Les eaux usées furent épandues à trois taux différents, soit 0.06, 0.19, et 0.31 m^3 m^{-2} j^{-1} aux lysimeters dotés de végétation, et à un taux de 0.19 m^3 m^{-2} j^{-1} aux lysimeters à sol découvert. Chaque traitement-lysimetre fut répété à trois reprises. Des eaux usées ayant subi un traitement secondaire provenant des usines d'épuration de Vaudreuil (2002 and 2003) and Pincourt (2004) servirent comme influent.

En 2002, une étude avec un sol sablonneux visa l'enlèvement de NH_4^+N, NO_3^-N, et de la demande chimique en oxygène (COD) de l'influent. Cette expérience fut répété en 2003 et 2004 avec des lysimètres remplis de sable. Toutes années et tous taux d'épandage confondus, la filtration par champ d'inondation enleva 62-84%, 96-99%, and 6-67% du total de l'azote dosé par la méthode de Kjeldahl (TKN), de NH_4^+-N, et de COD, respectivement. Pour le taux d'épandage de 0.19 m^3 m^{-2} j^{-1}, les lysimètres dotés de végétation enlevèrent légèrement plus de ces matières que les lysimètres à sol découvert. La majorité de la dégradation des matières organiques et de l'enlèvement de matières contaminantes eut lieu dans le premier 0.1 m du sol, où l'activité microbienne prédomina. La dégradation de matières azotés organiques and inorganiques provenant de l'influent augmenta les niveaux de

NO_3^--N levels dans l'effluent. L'augmentation du taux d'épandage n'eut qu'un effet mineur sur la teneur en azote du soil et des émissions de N_2O. Le bilan massique pour l'azote tint en compte 85-98% (2003) et 55-97% (2004) des apports en azote par le lessivage, la rétention dans le sol, et les émissions de N_2O, et le reste pouvant être attribué à la végétation et la volatilisation de gaz azotés excluant le N_2O. La végétation, même très pauvrement établie, par son influence sur la transformation des composés azotés, reduisa le lessivage d'azote à travers le sol de 6% (2003) et 41% (2004).

La filtration à travers le sol améliora la qualité de l'eau et diminua la teneur en métaux lourds de l'effluent. En 2003, dans les lysimètres dotés de végétation, pour les trois taux d'épandage, les teneurs moyennes en Cd, Cu, Ni, Pb, Zn, et As dans l'effluent diminuèrent de 20%, 3.5%, 52%, 71%, 65%, et 75%, respectivement, tandis qu'en 2004, les diminutions furent de 35%, 89%, 9%, 5%, 32 %, 56%, and 82% pour As, Cd, Cr, Cu, Ni, Pb, et le Zn, respectivement, par rapport à leur teneur dans les eaux épandues. Dans les lysimètres sans végétation, a part le Cu qui en 2004 augmenta, mais de façon non significative ($P>0.05$), tous les teneurs en métaux lourds diminuèrent. Même les basses teneurs en ces métaux dans les eaux épandues en 2004 (par rapport à celles de 2003) augmentèrent de 6 à 179% l'accumulation de métaux lourds dans le sol par rapport à leurs niveaux de 2003. L'augmentation d'intrants polluants, en parallèle à l'augmentation du taux d'épandage, réduisa le temps necessaire à ce que la teneur maximale admissible en métaux lourds du sol soit atteinte.

Une simulation, avec le modèle informatisé LEACHM-N, du NO_3^--N dans le lessivat suivant l'épandage d'eaux usées, montra que celle-ci diminua lorsque le taux d'épandage augmenta, puisque qu'à des taux élevés la dénitrification fut réhaussés dans la zone supérieur anoxique du sol. La simulation d'un épandage continu avec des eaux usées ayant une teneur basse, moyenne ou élevée en azote, montra une augmentation correspondante de la teneur en NO_3^--N du lessivat. La pollution par les nitrates advenant d'un épandage d'eaux usées à faible teneur en azote, quoique soit le taux d'épandage, fut minime sous des conditions climatiques tropicales tout comme sous des conditions humides. Pour toutes teneurs en composés azotés et taux d'épandage des eaux épandues, un épandage intermittent reduisa de 21-29%, par rapport à un épandage continu, la teneur en nitrates du lessivat. Des eaux usées avec une teneur élevée en composés azotés, tel qu'elles existent dans la plupart des pays en voie de

développement, pourraient être traitées en sol, avec un épandage intermittent, et ainsi reduire la pollution par le nitrate.

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CONTRIBUTION OF AUTHORS

This thesis has been written according to the rules and regulations of the Faculty of Graduate Studies and Research of McGill University Guidelines for a Manuscript Based Thesis, where it is stated that:

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The thesis must include the following:

(a) a table of contents;

(b) an abstract in English and French;

(c) an introduction which clearly states the rational and objectives of the research;

(d) a comprehensive review of the literature (in addition to that covered in the introduction to each paper);

(e) a final conclusion and summary;

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5. In general, when co-authored papers are included in a thesis the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitled "Contributions of Authors" as a preface to the thesis. The supervisor must attest to the accuracy of this statement at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers".

Manuscripts based on the thesis:

1. Kunjikutty S.P., S.O. Prasher, S. Barrington, Dutilleul.P, R. M. Patel, and S. H. Kim. 2005. Nitrogen and chemical oxygen demand reduction in municipal wastewaters by floodplain filtration technique. (Under preparation).
2. Kunjikutty S.P., S.O. Prasher, and S. Barrington. 2005. Nitrogen mass balance in simulated floodplain filtration system for municipal wastewaters. (Submitted for publication to Canadian Biosyems Engineering Journal).
3. Kunjikutty S.P. and S.O. Prasher. Removal of heavy metals from wastewater with a soil filtration system. (Under preparation).
4. Kunjikutty S.P. and S.O. Prasher. Simulation of nitrogen transport in soil under municipal wastewater application using LEACHN. (Under preparation).

All the experimental works, analysis of data, and preparation of above manuscripts were completed by the candidate, Sobhalatha P Kunjikutty, under the supervision of Dr. Shiv O. Prasher, who guided in the research study, and provided the necessary funds to carry out this research work.

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LIST OF SYMBOLS AND ABBREVATIONS

*	Significant
^0C	Degree Celsius
Al	Aluminum
AMINO	Agricultural Nitrogen Model
ANN	Artificial Numeral Network
ANOVA	Analysis Of variance
APHA	American Public Health Association
As	Arsenic
Avg.	Average
AWWA	American Water Works Association
B	Boron
BOD	Biological Oxygen Demand
BOD_5	5-day biological oxygen demand
C	Carbon
C: N ratio	Carbon to Nitrogen ratio
C1	Concentration 1
C2	Concentration 2
C3	Concentration 3
Ca	Calcium
CBOD	Carbonaceous oxygen demand
Cd	Cadmium
CEC	Cation exchange capacity
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
COD/N ratio	Chemical oxygen demand/Nitrogen ratio
Conc.	Concentration
Cr	Chromium
CREAMS	Chemicals, Runoff and Erosion from Agricultural Management Systems

LIST OF SYMBOLS AND ABBREVATIONS cont'd

CREAMS	Chemicals, Runoff, and Erosion from Agricultural Management Systems
Cu	Copper
d	Day
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DS	Dissolved solids
e.g.	Example
EF	Efficiency
EPA	Environmental Protection Agency (United States)
ET	Evapotranspiration (mm or mm day^{-1})
Fe	Iron
FOG	Fat, oil, and grease
FR	Flow Rate
GA	Genetic Algorithm
GC	Gas chromatography
GHG	Greenhouse Gas
GLEAMS	Groundwater Loading Effects of Agricultural Management Systems
h	Hour
HAV	Hepatitis A virus
IMAC	Interim Maximum Acceptable Concentration
K	Potassium
K_d	Soil-water partition coefficient (mg g^{-1})
kg	Kilogram
K_h	Hydraulic Conductivity (m day $^{-1}$)
K_{OC}	Soil sorption coefficient (g mL^{-1})
L	Litre
LACHNR	Convection-dispersion approach of LEACHN

LIST OF SYMBOLS AND ABBREVATIONS cont'd

LEACHM	Leaching Estimation and Chemistry Model
LEACHN	Nutrient sub-model of LEACHM
LEACHNA	Capacity model approach of LEACHN
m	Meter
M	Million
m^2	Square meter
m^3	Cubic meter
MAC	Maximum Acceptable Concentration (MAC)
MAE	Mean Absolute Error
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
meq	milliequivalent
Mg	Magnesium
mg	Milligram
Mn	Manganese
MPLP	Maximum Permissible Limit of Pollutant
N	Nitrogen
N_2	Molecular Nitrogen
N_2O	Nitrous Oxide
Na	Sodium
NCSWAP	Nitrogen, Carbon, Soil, Water And Plant model
NH_3	Un-ionized ammonia
NH_4^+	ionized ammonia or ammonium
NH_4^+-N	Ammonium-Nitrogen
Ni	Nickel
NLEP	Nitrate Leaching and Economic Analysis Package
nm	Nanometer
No.	Number
NO_2^-	Nitrite

LIST OF SYMBOLS AND ABBREVATIONS cont'd

NO_3^-	Nitrate
NO_3^--N	Nitrate-Nitrogen
NS	Non significant
NTRM	Nitrogen-Tillage-Residue Management
O_2	Molecular Oxygen
Org-N	Organic nitrogen compounds
P	Phosphorus
Pb	Lead
r	Correlation Coefficient
RMSE	Root Mean Square Error
RRMSE	Relative Root Mean Square Error
S	Sulphur
S.D.	Standard Deviation
S.E.	Standard Error
SAR	Sodium Absorption Ratio
SEM	Standard Error of Means
Sl	Slope
SS	Suspended solids
T	Time
TKN	Total Kjeldahl Nitrogen
TOC	Total organic carbon
Tr	Treatment
TSS	Total suspended solids
USDA-ARS	Agricultural Research Service of the U.S. Department of Agriculture
USEPA	United States Environmental Protection Agency
UV	Ultra violet
viz.	Namely
VOC	Volatile organic compounds

LIST OF SYMBOLS AND ABBREVATIONS cont'd

vs.	Versus
W	Week
WHO	World Health Organization
Zn	Zinc
μL	Microlitre
μm	Micrometer

CHAPTER-I

INTRODUCTION

Surface water is rapidly deteriorating throughout the world. The discharge of wastewater (point sources) with little or no treatment, agricultural runoff, and flood waters (non-point sources) are the main causes of surface water pollution. Although attention has been given to the control of non-point source pollution, point source pollution, particularly through municipal wastewater, has not been given due attention. Zhi-Yong et al. (2005) reported that the deterioration of water sources around Shanghai (China) was mainly attributable to discharge of untreated domestic wastewater and runoff, which, in turn, affected the quality of surrounding drinking water sources. As one liter of wastewater is sufficient to pollute about eight liters of fresh water, everyday discharge of large volumes of wastewater to rivers, lakes, and streams deteriorates water quality to a great extent (Michael, 2003). In drought-prone and tropical countries, water quality is very poor due to high level of pollutants from wastewater discharge, to the point where it is not even usable for industrial purposes. Although problems with wastewater are common in most developing counties, they are more pertinent in arid and semi-arid countries, where open irrigation canals receive untreated wastewater. This wastewater is then used for domestic purposes due to water shortages (e.g. Pakistan and Mexico). Currently, about 1.1 billion people in developing countries lack access to fresh water, causing a serious threat to their health and to the environment, which, in turn, has been affecting the social and economic growth of these countries (Michael, 2003).

As municipal wastewater receives a part of surface and agricultural runoff, fertilizers and pesticides are transported to water-bodies, and thus concentrations of these contaminants in water-bodies are increased. Runoff from highly fertilized agricultural lands increases nitrate pollution of most waterways. In addition, sewage outlets also contribute pesticides to water-bodies (Neumann et al., 2002; Gerecke et al., 2002). Although wastewater effluent from treatment plants are potential point sources of pathogens in surface water (Exall et al., 2004; Lipp et al., 2001), recent studies have reported their presence, even in runoff water (Smith and Perdek, 2004; Crainiceanu et al., 2003; Ferguson et al., 2003; and Conboy and Goss, 2000). The coliform bacterial concentrations found in runoff water are second to those present in sewer outflow (Kim et al., 2005). Waterborne diseases are mainly associated with pathogens in water (Balbus et al., 2004; Ferguson et al., 2003; Hunter, 2003); for example, diarrhea (waterborne illness) is caused by contaminated drinking water, while malaria and schistosomiasis (vector-borne diseases) are passed on by mosquitoes, which breed in contaminated water. These water-associated diseases kill more than 25 million people worldwide annually, the greater percentage being in developing countries.

Like runoff, a part of industrial wastewater also reaches municipal wastewater, thus causing heavy metals and/or synthetic organic compounds to enter surface water. Potentially toxic heavy metals (e.g. Cadmium, Chromium, Lead, and Mercury) are generally present in industrial wastewater. In many industrialized areas of the world, metal contamination of water-bodies is high and has adverse effects on human health and the environment. For example, in 1980, cadmium concentrations in the Rhine River (Europe) were 30-fold those in 1900, due to increased industrial effluent discharge (Evans et al., 2001). Likewise, from automobile industries, sulphur and nitrogen compounds also reach water-bodies. Studies showed that in developing countries groundwater is contaminated with arsenic (Bangladesh) and fluoride (India) (Hoeck, 2001). Though pharmaceutical wastes also reach municipal wastewater, very few studies have been done so far in this field, as its occurrence has only recently been recognized as an environmental concern (Heberer, 2002), and therefore only recently been detected in rivers (Weigel et al., 2004; Calamari et al., 2003) and estuaries (Thomas and Hilton, 2004). Thus, in general, municipal wastewater contains organic matter, nutrients (N and P), pathogenic organisms, heavy metals, pesticides and pharmaceutical wastes, and hence, its discharge to water-bodies deteriorates their water quality.

Wastewater is generally discharged to water-bodies after primary and/or secondary treatment. However, the level of wastewater treatment in most developing countries is minimal, and about 90% of wastewater is discharged directly into rivers and streams without any treatment (WWF, 2002). Although primary treatment removes about 40% of suspended solids and 30~40% of biological oxygen demand (BOD), and secondary treatment removes about 85% of total BOD from the wastewaters (Crities and Tchobanoglous, 1998), the water still contains substantial amounts of nitrate, ammonium, phosphorus, pathogenic bacteria, heavy metals, etc. This creates a threat to human health, the environment and aquatic life. In particular, the water deterioration due to discharge of untreated and/or partially treated wastewater to surface water sources adversely affects the large populations of downstream water users.

Wastewater disposal to water-bodies increases nutrient level and thereby causes eutrophication (Horn and Goldman, 1994), which depletes the dissolved oxygen in water, and hence, adversely affects aquatic life. Although standards are set for permissible levels of nitrate in drinking water [10 mg NO_3^--N L^{-1} (45 mg NO_3^- L^{-1}) USEPA, 2003], nearly three million individuals worldwide are affected by diseases (e.g. blue baby syndrome (methæmoglobinæmia)) brought on by nitrate contaminated drinking water intake (Cunte, 1997). Since there are many pollutants reaching water-bodies through wastewater, it must be treated to a tertiary level before discharge to water-bodies, in order to protect human health, aquatic life, and the natural environment.

The available tertiary treatment methods such as activated carbon, reverse osmosis or ion exchange methods are too sophisticated and prohibitively expensive for most developing countries. Although reduction of pollutants at the source is preferable, natural ecosystems, such as wetlands or soil filters can be used as a simple, inexpensive, and environmentally favorable treatment method. These land treatment methods are viable and successful in producing water, with quality and standards similar to that from advanced wastewater treatments (Leigh Albrecht, 1997). William (1999) assessed the suitability of wetlands to treat municipal and industrial wastewater, and agricultural and storm water runoff.

Although natural or constructed wetlands are often an alternative to treat wastewater, their initial cost of construction, energy input, and the availability of land with permeable soil for filtration, constrains their exploitation in many countries. Wide floodplains, however, are available with a large number of rivers and streams in most south-Asian developing countries due to their seasonal rainfall pattern. For example, Korea and most parts of India receive an average of 70% of total annual rainfall during two to three months of the rainy season (Kim et al., 2003; Kumar, 2003). These floodplains are predominantly made up of permeable alluvial materials, and are inundated only during the short rainy season. The floodplains usually remain uncultivated, weedy or bare during the major part of the year, and hence could effectively be used as a soil filter medium for wastewater treatment at no additional cost.

Floodplain filtration involves the spraying of wastewater over bare or vegetated land, where many of the organic contaminants are decomposed by microbial process in the rhizosphere during its percolation through the soil. The permeable soil allows the movement of air and water, which enhances biological degradation of organic matter by aerobic microorganisms in the rhizosphere. The predominant forms of nitrogen in wastewater such as organic nitrogen and ammonia (NH_3) are converted to ammonium ions, and these ions are then oxidized to nitrate (NO_3^-) through an intermediate nitrite production (nitrification) process. Finally, the nitrate is reduced to nitrogen gas, and is released to the atmosphere (denitrification). An aerobic environment promotes nitrification, whereas anoxic conditions promote denitrification, where the microbes use the oxygen from nitrate for the reaction. The rate of oxygen supply from the atmosphere to the soil is closely related to the air content of the soil (Collin and Rasmuson, 1988). Consequently, appropriate wastewater spray management can permit both nitrification and denitrification to occur simultaneously for the removal of nitrate and organic matter.

Plants convert NO_3^--N into plant biomass, therefore natural floodplains that usually support vegetation would be more effective in the removal of wastewater-N, as compared to bare soil. Floodplain vegetation supplies a topsoil with organic materials and establishes rhizosphere, an excellent habitat for microbes and worms. In the rhizosphere, oxygen is consumed largely for rapid nitrification of organic matter leading to anoxic conditions conducive to denitrification, thereby removing nitrogen and organic matter. High denitrification of N-rich drainage effluent in riparian soils and wetlands reduces the soil-N content [Cooper, 1990 (a)]. Thus, the contaminated water undergoes different biochemical reactions while filtering through the soil, and reemerges to the rivers and streams with better quality.

As the wastewater contains a large amount of organic matter, the efficiency of the treatment system is based on its removal/reduction from the wastewaters. The BOD of the wastewater measures the oxygen required for the biochemical degradation of organic material and oxidation of certain inorganic materials. In addition, chemical oxygen demand (COD), an indicator of the concentration of organic matter in wastewater, measures the oxygen required for the complete oxidation or the breakdown of organic matter to CO_2 (Living Machines, Inc., 2003). Because of the complete oxidation of organic matter, and quicker analysis, a reduction in the COD value is generally used as an indicator to determine the efficiency of municipal and industrial wastewater treatment processes.

Heavy metals could also be removed from wastewater by floodplain filtration. However, they may be fixed and/or integrated into sediments, plants, and microorganisms via adsorption and precipitation processes into insoluble compounds, or incorporated into lattice structures. Hence, wastewater application may increase heavy metal burden in the soil, and adversely affect plants and soil-microbes. Therefore, although filtration may reduce the heavy metals' level in the effluent, their accumulation in the soil could be harmful and could affect sustainability of land-based wastewater treatment. Hence, the heavy metal removals from the wastewaters, their accumulation in the soil, and how long the application will take to reach the maximum permissible levels (MPLP) of heavy metals in the soil, have to be estimated in this filtration system.

Floodplain filtration studies could be done in natural field conditions, however, such studies require a great deal of time and energy and are costly. Therefore, lysimeters could be used for this purpose. Although floodplain filtration seems to be a promising technique, it has not been evaluated for the amount and the rate of wastewater that can be applied to soil for efficient filtration. The biological degradation of organic matter in soil is dependant on soil microbes and contact time of wastewater in the soil, which in turn depends on application rate and soil properties. Furthermore, to protect groundwater, the wastewater should be applied only to specific soil and climate conditions, so as to create unsaturated water flow conditions in the soil to assure maximum biochemical treatment of the wastewater. This requires studies to determine an appropriate application rate that would be effective in contaminant removal.

Under natural conditions, floodplains do support some species of vegetation or could be bare; hence, studies would be needed to evaluate the effect of vegetation on contaminant removal. Effectiveness and sustainability of floodplain filtration can be evaluated by contaminant removal, N mass balance study, and assessment of maximum permissible limit of pollutants (MPLP) in the soil with wastewater application. It is difficult to evaluate the number of varying scenarios by field measurements, and results are site and contaminant specific; hence, modeling could be used as an alternative. Although several models are available, even with lysimeters, the nutrient version of Leaching Estimation And Chemistry (LEACHN) model can simulate transport of nitrogen in soil under different scenarios.

1.1 OBJECTIVES

The main goal of this study was to evaluate the suitability of a floodplain-soil filtration system in removing contaminants from secondarily treated municipal wastewater, and to investigate different management practices of wastewater application through mathematical modeling. The research aims to provide a low-tech wastewater treatment method to protect downstream rivers and streams from water quality deterioration.

The specific objectives of this study were to:

1. investigate the feasibility of a floodplain-soil filtration system in removing contaminants such as nitrate-N, ammonium-N, organic matter, and heavy metals from municipal wastewater,
2. estimate the optimum rate of wastewater application,
3. determine the adequate soil depth needed for efficient biochemical reactions in the removal of contaminants,
4. compare vegetation and bare soil filter effects in the removal of contaminants,
5. carry out a nitrogen mass balance,
6. assess the time to reach the maximum permissible limit of pollutants (MPLP) in soil for heavy metals with wastewater application, and
7. develop, through modeling, the best strategies for nitrate removal through soil wastewater applications.

The above objectives were met through extensive studies carried out on vegetated and bare floodplain-simulated field lysimeters, under different wastewater application rates. Experiments were conducted at the Macdonald campus of McGill University. Studies were carried out over a period of three years (summer months of 2002-2004), and computer modeling was done simultaneously.

1.2 THESIS ORGANIZATION

This thesis contains ten chapters and one appendix. Chapter 1 introduces the subject, followed by a listing of the objectives and scope of this research. Chapter 2 presents a general literature review concerning this research study. The results of this study are reported in Chapters 3 through 6 as four papers with connecting texts. The titles of the four papers included in the thesis are:

1. Nitrogen and chemical oxygen demand reduction in municipal wastewaters by floodplain filtration technique.
2. Nitrogen mass balance in the simulated floodplain filtration system for municipal wastewaters.
3. Removal of heavy metals from wastewaters and their accumulations in soil with soil filtration system.
4. Simulation of nitrogen transport in soil under municipal wastewater application using LEACHN.

Chapter 7 summarizes the research findings and lists the main conclusions derived from this work. Major contributions to knowledge and suggestions for future research are listed in Chapter 8. An example of an input file used for the LEACHN model study is provided in Appendix I. The data collected in this research, as well as the input data file for the model simulation, are available on CD from the author or her supervisor upon request.

1.3 SCOPE

In this study, the results are limited to lysimeters, homogeneously filled to a depth of 0.9 m with a sandy soil (3.5% O.M) or sand (0.5% O.M), under three different wastewater application rates (0.06, 0.19 and 0.31 m^3 m^2 d^{-1}). The lysimeters were placed outdoor and shielded with a rain cover. The aboveground installation of the lysimeters might lead to higher soil temperature than in a natural soil profile. This could affect the rate of biochemical reactions and growth of microbes. The vegetative cover, used in this study, was sod instead of natural floodplain vegetation. The experiment was done during the summer months of 2002, 2003, and 2004 for 7, 9, and 6 weeks, respectively; hence, vegetation might not have established an active rhizosphere. Therefore, the results of this study may not be directly applicable to other field conditions, and such application of the results needs further preliminary studies, concerning characteristics of influent wastewater, soil, vegetation, and climatic factors.

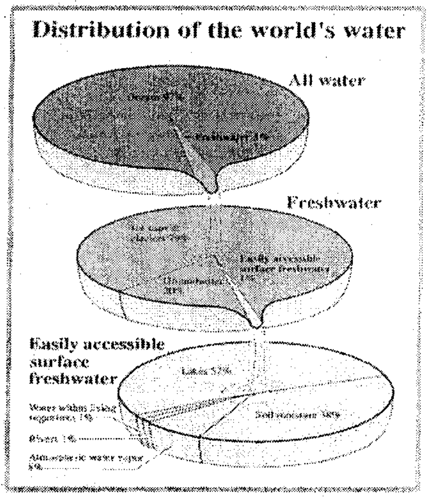
CHAPTER-II

LITERATURE REVIEW

In this chapter, the relevant literature related to issues associated with municipal wastewater disposal to water bodies is reviewed. The subjects of this review are freshwater decline, downstream water quality, wastewater, municipal wastewater treatment methods, land treatment of wastewater, and modeling of pollutant transport through soil with wastewater application. In the wastewater section, different kinds of wastewater, problems associated with wastewater disposal to water-bodies, and pollutants in wastewater are also discussed.

2.1 FRESHWATER DECLINE

Water is vital for all life on Earth. More than 97% of the Earth's water is in oceans, leaving only about 2.5% on land. Most human civilizations emerged in or near valleys, providing sufficient evidence of human needs for water. The declining trend in available fresh water and its finite nature has been the cause of quite some concern around the world. Figure 2.1 shows how small the amount of available fresh water is as compared to total water. In many parts of the world, fresh water availability is becoming inadequate to meet the nation's water needs. Currently in developing countries, 1.1 billion people lack access to fresh water. Worldwide 7 billion people in 60 countries may be faced with water scarcity by the middle of the 21^{st} century (by 2050) [Michael, 2003]. In coming decades, the accelerating population growth, surface water pollution, and climate change together may produce a drastic decline in fresh water supply. The deterioration of the surface water quality by wastewater disposal will further hasten the decline in fresh water availability. Thus, the world's primary sources of water supply will need to be increased to meet its growing domestic, agricultural, and industrial needs.



http://www.umich.edu/~gs265/society/waterpollution.htm

Fig.2.1 World's Fresh Water Availability

2.2 DOWNSTREAM WATER QUALITY

Surface water pollution is very serious, especially river water pollution, as rivers are generally the primary source of drinking water for towns and cities. Water quality deterioration greatly affects the downstream end users. Natural calamities such as flooding and drought, human activities such as mining, dam construction, etc., and wastewater disposal are the main causes of water quality deterioration. River flooding also has an influence on nutrient cycling in riverbeds. Flooding will cause both erosion and deposition of eroded and suspended materials and absorbed nutrients (Pinay et al., 1992). This influences soil physio-chemical conditions such as redox potential and pH, which regulate the effect of the biochemical reactions namely, soil organic matter decomposition, nitrification, denitrification, N-mineralization and P availability (Delaune et al., 1981, and Patric Jr et al., 1985).

Human activities also interfere with the natural flooding regime of the floodplain. Gravel mining in floodplains, dam construction, and other human interferences have caused the water table to lower, causing more frequent summer droughts in floodplains (Spark, 1995). This modification of water level fluctuations, especially in the summer drought period, will also affect nutrient related biological processes in floodplains (Oorschot et al., 2000). Low water levels in waterways may reduce nutrient retention through plant uptake and nitrogen removal through denitrification; it also may increase organic matter accumulation and nitrate leaching through soil to groundwater (Walbridge et al., 1993).

The municipal wastewater discharge to water bodies during the rainy season may not result in high environmental problems due to high dilution and sufficient biodegradation to manage the incoming pollution load; however, during drought season, pollution levels and its effects on the environment may exceed acceptable levels and will be more serious in downstream regions (Meybeck and Helmer, 1992). It may therefore adversely affect the environment, aquatic life and human health.

Generally, nutrient removal and retention in floodplains are important for improving river water quality (Haycoke et al., 1993). In metropolitan areas of major cities in the USA (e.g. Atlanta, Columbus, Abany, and Phoenix), significant increases in nutrient concentrations and pollutant loads were observed from the upstream to the downstream of waterways. During the period 1972 to 1990, nutrient concentration in surface waters was high enough to warrant concerns about accelerated eutrophication due to phosphorus, and toxicity to fish due to dissolved ammonia concentrations, mainly in downstream of wastewater treatment outfalls in these areas (Elizabeth et al., 1996). Even though problems are seen in developed countries, they are discharging their wastewater to water-bodies after secondary treatment. However, in most of the developing countries, the level of treatment is trivial and thus, 90~95% of domestic sewage and 75% of industrial wastewater are discharged into surface waters without any treatment (Allaoui, 1998; Carty, 1991).

In India, 70% of the available water is polluted, and increasing river water pollution is one of the biggest threats to public health (Dewaram, 2002). The downstream water of Malaprabha River (India) exceeds the acceptable limits of pollution, which indicates a severe degradation of its quality due to sewage, wastewater, and agricultural runoff. The chemical mass balance of its water quality showed dominance of bicarbonate, sodium and chloride towards downstream, as compared to upstream (Purandara et al., 2004). It was observed in the Yellow River of China that the chemical oxygen demand (COD) and ammonium levels sharply increased due to abundant discharge of influent wastewater, and thereby deteriorated water quality, and adversely affected the aquatic life and environment (CGIAR, 2003; Zhi-Yong et al., 2005). Thus, it seriously affected the agriculture, human health and livelihood in the downstream region of Yellow River (China). Wastewater discharge along with water flow reduction in the Ganges (India) has negatively affected the downstream river water quality and the environment (Morshed, 2003). As rapid growth is occurring throughout arid regions of the world, water and wastewater infrastructure and management are emerging as critical concerns for sustaining industrial growth and improving standards of living.

2.3 WASTEWATER

Wastewater can be classified as domestic/municipal, commercial, or industrial. Municipal wastewater is derived principally from dwellings, business buildings, institutions, sanitary wastewater, and sewage. Commercial wastewater includes non-toxic, non-hazardous wastewater from commercial facilities, normally similar in composition to domestic wastewater, but may occasionally have one or more of its constituents exceed typical domestic maxima. It may include wastewater from commercial and institutional food service operations, commercial laundry facilities, and animal holding facilities. Industrial wastewater means wastewater from manufacturing, commercial, mining, and silvicultural facilities or activities, including the runoff and leachate from areas that receive pollutants associated with industrial or commercial storage, handling or processing.

2.3.1 Problems associated with wastewater

Wastewater contains varying levels of pathogenic organisms, nutrients, heavy metals, organic matter, pesticides, pharmaceutical wastes, etc., based on the degree of treatment provided. Water quality issues mainly arise when increasing amounts of untreated or partially treated wastewater is discharging to water bodies that will eventually be used for water supply. The water of the Mississippi River and many other rivers in the eastern United States are used for municipal and industrial water supplies, and as repositories for the resulting treated wastewater. Approximately, 4300 M m^{-3} of effluent (in 1991) is discharged into Canadian rivers and the associated pollutants and water quality deterioration makes municipal wastewater a major concern in Canada (Marks el. al., 2002). In southern California, a semiarid region, increasing amounts of reclaimed wastewater are being used for groundwater recharge to augment existing potable water supplies (Tchobanoglous et al., 2003). In developed countries, municipal wastewater generally undergoes the equivalent of secondary treatment prior to disposal to water bodies, whereas in many developing countries, the wastewater may be discharged after primary treatment or even without any treatment (Allaoui, 1998; Carty, 1991). Wastewater, even after secondary treatment, may contain nutrients, heavy metals, pathogens, and organic matter. Hence, the discharge of treated or untreated wastewater to water bodies can cause serious problems to human health, environment, and aquatic life.

2.3.1.1 Health problems

Water-borne diseases and aquatic vectors continue to be the largest single cause of human illness and death around the world. Eighty percent of all diseases and more than one-third of all deaths in developing countries are water related (ICWQ, 2002). Infectious diseases are transmitted either through direct contact with wastewater or consumption of the wastewater-irrigated crops. These diseases are mainly associated with pathogens in water (Balbus et al., 2004; Ferguson et al., 2003; Hunter, 2003); for example, diarrhea (waterborne illness) is caused by contaminated drinking water, while malaria and schistosomiasis (vector-borne diseases) are passed on by mosquitoes, which breed in contaminated water.

Ingestion of nitrate-contaminated drinking water can induce blue baby syndrome (methanoglobinemia) in infants and can increase the risk of cancer within the digestive tract (Miaco, 1989; Cunte, 1999; L'hirondel and L'hirondel, 2002). In developing countries, these problems are becoming a major concern. In China, many people do not have access to a safe water supply or proper sanitation facilities. This is in part a result of their having fewer wastewater treatment facilities *per capita* than most developed nations, and their intensive use of lands and waters for agriculture and fish farming (Lai, 1995).

Endocrine disrupting chemicals are a special health concern, which can emerge with the uptake of deteriorated water. It can mimic hormones produced in vertebrate animals by causing an exaggerated response, or block the effect of a hormone in the body (Trussell, 2001), can cause testicular, prostate, and breast cancers (Peggy et al, 2000), and cause problems with development, behavior, and reproduction in a variety of species (Tchobanoglous et al., 2003). Although there are many human health problems with the uptake of deteriorated water, the latest concerns with wastewater and human health are: the lack of sufficient information regarding the health risks posed by some microbial pathogens and chemical constituents in wastewater, the nature of unknown or unidentified chemical constituents and potential pathogens, and the effectiveness of treatment processes for their removal (Tchobanoglous et al., 2003).

2.3.1.2 Environmental problems

Surface water contamination may be a consequence of wastewater disposal and runoff from agricultural land irrigated with contaminated wastewater. Wastewater disposal to water-bodies increases nutrient level and thereby causes eutrophication (Horn and Goldman, 1994), which depletes the dissolved oxygen in water, and hence, adversely affects aquatic life. Excessive phosphorus levels can result in nuisance algae growth in rivers and lakes. Water reclamation plants are required to minimize the amount of phosphorus discharged in their effluent in order to prevent algal growth in the receiving waters. Nitrate leaching can contribute to the eutrophication of watercourses, to the detriment of aquatic fauna. Israel has suffered massive nitrate contamination of groundwater as a consequence of large-scale water recycling (William, 2002). Excessive eutrophication and algal growth will decrease the oxygen content in the receiving water bodies, which, in turn, affect the aquatic life. Effluents containing chlorine residuals are also toxic to aquatic life.

Soil contamination may be due to salinity, accumulation of trace metals and water logging. Odor with wastewater discharge is another serious environmental concern to the public (Tchobanoglous et al., 2003). New techniques for odor measurement are used to quantify the development and movement of odors that may emanate from wastewater facilities, and special efforts are being made to design facilities that minimize the development of odors, contain them effectively, and provide proper treatment for their destruction. Many industrial wastes contain volatile organic compounds (VOC) that may be flammable, toxic, and odorous, and they may be contributors to photochemical smog and tropospheric ozone (Tchobanoglous et al., 2003).

2.3.1.3 Other problems

The other main problem is reduced crop yield / production as a consequence of imbalanced concentrations of key constituents necessary for crop growth present in the irrigation wastewater, and widely varying crop susceptibilities to various elements present in it (William, 2002). Another concern is the presence of high levels of certain heavy metals (e.g. Cd, Cr, Cu, Hg, Ni, Pb, and Zn) in wastewaters, which, in turn, accumulate in the soil with irrigation and land application. Usually, in wastewater, some of these metals occur in small amounts, and are necessary for plant growth (e.g. Cu, Ni, and Zn). However, excess amount of these elements can damage the plant growth, and thereby can reduce crop yield (ACES, 2000). The Cd present in wastewater can even enter the food chain, and with its high concentrations, it can be harmful to plant and human health (ACES, 2000).

2.3.2 Pollutants in wastewater

Municipal wastewater is a complex mixture of suspended solids, waste, debris and chemicals from residential, commercial, and industrial sources (Mark et al., 2002). The concentrations of pollutants are very low in municipal wastewater compared to industrial wastewater, as it usually contains 99% water. As discussed earlier, the municipal wastewaters, even after secondary treatment, often contain many contaminants. Hence, the important constituents of concern in wastewater treatment are discussed below in detail.

2.3.2.1 Nutrients

Wastewater often contains large amounts of the nutrients, which promote plant growth. Microorganisms only require small amounts of nutrients in biological treatment of wastewater, so there is normally an excess amount available in treated wastewater. In severe cases, excessive nutrients in receiving waters cause algae and other plants to grow quickly, thus depleting oxygen in the water. Deprived of oxygen, fish and other aquatic life die and emit foul odors.

2.3.2.1.1 Nitrogen

Wastewater naturally contains several forms of nitrogen, and the water reclamation process relies on bacteria to convert nitrogen in the wastewater into forms that are not harmful to the environment. Total Kjeldahl Nitrogen (TKN), also known as organic nitrogen, is the most commonly found form of nitrogen in wastewater. The nitrogen cycle is composed of four processes, defined as nitrogen fixation, ammonification, nitrification and denitrification. The decomposition of organic wastes in the water reclamation plant converts TKN to ammonia, a very damaging water pollutant. Removal of ammonia is required because of its toxic effect on fish and other aquatic life in the receiving water. Within the biological section of the water reclamation plant, ammonia is converted to nitrogen gas by specific types of bacteria through the processes known as nitrification and denitrification. The nitrification process produces nitrite and nitrate, which are common inorganic forms of nitrogen. These forms of nitrogen can be easily taken up by algae and other aquatic plants, potentially triggering nuisance of algae blooms in the receiving water, if present in high concentrations in the effluent discharged from the water reclamation plant. Other than wastewater, runoff from highly fertilized agricultural lands also increases nitrate pollution of most waterways.

Nutrient stimulated algae production is of most concern in lakes and estuaries. It could be controlled by physical factors, such as light penetration, timing of flow, and type of substrate available (McCabe et al., 1985). If sufficient phosphorus is available, high concentrations of nitrates along with P will lead to phytoplankton (algae) and macrophyte (aquatic plant) production. In contrast to freshwater, nitrogen is the primary limiting nutrient in the seaward portions of most estuarine systems (Paerl, 1990). The recommended level of nitrogen in estuaries to avoid algal blooms is 0.1~1 mg L^{-1} (NOAA/EPA, 1988). Toxic algae, like the occurrence of red tide, have been associated with eutrophication in coastal regions and may result in paralytic shellfish poisoning (Mueller et al., 1987). Algal blooms shade submerged aquatic vegetation, reducing or eliminating photosynthesis and productivity (Dennison et al., 1993; Batiuk et al., 1992).

Nitrogen mineralization is low or absent in treated wastewater irrigated fields. It will not compensate for the loss of nitrogen, when the wastewater is treated, and the application of nitrogen fertilizer will be required to maintain the same level of crop production. The characteristics of the soils may not deteriorate after years of application of wastewater, but further irrigation, even with treated wastewater, might increase sodicity and salinity and pose a threat to future crop production (Ramirez-Fuentes et al., 2002). The groundwater quality is highly disturbed by the increased inputs of nitrogen fertilizers. The riparian forests have been demonstrated to be capable of removing nitrate from agricultural drainage and thus play an important role in the regulation of fluxes between rivers and adjacent agro-systems (Cooper, 1990 (b); Lawrence, 1992; Pinay et al., 1993).

Soil nitrate concentration will vary seasonally with temperature and moisture levels. Fall and winter thoroughly remove all nitrates from the soil. No nitrate is naturally added to the soil during late fall and winter because the cold weather prohibits the mineralization and nitrification processes. Some leaching may occur in the spring if crops are not established enough to absorb the nitrogen (Gower, 1980). The limits of nitrate nitrogen for human consumption, aquatic life, and the brewing industry are 10, 90, and 30 mg L^{-1}, respectively; and the total of nitrate and nitrite nitrogen in estuarine water and the livestock industry are 0.1~1 and >100 mg L^{-1}, respectively (AWWA, 1990).

The toxicity of nitrate in humans is a result of the reduction of nitrate to nitrite. By reacting with hemoglobin, nitrite forms methanoglobin, a substance that does not bind and transport oxygen to tissues. Thus, methanoglobin formation may lead to asphyxia. Normally, methanoglobin accounts for 1~2% of globin in the body, but a level greater that 3% is defined as methanoglobinemia. Therefore, if the nitrate concentrations in drinking water are above 10 mg L^{-1} of NO_3^--N or above 45 mg L^{-1} of NO^{3-}, it could cause methanoglobinemia (Blue baby syndrome), mainly in infants (Straub, 1989).

2.3.2.1.2 Phosphorus

Lake and reservoir sediments serve as P sinks, and the particles containing P settle to the substrate and are rapidly covered by sediment. Therefore, some P is removed permanently from bio-circulation this way (Smith, 1990; Holtan et al., 1988). Continuous accumulation of sediment will leave some P too deep within the substrate to be reintroduced into the water. Recycling of P often stimulates phytoplankton blooms. Phosphorus in fresh and marine water exists in either a particulate or a dissolved phase. The dissolved phosphorus (usually orthophosphate) is assimilated by phytoplankton and altered to organic phosphorus and then ingested by zooplankton. Continuing in the cycle, the inorganic P is rapidly assimilated by phytoplankton (Smith, 1990; Holtan et al., 1988). In the soil, it is rapidly immobilized as calcium or iron phosphates. The natural background levels of total P are generally less than 0.03 mg L^{-1}. Most of the P in soils is adsorbed to soil particles or incorporated into organic matter (Smith, 1990; Craig et al., 1988; Holtan et al., 1988). Sorption is the main P removal mechanism in soil. The sorption of P to Al and Fe components is important for its retention in filter materials (Sakadevan and Bavor, 1998), and co-precipitation to Ca and Al is also an important retention mechanism in lightweight aggregates (Zhu, 1998; Jenssen and Krogstad, 2003).

Phosphorus in wastewater exists mainly in organic and inorganic forms, where more than half of total phosphorus is in organic forms. Common forms of organic phosphorus are inositol phosphates, phospholipids, phosphate sugars and nucleic acids (Pierzynski et al., 2000). The typical levels of phosphate-P in municipal wastewater and total-P in secondary treated effluent were reported to be in the range of 4~16 (Tchobanoglous et al., 2003) and 5~40 mg L^{-1} (Asano et al., 1984; Treweek, 1985), respectively.

With wastewater irrigation, P can be treated as a valuable fertilizer, and thereby can reduce the pollution to surface and groundwater (Hylander et al., 1999). Plants and other soil organisms take up inorganic phosphate and incorporate it into their tissue. Vegetative uptake of soil phosphorus occurs only from the inorganic forms. Plant roots will absorb phosphate ions ($H_2PO_4^-$, HPO_4^{-2}) dissolved in soil-water and incorporated into microbial cell material and organic matter (Evanlou.V.P, 1998). $H_2PO_4^-$ is the dominant phosphate ion in soils (Pierzynski et al., 2000). In the treatment of wastewater by wetlands, infiltration beds, and constructed filter wells, P in the wastewater can be entrapped into the soil (Roseth, 2000; Brooks et al., 2000; Hill et al., 2000; Agyei et al., 2002; Drizo et al., 2002; Cameron et al., 2003), and thereby increase the level of P in the soil. Biological and chemical processes in the soil-water system constantly change soil phosphorus from one form to another. Microbial decomposition of organic P results in the release of soluble organic P, which eventually is converted into stable inorganic forms of P.

The discharge of wastewater with high nutrient levels into water bodies can accelerate eutrophication (Pretty et al., 2003). If sufficient P is available, the elevated concentrations of nitrates will lead to algal blooms. Although 0.08~0.10 mg L^{-1} of orthophosphate in water may trigger periodic algal blooms, long-term eutrophication will usually be prevented if total P levels and orthophosphate levels can be reduced below 0.5 and 0.05 mg L^{-1}, respectively (Dunne and Leopold, 1978). A reduction in P loading alone may not be effective in reducing algal blooms (Maki et al., 1983) because a reduction of nitrate is also needed. If the streams discharge into lakes or reservoirs, the amount of P should not exceed 0.05 mg L^{-1} in the stream water, and within a lake or reservoir, the level should be below 0.025 mg L^{-1} to control algal growth (USEPA, 1986). Surface waters that are maintained at 0.01~0.03 mg L^{-1} of total P tend to remain uncontaminated by algal blooms. Phosphate in water itself does not have notable adverse health effects, however, phosphate levels greater than 1.0 mg L^{-1} may interfere with coagulation in water treatment plants. As a result, organic particles that harbor microorganisms may not be completely removed before distribution to water supply systems.

2.3.2.2 Organic pollutants

The organic matter present in wastewater, derived from both animals and plants, are normally composed of a combination of carbon, hydrogen, oxygen, and in some cases, nitrogen. The principal groups of organic substances found in wastewater are proteins (40~60%), carbohydrates (2~25%), and fats and oil (10%) [Bal et al., 1999]. Suspended matter represents the organic and inorganic materials in the wastewater. A substantial portion of organics consists of biodegradable materials, which serve as food sources for bacteria and other microorganisms. Microbial degradation of organic matter ends up in products, such as carbon dioxide, water, phosphate and nitrate. General forms of these reactions are as given below, and each of these reaction steps consumes dissolved oxygen (Dunne et al., 1978).

Carbohydrates ---> Carbon dioxide
---> Water
Proteins ---> Amino Acids --->Ammonia --->Nitrite ---> Nitrate
---> Sulfate
---> Phosphate

High organic inputs trigger de-oxygenation, and hence, if excess organics are introduced to the system, there is a potential for complete depletion of dissolved oxygen, thereby potentially having an adverse affect on aquatic life. The only organisms that can endure this situation are air-breathing insects and anaerobic bacteria (Gower, 1980).

Organic levels in the surface water decrease with distance from the source of wastewater disposal; however, in a standing water body such as a lake, currents are generally not powerful enough to transport large amounts of organics. In a moving body of water, the saprotrophic organisms (organisms feeding on decaying organic matter) break down the organics during transportation away from the source. Hence, there is a decline in the oxygen demand and an increase of dissolved oxygen in the water. Due to high levels of organic matter in the wastewater, some areas encourage the practice of disposal or discharge of treated water offshore, in order to protect the waterways (Kennish, 1992). Organic matter in wastewater is considered to be a pollutant and should be removed as much as possible before discharging the water into water-bodies. However, fortunately, the organic matter in soil is considered as a valuable constituent rather than as a pollutant.

2.3.2.2.1 Biological oxygen demand (BOD)

Biological oxygen demand (BOD) is defined as the amount of oxygen consumed during degradation of organic materials. The BOD of the wastewater measures the oxygen required for the biochemical degradation of organic material and oxidation of certain inorganic materials. Five-Day biochemical oxygen demand (BOD_5) is commonly used to measure natural organic pollution and is defined as the amount of oxygen required by bacteria to decompose organic matter for a specified time (usually 5 days) under aerobic conditions. The amount of oxygen reported with this method represents only the carbonaceous oxygen demand (CBOD) or the easily decomposed organic matter. Nitrification is not expected until the carbonaceous BOD drops below approx. 20 mg L^{-1} in a wastewater treatment with trickling filters (Parker et al, 1998). Under low BOD conditions, even if nitrification occurs, denitrification is limited by the lack of a carbon source in the deeper depth of the biofilm in wastewater treatment (Timberlake et al., 1988). However, since the levels of BOD and total suspended solids (TSS) are used as wastewater treatment standards, high BOD concentrations of the treated wastewater are often considered as a failure of the treatment system (Benefield, 2002).

2.3.2.2.2 Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. It is often used as an indicator of the concentration of organic matter in wastewater and natural waters, and measures the oxygen required for the complete oxidation or breakdown of organic matter to CO_2 (Living Machines, Inc., 2003). Because of the complete oxidation of organic matter, and quicker analysis, generally a reduction in the COD value is used as an indicator to determine the efficiency of municipal and industrial wastewater treatment processes. Typical values the of BOD: COD ratio for untreated municipal wastewater are in the range of 0.3~0.8 (Tchobanoglous et al., 2003). Wastewater with ratios higher than 0.5 can be biologically treated, whereas, if the ratio is lower than 0.3, it can be presumed that the wastewater contains some toxic compounds (Tchobanoglous et al., 2003).

Numerous studies have been performed on COD and nitrogen removal in membrane bioreactors supplied with both air and oxygen (Osa et al., 1997). They found that nitrogen removal efficiency was influenced by the COD: N ratio in the influent wastewater. Less than 5% nitrogen removal was achieved at a COD: N ratio of about three. In domestic wastewater, the COD: N ratio is typically 5~8. At a value of about five, the COD of the added organic substrate is approximately equal to the nitrogenous oxygen demand (NOD) for nitrification. A study of an aerated bioreactor used to treat synthetic wastewater containing ammonium acetate and trace nutrients showed COD removals in excess of 95% in six hours of nominal retention (Michael et al., 2003).

2.3.2.2.3 Total organic carbon (TOC)

Total organic carbon (TOC) is a measure of the organically oxidizable content of a water sample. In the TOC determination, organic carbon converts to carbon dioxide using a combination of heat and oxygen, ultraviolet radiation, and chemical oxidation. TOC is often used as a substitute for the BOD test (Tchobanoglous et al., 2003), and hence can also be considered as a standard measure of wastewater pollution. The TOC test is also gaining favor as it takes only 5~10 minutes to complete. The typical TOC level of municipal wastewater per capita is usually below 135 mg L^{-1}. The BOD: TOC ratio of municipal wastewater is in the range of 1.2~2.0, whereas, its values in secondary treated effluent range from 0.2 to 0.5 (Tchobanoglous et al., 2003).

TOC removal generally becomes more difficult, as alkalinity increases and TOC decreases. When alkalinity is high, more acid must be added to force the pH down (the optimal pH range for coagulation with alum is 5.5 to 6.5), therefore just adding coagulant might not be enough in water treatment plants. Fewer opportunities for particles to contact each other and form flock, is another reason for the difficulty in TOC removal. Water systems with an ultraviolet radiation (UV) reaction chamber (designed to destroy organic carbon compounds) in most modern labs are capable of producing water with a low TOC level. As opposed to a specific organic compound, TOC provides a generic test of the overall organic carbon content of a system, and hence, will show a trend or alert the user of the potential organic matter in the system.

2.3.2.2.4 Pesticides

The United States environmental protection agency (USEPA) defines a pesticide to be any substance that is intended to prevent, destroy, repel, or mitigate any pest (Ecobichon, 1991). This includes insecticides, herbicides, fungicides, fumigants, algaecides, and other substances. Herbicides are widely used in agriculture, and hence, detected in surface and ground waters (Barbash, 1996). Herbicides account for 75% of pesticide use in U.S. agriculture (Wauchope et al., 1994), and are more frequently found at higher concentrations in streams or surface water than in ground water (USGS, 1998).

The most common types of herbicides found in the surface water of the U.S.A. and Canada are atrazine, metolachlor, and metribuzine (Smith and Cullum, 1992; Logan et al., 1993; Munster et al., 1994). Among these, atrazine is one of the most frequently used pesticides in agriculture, and due to its wide use, it persists in soil, and moves into surface and groundwater (USEPA, 2001). Metolachlor is also one of the top pesticides detected in surface waters (USEPA, 1995). For atrazine, maximum contaminant level goal (MCLG) and maximum contaminant level (MCL) have been set at 0.003 mg L^{-1}, for metolachlor, the interim maximum acceptable concentration (IMAC) is set as 0.05 mg L^{-1}, and for metribuzin, the maximum acceptable concentration (MAC) is set as 0.08 mg L^{-1} (EPA, 2002). According to Canadian standards, the acceptable levels of metolachlor and metribuzin are the same as that of the EPA limits, but for atrazine, the level is set as 0.005 mg L^{-1} (Health Canada, 2004).

Pesticides are transported to aquatic systems via: surface runoff, direct fallout from spraying of nearby fields, adsorption of the compound into soil or organic particles that are then eroded and carried to the water body, the compound carried by overland and/or subsurface flow, and dry or wet atmospheric deposition. Point sources include direct application of pesticides, release of effluent from pesticide manufacturing plants, and spills during mixing, loading, or transport. In addition to runoff from agriculture land, wastewater discharge also contributes pesticides to water-bodies (Neumann et al., 2002; Gerecke et al., 2002). The degree and ease of pesticide transport depends on five main factors (Wauchope et al., 1994). It include the time, frequency, site and amount of pesticide, the formulation type (granules, powder or liquid), and application method (surface, incorporated, or in-furrow). Mobile pesticides do not bind strongly to soil particles and are more likely to leach. If a pesticide is too rapidly leached to the subsurface or carried in runoff to a water system, contamination of a water supply may occur. Sandy soils drain rapidly and thus are susceptible to leaching problems. Clay soil is less porous, so water will pool at the soil surface and run off instead of infiltrating. Therefore, soils with high organic matter content will better adsorb pesticides.

These pesticides are mainly released to wastewater through agricultural runoff and from manufacturing facilities. Numerous detections of atrazine at concentrations above the MCL in ground water were observed in different states of the United States (EPA, 2002).

Metribuzin was detected in municipal water supplies in Nova Scotia (1986), Ontario (1979~1986), Manitoba (1986), and Alberta (1978~1986), and their detection limits were in a range of 0.01~1.0 mg L^{-1} (Heibsch, 1988). The maximum concentration of metribuzin, determined in a sample of well water in Ontario, was 300 mg L^{-1} (Frank and Logan, 1988), and in surface water samples from two Ontario river basins was 1.1 mg L^{-1} (mean concentration detected during 1981~1985; Hiebsch, 1988).

2.3.2.2.5 Oil and grease

The term *fat, oil, and grease* (FOG) used previously in literature is now replaced by the term *oil and grease*. When large amounts of oil and grease are spilled out, they can be transported directly to water-bodies or can be a part of wastewater, which, in turn, will reach waterways. They increase BOD of the receiving water, and may float on the surface, causing aesthetically unpleasant conditions (Tchobanoglous et al., 2003). They can trap trash, plants and other materials, causing foul odors and attracting flies and mosquitoes and other disease vectors. In some cases, too much oil and grease can cause septic conditions in ponds and lakes by preventing oxygen from reaching the water. Fatty organic materials from animals, vegetables, and petroleum are not quickly broken down by bacteria and can cause pollution in the receiving environment. The typical range of FOG of municipal wastewater is in the range of 50~150 mg L^{-1} (Benefield, 2002). The presence of grease in wastewater can interfere with the aquatic life of surface waters and can create hideous films on water surfaces (Tchobanoglous et al., 2003).

2.3.2.3 Other inorganic pollutants

Inorganic pollutants include dissolved solids such as salt and minerals, heavy metals, and compounds of Na, K, Ca, Mg, Cd, Cu, Pb, Ni and Zn, and are common in both residential and nonresidential sources of wastewater.

2.3.2.3.1 Heavy metals

Recently, the presence of heavy metals in water is receiving greater prominence in water quality issues. Uncontrolled heavy metal inputs are undesirable, as they are very difficult to remove from the soil; once they accumulate in the soil they will cause potentially harmful effects in the future. Potentially toxic heavy metals (e.g. Cadmium, Chromium, Lead, and Mercury) are generally present in industrial wastewater, hence, they are often present in municipal wastewaters. Urban storm water runoff often contains metals from roadways and atmospheric fallout (Connell et al., 1984). Domestic wastewater effluent contains metals from metabolic wastes, corrosion of water pipes, and consumer products. Industrial effluents and waste sludge may substantially contribute to metal loading (Connell et al., 1984). The toxic effects of these metals can interfere with biological waste treatment processes (Bal, et al., 1999). Heavy metals are found in river waters as well. For example, cadmium was found in the rivers of Europe (Rhine River) [Evans et al, 2001) and Bangladesh, and fluoride in Indian rivers (Hoeck, 2001). Living organisms require trace amounts of heavy metals like Co, Cu, Fe, Mn, Mo, and Zn. However, excessive levels of these metals can be detrimental to the organism. Non-essential heavy metals of particular concern to surface water systems are Cd, Cr, Hg, Pb, As, and An (Kennish, 1992).

Heavy metals exist in waters in colloidal, particulate or dissolved phases, although dissolved concentrations are generally low (Kennish, 1992). The solubility of trace metals in surface waters is predominately controlled by the pH of the water, the type and concentration of ligands on which the metal could adsorb the oxidation state of the mineral components, and the redox environment of the system (Connell et al., 1984). The behavior of metals in natural waters is a function of the sediment composition of substrate and suspended material and the water chemistry. A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal-carbonate complexes, releasing free metal ions into the water (Connell et al., 1984).

Ingestion of metals such as Pb, Cd, Hg, As, Ba and Cr may pose great risks to human health. Trace metals, such as Pb and Cd, will interfere with essential nutrients of similar appearance, such as Ca (Ca^{2+}) and Zn (Zn^{2+}). Because of charge similarities, Pb can substitute for Ca and is infused into human bone. Lead that is stored in bone is not harmful, but when high levels of Ca are ingested later, the Pb in the bone may be replaced by Ca and the free Pb in the system may cause nephrotoxicity, neurotoxicity, and hypertension. Cadmium may interfere with the metallothionein's ability to regulate Zn and Cu concentrations in the body. Metallothionein is a protein that binds to excess essential metals to render them unavailable. When Cd induces metallothionein activity, it binds to Cu and Zn, disrupting the homeostatic levels (Kennish, 1992). Mercury in water (the only metal that bioaccumulates) may often be transformed by microorganisms into the toxic methyl mercury form. However, most of the other heavy metal removal mechanisms in soil are through reactions such as, adsorption, co-precipitation, precipitation, cation and anion exchange, complexation, oxidation/reduction, microbial activity, hydrophobic partitioning, and plant uptake (Matagi et al., 1998). Chronic Hg poisoning is usually a result of industrial exposure or a diet consisting of contaminated fish, and may cause liver damage, neural damage, and teratogenesis (USEPA, 1987). Arsenic ingestion can cause severe toxicity through ingestion of contaminated food and water.

Elevated metal levels in natural waters may cause sub-lethal effects in aquatic organisms, mainly resulting in changes to their morphology, physiology (growth retardation), enzyme activity, behavior, and reproduction (Connell et al., 1984). Many organisms are able to regulate the metal concentrations in their tissues. Fish can excrete excess essential metals, such as Cu, Zn, and Fe. Some can also excrete non-essential metals, such as Hg and Cd (Connell et al., 1984). The ability of fish and invertebrates to adsorb metals is largely dependent on the physical and chemical characteristics of the metal (Kennish, 1992). With the exception of Hg, little metal bioaccumulation has been observed in aquatic organisms (Kennish, 1992). Aquatic plants are not able to successfully regulate the uptake of metals (Connell et al., 1984).

Metals may enter the systems of aquatic organisms via three main pathways; (i) Free metal ions that are absorbed through a respiratory surface (e.g., gills) are readily diffused into the blood stream, (ii) Free metal ions that are adsorbed onto body surfaces are passively diffused into the blood stream, and (iii) Metals that are sorbed onto food and particulates may be ingested, as well as free ions ingested with water (Connell et al., 1984). Accumulation of cadmium usually occurs in plant roots, but may also occur throughout the plant (De-Voogt et al., 1980).

2.3.2.4 Pathogens

Many disease causing viruses, parasites, and bacteria are present in wastewater. Wastewater effluent is well known as the potential point source of pathogens in surface water (Exall et al., 2004; Lipp et al., 2001). However, recent studies showed their presence even in runoff water (Smith and Perdek, 2004; Crainiceanu et al., 2003; Ferguson et al., 2003; and Conboy and Goss, 2000; Kim et al., 2005). The pathogens often originate from people and animals who are carriers of a disease. Thus, apart from the removal of organics, another important wastewater treatment concern is often the removal of as many pathogenic bacteria and viruses as possible before discharging of the wastewater to water-bodies (Bal et al., 1999). They are minute in size and can enmesh in suspended solids in the wastewater. The suspended solids can provide shields to protect bacteria and viruses from the added disinfecting agents in the treatment. Cases of illness caused by parasitic protozoa Giardia lambia and Cryptopordium are quite common in North America (Barbara Butler and Colin Mayfield, 1996; CDCP, 2000). Other diseases include hepatitis A, typhoid, polio, cholera, and dysentery. Outbreaks of these diseases can occur as a result of polluted drinking water uptake, eating contaminated fish, or recreational activities in polluted waters (Barbara Butler and Colin Mayfield, 1996).

2.3.2.4.1 Bacteria

Bacteria are small, simple, and the most abundant organism on earth. Most bacteria are only one micrometer (μm) in diameter, but they can range in size from 0.1~>10 μm. Bacteria are able to survive in a wide range of environmental conditions. Bacteria can be useful to humans in many ways, such as decomposing organic substances and unwanted synthetic chemicals (e.g. pesticides, dyes, and petroleum) that are released into the environment. Additionally, bacteria provide many antibiotics, such as penicillin, bacitracin, erythromycin, streptomycin, and tetracycline.

Bacteria can also be harmful. In addition to the toxin-producing bacteria, there are also a wide variety of pathogenic bacteria (Table 2.1). Bacteria can also cause many crop-destructive plant blights (Raven et al., 1986). Since 1880, coliform bacteria have been used to assess the quality of water and the likelihood of pathogens being present. Although several of the coliform bacteria are not usually pathogenic themselves, they serve as an indicator of potential bacterial pathogen contamination. It is generally much simpler, quicker, and safer to analyze for these organisms than for the individual pathogens that may be present.

Table 2.1: Human pathogenic bacteria

Bacteria	**Disease**
Bacillus anthracis	Anthrax
Bordetella pertussis	Whooping cough
Corynebacterium diphtheriae	Diphtheria
Mycobacterium tuberculosis	Tberculosis
Salmonella sp.	Salmonellosis, Typhoid fever
Shigella sp.	Bacillary Dysentry
Streptococcus pyogenes	Scarlet Fever
Vibrio cholera	Cholera
Yesinia pestis	Bubonic Plague

The fecal coliform to fecal streptococci ratio (FC: FS) provides an indicator of the origin of pollution of surface waters. A ratio of 4 or more indicates contamination of human origin, where as, a ratio below 0.7 is an indication of animal pollution (Geldreich and Kenner, 1969); however, this ratio is only valid for recent (24 hours) fecal pollution. They are valuable pollution indicators in the study of rivers, streams, lakes, and marine systems, especially when dealing with fecal coliform bacteria. Klebsiella, a microorganism of coliform group may be present in water distribution systems. It is also found as a major coliform population of municipal and industrial wastewater, where high amounts of nutrients to bacterial growth are available (Marial and Csaba, 1999).

Coliform bacteria concentrations in water and wastewater are determined using methods specified by the Environmental Protection Agency (EPA) and Standard Methods for the Examination of Water and Wastewater (AWWA, APHA, and WEF, 1992). Researchers estimate that 40% of private water supplies and 70% of spring-fed supplies contain coliform bacteria (Kubek et al., 1990). Immersion in bacteria-contaminated water can result in infections of the eyes, ears, nose, and throat (Mueller et al., 1987). From bacteriological data, it was estimated that fecal coliform concentrations of 200 per 100 ml would cause illnesses in

8 per 1,000 swimmers at fresh water beaches and 19 per 1,000 swimmers at marine beaches (USEPA, 1986). Heterotrophic Plate Count (HPC) represents the aerobic and facultative anaerobic bacteria that use carbon and energy from organic compounds. It was found to be the most sensitive indicator for determining the removal and inactivation of microbial pathogens in reclaimed wastewater, and hence was used as a wastewater treatment standard in the treatment plant (AWWA, 1987; Grabow, 1990; Reasoner, 1990).

Recently in the year 2001, due to the uptake of contaminated water, nearly 2000 people were infected with Cryptosporidiosis in North Battleford city (Canada). Another serious outbreak occurred in the year 2000 in Walkerton city (Canada), where seven people died and more than 40% of the population became ill, by drinking water contaminated with a highly dangerous strain of E.Coli bacteria (Encyclopedia, 2005).

2.3.2.4.2 Viruses

Viruses are a group of infectious agents ranging from 10~25 nanometers (nm) in diameter. The protein or lipoprotein cover of viruses determines to what surface the virus will adhere (AWWA, 1990). Members of the enteric viruses infect the gastrointestinal tract of humans and animals, and are excreted in feces. If the feces enter a surface water system, usually possible through wastewater disposal, there is potential for the spread of waterborne diseases. Enteric viruses of particular concern in water are hepatitis A, rotaviruses, adenoviruses, enteroviruses, and reoviruses.

Hepatitis A virus (HAV) is readily transmitted through water. Rotaviruses cause acute gastroenteritis, especially in children. Both HAV and rotaviruses can be removed from drinking water through coagulation, flocculation, and filtration (AWWA, 1990). Adenoviruses and Enteroviruses can infect both the intestine and the upper respiratory tract. Adenoviruses have been detected in wastewater and contaminated surface water, but not in drinking water, whereas, enteroviruses have been detected in wastewater, natural water, and even in drinking water (AWWA, 1990). The maximum contaminant level (MCL) for viruses is zero viruses per 100 ml sample of drinking water. The MCL is simply the level which can be achieved by the best available technology (Kubek et al., 1990).

Bacteriophage, a major type of indicator organism for viral population is similar to enteric viruses, but is more easily and rapidly detected in environmental samples and is found in higher numbers than enteric viruses in wastewater and other environments (Bitton, 1980, Goyal et al., 1987). Coliphages serve as indicators for assessing the removal efficiency of water and wastewater treatment plants (Bitton, 1987). In water treatment plants, coliphages help provide information concerning the performance of water treatment processes such as coagulation, flocculation, sand filtration, adsorption to activated carbon, and disinfection (Payment, 1991).

2.3.2.5 Soil solids

Solid materials in wastewater can contain a variety of solid materials varying from rags to colloidal materials, which includes organic and inorganic materials and organisms (Tchobanoglous et al., 2003). The solids must be reduced by treatment, or they will increase BOD in the receiving waters and facilitate microorganisms to escape from disinfection.

There are three types of soil solids: settleable, suspended, and dissolved solids. Settleable solids include sand, grit, and heavier organic and inorganic materials; these solids settle out from the rest of the wastewater stream during the preliminary stages of treatment. Suspended solids (SS) will resist settling and remain suspended in wastewater. Wastewater should be treated to remove SS, otherwise, they will clog the soil or reduce the effectiveness of the disinfection systems. Dissolved solids (DS) are small particles of certain wastewater materials that can dissolve in water. Some dissolved materials are consumed by microorganisms in wastewater, but others, such as heavy metals, are difficult to remove by conventional treatment. Excessive amounts of dissolved solids in wastewater can have adverse effects on the environment. The typical ranges of SS and DS in the municipal wastewater (per capita) are 225 (Tchobanoglous et al., 2003) and 200~1300 mg L^{-1} (Treweek, 1985; Asano et al., 1985), respectively.

2.3.2.6 Gases

The gases relevant in wastewater are dissolved oxygen and green house gases. Dissolved oxygen is the oxygen that is present in water, while, a green house gas can be any gas molecule which absorbs infrared light in the spectral region of 5~20 μm. These include molecules of water vapor, carbon dioxide, carbon monoxide, methane, certain volatile organic compounds, and nitrous oxide.

2.3.2.6.1 Dissolved oxygen

Oxygen enters the water by photosynthesis of aquatic biota and by the transfer of O_2 across the air-water interface. The amount of O_2 that can be held by water depends on the water temperature, salinity, and pressure (Tchobanoglous et al., 2003). Gas solubility increases with decreases in temperature and salinity, whereas, it decreases as pressure decreases. In flowing water, O_2 rich water at the surface is constantly being replaced by water containing less O_2 as a result of turbulence, creating a greater potential for an exchange of O_2 across the air-water interface. Oxygen losses readily occur when water temperatures rise, plants and animals respire, and microbes aerobically decompose organic matter. Microbes use O_2 as energy to break down long-chained organic molecules into simple, more stable end products such as carbon dioxide, water, phosphate, and nitrate (Dunne et al., 1978). The introduction of excess organic matter may result in a depletion of O_2 from the aquatic system. In wastewater, dissolved oxygen (DO) can restrain nitrate reduction by inhibiting nitrate reduction enzymes (Tchobanoglous et al., 2003). In the treatment of municipal wastewater, DO concentrations above 0.2 mg L^{-1} inhibited the denitrification for a *Pseudomonas* culture (Terai and Mori, 1975) and for an activated sludge process (Dawson and Murphy, 1972).

2.3.2.6.2 Nitrous oxide

Nitrous oxide (N_2O) is one of the greenhouse gases, 280 times as effective as CO_2 in causing global warming (Houghton et al., 1996). It is a low concentration constituent in the atmosphere, which represents 0.3 $\mu l\ L^{-1}$ within the atmosphere by volume basis (Rolston, 1981). Being chemically inert in the lower atmosphere, N_2O slowly diffuses into the stratosphere, where it participates in photochemical reactions. This can lead to the destruction of the earth protecting ozone layer (Crutzen, 1981), causing increased incidences of skin cancer (Peoples et al., 1995).

The sources of N_2O fluxes are terrestrial, aquatic and man-made. The main source of N_2O emissions from agricultural soils is from the microbial processes of nitrification and denitrification (Firestone and Davidson, 1989), which are commonly stimulated by fertilizer application (Clayton et al., 1994). Furthermore, the land spreading of farmland manure has been identified as a significant contributor of N_2O (Goulding and Webster, 1989). Little research appears to have been done on the effects of sludge application to soils of fine or medium texture (Smith, 1996), although Moiser et al. (1982) found rather low N_2O fluxes from coarse textured soils. Digested sewage sludge contains a similar amount of total nitrogen to farmyard manure (Aitken, 1997). A study of sewage sludge amended with soil revealed that the automated N_2O sampling chamber was especially useful in detecting the marked temporal variability of N_2O and CO_2 gases associated with the diurnal temperature change and rainfall (Scott et al., 2000). The high cumulative emissions of N_2O from sewage sludge amended soil were attributed to the high nitrogen, carbon, and moisture levels in the soil (Scott et al., 2000).

2.4 MUNICIPAL WASTEWATER TREATMENT METHODS

Wastewater treatment facilities are designed to fit into the communities that they serve. The goal of wastewater treatment is the removal of contaminants from the water in order to decrease the possibility of detrimental impacts on human life and the rest of the ecosystem. Municipal wastewater systems are normally designed to treat influents that are essentially domestic in nature. Such systems are ineffective in removing some industrial pollutants and may even be damaged by them. However, municipal wastewaters do receive some amounts of industrial wastewater and runoff from agriculture land. The general treatment approaches for municipal wastewater treatment fall into three major categories: primary treatment, secondary treatment and tertiary (advanced) treatment (PPA, 1998).

2.4.1 Primary treatment

Primary treatment consists of physical or mechanical operations to remove large objects by screens (filters) and remove sediment and organic matter in settling chambers. The objective of this treatment is to produce an effluent quality with less than 130 mg L^{-1} of BOD_5 and total suspended solids (TSS) (Environment Canada, 2003). It eliminates approximately 60% of total suspended solids, 35% of BOD and 50% of pathogens. Dissolved impurities are not eliminated (Crities and Tchobanoglous, 1998).

2.4.2 Secondary treatment

Secondary treatment standards for wastewater are concerned with the removal of biodegradable organics, total suspended solids, and pathogens. Secondary treatment involves a combination of biological or chemical, and mechanical processes, or processes using gravity to eliminate dissolved materials and colloidal as well as suspended matter. This degree of treatment is considered to result in the removal of at least 85% of suspended solids and BOD (Crities and Tchobanoglous, 1998). Many more stringent standards that deal with the removal of nutrients, heavy metals, and priority pollutants have been recently developed (Tchobanoglous et al., 2003). Activated sludge and trickling filters are two of the most common secondary treatment methods. It is accomplished by the combined action of organic and inorganic wastes, microorganisms, and oxygen in trickling filters or in the activated sludge process. This treatment removes floating and settleable solids and about 90% of the oxygen-demanding substances and suspended solids. It also removes some amounts of P (8~25%) and N (10~30%) from the wastewaters. It produces an effluent quality with less than 45 mg L^{-1} of BOD_5 and TSS (Environment Canada, 2003).

In most cases, secondary treatment processes are biological in nature, designed to provide a proper environment for biological breakdown of soluble organic materials either in aerobic or in anaerobic processes. A variety of microorganisms which play an important role in wastewater treatment, are bacteria, protozoa, rotifers, fungi, and algae. The basic input needed for secondary biological treatment are the availability of appropriate microorganisms, good contact between organisms and organic material, O_2 availability, and the maintenance of other favorable environmental conditions depending on the process (PPA, 1998).

2.4.3 Tertiary treatment

Tertiary or advanced treatment methods are utilized when the effluent is discharged to a sensitive receiving environment or in water reuse applications. The process can be accomplished using a variety of physical, chemical, or biological treatment processes to remove targeted pollutants. It is an advanced level of treatment to remove constituents of concern including nutrients, toxic compounds and increased amounts of organic matter and suspended solids. The purpose of tertiary treatment is to produce a high quality effluent using the best available technologies. These systems can achieve high removal of organic material, suspended solids, and nutrients (PPA, 1998). Tertiary treatment uses the addition of chemical products, or physical/biological processes to improve the quality of effluents. It is used to eliminate more than 85% of total solids and BOD, or to reduce the concentration of nutrients (Crities and Tchobanoglous, 1998). These processes can eliminate more than 99% of all wastewater impurities. Activated carbon, reverse osmosis, and ion exchange are some of the main tertiary treatment methods. These methods are very expensive and use advanced techniques.

A number of studies (Sheikh et al., 2000a, and b) have reported that tertiary treated municipal wastewater is safe for irrigation of food crops, without pathogenic agents transmitting diseases (Ayres et al., 1992, Oragui et al., 1993). As primary and secondary treatment removes only 10% and 30% of P from the wastewater (Smith, 1990), tertiary treatment is required to remove additional P before discharging to water-bodies.

2.5 LAND TREATMENT / FLOODPLAIN-SOIL FILTRATION TECHNIQUE

When municipal wastewaters receive some amounts of industrial wastewater, tertiary treatment is often required to meet treatment goals. However, in rural areas, land is more available and wastewater is from domestic sources with minimal industrial inputs. In these areas, constructed wetlands, as a component of a treatment process, provide a low energy, low-tech method of removing pollutants. According to Westerhoff and Pinney (2000), simple wastewater land treatment processes coupled with groundwater recharge systems offer a potential option for water and wastewater management.

The texture, structure, and chemistry of soil and the associated biological activity make it ideal to treat wastewater to protect surface and ground water. The suspended solids in wastewater are easily filtered out through soil. Soil pores must be fine enough to trap suspended solids and disease causing organisms. The application of wastewater to agriculture land from municipal treatment plants, agricultural processing plants, and industrial sources has been practiced in many countries for a long time. Land application of wastewater is an economically attractive treatment, which provides recycled water for rural communities (ACES, 2000).

Land application techniques consist of three categories: slow irrigation, overland flow, and rapid infiltration. Slow irrigation is the most widely used land application method as compared to overland or rapid infiltration method. Rapid infiltration technique is also common, in which wastewater quickly moves through the soil until it becomes part of the groundwater. Other land application techniques such as subsurface adsorption beds, deep-well injection, and evaporation ponds are limited in their applicability due to high construction and maintenance costs (ACES, 2000).

Although there are different land treatment methods available for wastewater (wetlands, soil aquifer, soil filter beds, lagoons, etc.), wetland treatment is the main treatment method adopted in many parts of the world since the 1950's. Wetlands, commonly known as biological filters, are known to be well suited for treating municipal, agricultural, and industrial wastewater, storm water and runoff (William, 2002). During the early 1950s, studies on the feasibility of using wetlands in treating wastewater were initiated in Germany; and in the late 1960s, such studies began in the United States (DeBusk, 1999). During the 1970s, its scope in wastewater treatment increased dramatically and thus gained worldwide popularity (DeBusk, 1999). However, the use of wetlands for meeting wastewater treatment and water quality guidelines has only been seriously studied and implemented during the past few decades.

In wetlands, a wide range of physical, chemical and biological processes are involved in the removal of contaminants from wastewaters. Wastewater treatment using wetlands was found to remove more than 90% of nitrogen (Fennessey and Mitsch, 1991). Similar studies also showed nitrogen (Breaux and Day, 1994; Zhang et al., 2000), organic matter and suspended sediment removal (Ewel and Odum, 1984; Kadlec and Knight, 1996; Boustany et al., 1997; Gemma et al., 2003; Day et al., 2003). To overcome the problem of high nutrient levels in secondary treated wastewater in Australia, they opted partially for effluent treatment through artificial wetlands (Gardner et al., 2001).

In wetlands, flocculation is enhanced by increased pH, turbulence, concentration of suspended matters, ionic strength, and high algal concentration. In sediments, metals are adsorbed to clay and organic matter by electrostatic attraction (Patric et al., 1990). For chemicals such as heavy metals, more than 50% can easily be adsorbed onto particulate matter in the wetland and thus be removed from the water by sedimentation (Muller, 1988).

Co-precipitation of heavy metals with secondary minerals, such as hydrous oxides of Fe, Al, and Mn, is an important adsorptive mechanism in wetland sediments. Precipitation is also one of the major mechanisms by which metals are removed from wastewater and deposited in the sediments. In wetlands, P in the wastewater could become trapped in the soil thereby increasing the level of P in the soil (Roseth, 2000; Agyei et al., 2002; Cameron et al., 2003).

Observations and studies showed that both natural and artificial wetlands have a capacity to purify wastewater containing heavy metals (Matagi, 1993: Tam and Wong, 1994; Mbeiza, 1993; Denny et al., 1995). The four main processes by which heavy metals are removed in wetlands are physical, chemical, biological and biochemical. These processes occur mainly in compartments of wetlands like water, biota, substratum and suspended solids; emergent plants influence metal storage indirectly by modifying the substratum through oxygenation, buffering pH and adding organic matter (Dunbabin and Bowmer, 1992). The concentration of heavy metals removed from solution in wetlands is determined by interacting processes of sedimentation, adsorption, co-precipitation, cation exchange, complexation, microbial activity and plant uptake.

Microorganisms in water and wastewater can remove heavy metals directly from wetlands mainly by two major mechanisms: metabolism dependent uptake of metals into their cells at low concentrations and bio-sorption, a non-active adsorption process binding metal ions to the extra-cellular charged materials or the cell walls. Phytoplankton, the microorganism most often present in water, plays an important role in heavy metal dynamics in wetlands (Hammer and Bastian, 1989). Algae can assimilate Zn, Cu, and Ni, into their tissue in alkaline conditions (Hammer and Bastian, 1989).

Lagoons have been used as a process for wastewater treatment for centuries. In the 1920's artificial ponds were designed and constructed to treat wastewaters. By 1950, the use of ponds had become recognized as an economical wastewater treatment method for small municipalities and industries. In U.S, as of 1980, approximately 7,000 waste stabilization lagoons were in use, and today, one third of all secondary wastewater treatment facilities include a pond system of one type or another (DEP, 2003).

In Norway, filter beds have been used to remove phosphorus from sewage water since the beginning of the 90's. Due to its excellent performance and low maintenance, filter beds have become a widespread method for onsite sewage treatment in Nordic countries. The clean water obtained after the treatment process is discharged into streams, rivers, lakes or infiltrates into the ground (Rystad and Sortehaug, 2004). As in wetlands, P in wastewater could be trapped in the soil of filter beds, and hence its level could increase in the soil (Brooks et al., 2000; Hill et al., 2000; Drizo et al., 2002; Cameron et al., 2003).

In soil aquifer treatment of wastewater, sewage effluent is degraded or treated by biodegradation and sorption in soil (Wilson et al., 1995). In a study with soil aquifer treatment, the treated wastewater met the public health, agronomic and aesthetic quality requirements for the use of treated effluent for irrigation (Bouwer, 1985). The reclaimed water obtained after soil treatment is suitable for a variety of non-potable uses such as unrestricted agricultural uses, industrial uses, non-potable municipal uses, and recreational uses (Kanarek and Micheal, 1996).

The effluent obtained from the sand filtered treatment was of high quality, with typical biochemical oxygen demand (BOD) concentrations and suspended solids (SS) of 5 mg L^{-1} or less and 80% or more nitrification of the applied ammonia. Limited phosphorus removal was observed, however, significant reductions of fecal coliform bacteria were achieved by this treatment [USEPA, 1999(a)]. The performance of the filter is typically higher in areas of warmer climate, as compared to colder climate areas. However, the land area required may be a limiting factor for the treatment, it could create odor problems from open filters and its cost can be high if appropriate filter media are not locally available (CSPC, 1998).

Nitrogen removal from wastewater was also observed in other land treatment studies such as in riparian soils (Jacobs and Gilliam, 1985; Cooper, 1990 (a and b); Magg et al., 1997; Grimaldi and Chaplot, 2000), shallow aquifers (DeSimone and Howes, 1998), estuarine headwaters (Thompson et al., 2000), and vegetated and forested filter strips (Groffman et al., 1991). These wastewater land-treatment studies demonstrate the potential of soils use as an effective filtering media for the removal of nitrogen compounds, thus indicating that soil filtration could be used as a tertiary wastewater treatment process.

Thus, the land treatment can remove most of the contaminants to a certain level from the wastewaters, thereby increasing the quality of the water, which, in turn, improves the receiving surface water quality. However, land availability for treatment is scarce in many developing countries, which mainly face the problems with wastewaters. However, wide floodplains, low-lying areas on either sides of rivers and streams, are available in these countries, hence these area could be used as soil filter for wastewater treatment. Therefore, the floodplain-soil filtration technique, a wastewater land-treatment method, can be considered as a low cost, technically, and environmentally favorable treatment method.

The floodplains associated with most rivers and streams, will inundate only during rainy season, and will be uncultivated and weedy for most part of the year. In tropical developing countries like Korea and India, their seasonal patterns of rainy season (less than 3~4 months in a year; Kumar, 2003; Kim et al., 2003) allow floodplains to be used for treating wastewaters during a major part of the year,. The vegetation in the floodplains developed a rhizosphere, an excellent habitat of microbes and worms, with the supply of organic matter and oxygen in the top soil zone (Pierzynski et al., 1994), thereby enhancing the biochemical reactions, which remove most of the contaminants from the wastewaters.

Sanchez-Perez et al (1991) found that the floodplain soil greatly reduced the nitrate of floodwater which infiltrated through the vegetative-root-soil system. In another study, floodplains in Eastern France retained 95% of the nitrate load in groundwater, and thereby reduced the retention in the stream network (Jose et al., 1999). In this study, only the stream flow and nitrate concentrations in the groundwater and surface water were monitored compared to the analysis of direct filtered water from a floodplain-soil system in the current research study. Chung et al. (2004) reported that floodplain filtration successfully removed organic matter and nitrate from contaminated river waters of Korea. This study was with contaminated river water, as opposed to municipal wastewater as in the current study. Although, this study was similar to one part of the current study, there were no replicated or repeated studies to reinforce the findings and monitor the long-term effectiveness of the floodplain-soil in contaminant removal. Apart from nitrogen and organic matter removal, heavy metal removal from wastewaters, their accumulation in soil to assess long-term feasibility of floodplain-soil filtration, and green house gas (N_2O) emission from wastewater applied to the soil surface were also monitored in the current study. Moreover, the treatment under different flow rates and vegetative cover were replicated and repeated three times (years) with two different soils. Modeling was also done to develop a better and safer wastewater land-application strategy to reduce nitrate pollution.

2.6 MODELING OF NITROGEN TRANSPORT IN SOIL

Nitrogen is the main factor in determining the amount of bio-solids or wastewater that can be applied to land. Nitrogen is more mobile than phosphate in both water and soil, and is associated with organic matter. Ammonium nitrogen is soluble in water, but it could be weakly retained in soil due to its positive charge. However, nitrate nitrogen is very soluble in soil solutions and leaches into ground water, posing a threat to ground water. The field studies to determine nitrogen movement in soil require more labor, capital and time. The results are specific to the site also. Hence, modeling, either with analytical or numerical models can be used as an alternative to predict the fate and transport of nitrogen in the soil. Analytical models use very simple water flow and transport conditions, whereas numerical models approximate the equations for very complex flow and transport conditions.

Models can be used to predict the fate and transport of nitrogen through soil, and can even be used to simulate under different wastewater application scenarios. Hence, they can be used to explore better management options for wastewater land application to reduce the risk with nitrate leaching through the soil. The main focus of the model is to forecast the amount and interval of wastewater application to land. The objective of the technique was to apply an optimum quantity of wastewater on land, which will reduce the surface and groundwater contamination. Short and long-term land-treatment management decisions can be taken by analyzing the soil absorption capacity to the designed effluent-irrigation rate, the amount of NO_3^--N concentration in the leachate, and the plant's N uptake capacity (Mahmood, 2003).

There are several models (nearly 20 according to Donald and Alker, 2004), available to simulate fate and transport of nitrogen in the soil (Tsuji et al., 1994; Shaffer et al., 1991(a)); Wagnet and Hutson, 1989). Although most of these soil-nitrogen models are based on field study results, and can be applied to simulate fate of N in the crop root zone depth (Hansen et al., 1994), some others can predict NO_3^--N leaching beyond the root zone depth, by taking soil, climate, management practices, vegetation and soil-water interaction characteristics into account (e.g. CREAMS: Knisel, 1980; GLEAMS: Leonard, 1987; NTRM: Shaffer and Larsen, 1987; LEACHN: Wagenet and Hutson, 1989; SOILN: Jansson et al., 1991, Bergstrom and Jarvis, 1991; CREAMS-NT: Deizman and Mostanhimi, 1991; NLEAP: Shaffer et al., 1991(b); CENTURY: Metherell et al., 1993; ManureN: Sri Ranjan et al., 1995; MANIMEA: Hengnirun, 1996; and DRAINMOD-N, Brevé et al. 1997).

Chemicals, Runoff, and Erosion from Agricultural Management Systems (CREAMS) model is a continuous simulation model developed by the Agricultural Research Service of the U.S. Department of Agriculture (USDA-ARS; Knisel, 1980). It does not require a field-level data set for model calibration and necessary parameters needed are easily available or estimated (Knisel and Foster, 1981). This can be used to estimate field scale nutrient, pesticide, and soil losses. This model was used to analyze the impact of agriculture crops on chemical and soil losses through runoff (Crowder et al., 1985).

Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) is a continuous, field-scale simulation model, developed as an extension of the CREAMS model. It assumes a field with homogeneous land use, soil and precipitation. It was developed to evaluate the impact of management practices on pesticide and nutrient leaching within, through, and below the root zone, but was not developed as an absolute predictor of pollutant loadings (Leonard et al., 1987).

Nitrogen-Tillage-Residue Management (NTRM) developed by USDA-ARS, is a model to used simulate nitrogen, tillage, and crop-residue management (Shaffer and Larson, 1987). It has sub-models for temperature, soil-carbon, and nitrogen transformations, unsaturated water flow, crop and root growth, evaporation and transpiration, interception and infiltration, tillage, chemical equilibria processes, solute transport, and crop residues; so, it can simulate physical, chemical, and biological processes.

Leaching Estimation And CHemistry Model (LEACHM) developed by Wagnet and Hutson (1987), is a deterministic model, which describes water and solute movement, transpiration, plant uptake, and chemical reactions in unsaturated soil zones. This model has four different versions, LEACHW for water regime only, LEACHN for nutrient, LEACHP for pesticides, and LEACHC for chemicals. LEACHN model simulates NO_3^--N based on chemical, physical, and biological processes in the soil-water-plant system. It can be used to simulate nitrification, denitrification, ammonia volatilization, and plant uptake of fertilizers.

The SOILN model was designed to simulate transport and transformations of nitrogen in the soils, and its uptake by plants. It uses some of the SOIL model output as its input (Ekerston et al., 1994). The SOIL model works under a steady-state water flow condition, and gives relative potential for degradation-reaction, evaporation, and leaching of chemical or contaminants through the soil, and these rates can be used to estimate half times for losses by these processes. Many modules of this model, describing mineralization, nitrification, and denitrification processes in the soil are similar to those in LEACHN (Jansson et al., 1991), and both these models consider homogeneous multi-layer soil profiles. However, the SOILN model requires more than 140 parameters for its calibration, and hence, it is very difficult to use this model to predict nitrate-N leaching through the soil.

The CREAMS-NT model is a modified version of the CREAMS model, developed to simulate nitrogen transformations and transport following land application of organic waste (Deizman and Mostaghimi, 1991). This model considers nitrogen input through fertilizer applications and nitrogen losses through volatilization, denitrification, plant uptake, leaching, and over land flow.

The Nitrate Leaching and Economic Analysis Package (NLEAP) is a field-scale model developed to determine the potential NO_3^- leaching associated with agricultural practices [Shaffer et al., 1991(b)], which develops an N budget and calculates NO_3^--N leaching as a function of soil, management, and climatic factors.

The CENTURY model is used to simulate the long-term dynamics of carbon, nitrogen, phosphorus, and sulfur for different soil-plant systems. It has different plant production sub-models, which are linked to a common soil organic matter sub-model, which simulates the flow of C, N, P, and S through plant litter and different organic/inorganic pools in the soil (Metherall et al., 1993).

The ManureN model was developed to simulate crop production and irrigation management practices under various manure application strategies (Sri Ranjan et al., 1995). It includes the simulation of ammonia volatilization, mineralization, nitrate leaching, and nitrogen uptake by plants. However, nitrogen losses through surface runoff and ammonia loss from soil are not included in this model. It works in an interactive, user-friendly environment. The results are in the graphical form for nitrate and soil moisture profiles.

MAnurial NItrogen Management: Environmental Aspects (MANIMEA) is a one-dimensional, dynamic model that simulates nitrogen transformations such as volatilization, mineralization-immobilization, and denitrification, nitrogen transport through runoff and leaching, plant uptake, and adsorption, in a homogeneous, unsaturated soil (Hengnirun, 1996).

The DRAINMOD-N is a quasi two-dimensional flow model, that simulates the movement and fate of N in the shallow water table, mainly for artificially drained soils (Brevé et al., 1997). This model was used to estimate the accumulated nitrate loss in drainage and subsurface water, and to evaluate different water pollution scenarios (Yang et al., 2002). A new version of DRAINMOD-N (DRAINMOD-N II) evaluated the combined effects of soil variability, vegetation, drainage intensity, climate, and management practices on the hydrology and nitrogen transport in forests, and performed reasonably well in predicting N concentrations and cumulative N loads (Andrew, 2004). This model has also performed well in simulating N dynamics in agro ecosystems (Youseff et al. 2004).

Among all of the above described models, NLEAP, CENTURY, and LEACHN were developed for use at the farm and regional level, in contrast to point and field level applications (Wylie et al., 1994; Bleecker et al., 1990; Burke et al., 1989). The water and chemical kinetics used in LEACHN make it more straightforward to use in field level studies. It needs a smaller parameter set, and can estimate the critical soil and hydraulic properties that affect chemical transport in the soil, rather than using the calculated values, derived from established relationships, hence increasing the prediction accuracy. Therefore, LEACHN appeared to be a more robust and simpler model. Moreover, among the above models, the LEACHN model has well-described N-simulation algorithms (Alan et al., 1999; Donald and Alker, 2004), and has been tested in many regions of the world (Jemison et al., 1994; Ramos and Carbonell, 1991). In a study by Jabro et al. (1995), the amounts of nitrate leaching through soil were well predicted with LEACHNA (capacity model approach) and LACHNR (convection dispersion equation approach) of LEACHN (nitrogen version of LEACHM model). In recent years the LEACHN model has been widely used in the nitrate leaching estimation studies (Mahmood, 2003; Jabro et al., 1995; Jabro et al., 1993; Soulsby and Reynolds, 1992; Pennell et al., 1990). In another study, a land treatment system with the LEACHN model was used to (i) develop a quantitative model to predict fate and transport of water and solute movement in field soils under a range of effluent application rates, (ii) improve the effluent-irrigation scheduling and reduce the magnitude of risk of groundwater contamination by predicting the future outflows and (iii) provide information for the design and sustainable management of effluent-irrigated land treatment systems (Mahmood, 2003). Consequently, the LEACHN model was selected in this proposed research study to simulate the fate and transport of nitrogen compounds in land receiving wastewater to explore various scenarios, in order to select the best management strategy for reducing N pollution associated with wastewater-land application.

2.7 CONCLUDING REMARKS

One of the main causes of water quality deterioration is the disposal of partially treated, and/or untreated wastewater to water-bodies. Likewise, one of the solutions for solving the problem of ever-increasing demand for water is to reuse wastewater. Municipal wastewater is frequently discharged into water-bodies, and it is better than industrial wastewater for reuse purposes. However, it may contain many contaminants like nitrates, phosphorus, organic matter, heavy metals, and pathogenic organisms, which can cause serious health and environmental problems.

Municipal wastewater is treated in several stages to remove contaminants before discharging it into water bodies. In developed countries, these stages include primary, secondary, and in some cases, even a tertiary treatment, as opposed to most developing countries, in which water is discharged after primary or secondary treatment or even without any treatment, leaving a nutrient rich, contaminated water which flows to the rivers and streams. Many rural communities on the downstream side of these water bodies are solely dependent on these sources for their domestic purposes. Since these communities rely on these sources for their potable use too, the water has to be of safe quality. A better and more cost-effective technology for the treatment of wastewater is essential in developing countries, more so than in developed countries.

As seen from the above-cited literature, soil filtration or land application has been found to be quite an effective and inexpensive method for wastewater treatment. Most of the rivers and streams in many developing countries are characterized by their wide floodplains on either side of the rivers to accommodate the flooding, and they remain weedy and uncultivable during most of the summer season. These floodplains can thereby be used as soil filters. Even though some studies have already been done in this field, the efficiency of the floodplain-soil filtration for different contaminant removal and the adequate amount of water that can be applied to get safe, treated water is still not known. Hence, there is a need to study this problem under controlled conditions like a lysimeter system. Both field and lysimeter studies can be slow, time consuming, labor intensive, and yield site-specific results. Modeling can be a solution for these problems. It can simulate field scenarios and optimal wastewater loading rates, which can then be applied to a specific soil filtration system, to yield a safer and better quality of downstream river waters.

PREFACE TO CHAPTER III

According to the literature, surface water quality is rapidly deteriorating mainly due to the discharge of partially treated and/or untreated wastewater to water-bodies; therefore, it must be further treated to remove the contaminants. Available tertiary treatments are too complex and expensive for many developing countries, which are mainly facing problems with wastewaters. A low-tech, inexpensive, environmentally favorable land treatment method - floodplain-soil filtration - was studied in simulated floodplain field lysimeters for its efficiency in removing contaminants from secondary treated municipal wastewaters. Although there are many contaminants in the wastewaters, the major constituents such as nitrogen and organic matter removal was studied with sandy soil in 2002 and was repeated in 2003 and 2004 with sand.

The biochemical reactions of organic matter degradation, and the removal of N (NH_4^+-N and NO_3^--N) and COD with two different soils under three different flow rates (0.06, 0.19, and 0.31 m^3 m^{-2} d^{-1}) in vegetated lysimeters and at a flow rate of 0.19 m^3 m^{-2} d^{-1} in bare lysimeters, was undertaken to examine simulated floodplain filtration's efficacy in contaminant removal, efficiency of different application rates, effective soil depth for biochemical reactions, and to compare the effect of vegetation on these soil reactions.

Research paper based on the chapter:

Kunjikutty S.P., S.O. Prasher, S. Barrington, R. M. Patel, P. Dutilleul, and S. H. Kim. 2005. Reduction of nitrogen and chemical oxygen demand from municipal wastewater by floodplain filtration technique. (under preparation).

CHAPTER-III

NITROGEN AND CHEMICAL OXYGEN DEMAND REDUCTION IN MUNICIPAL WASTEWATERS BY FLOODPLAIN FILTRATION TECHNIQUE

ABSTRACT

Natural floodplains were simulated in field lysimeters to investigate the feasibility of their use in the treatment of wastewaters. Secondary treated municipal wastewater was applied at three flow rates of 50, 30, and 10 L d^{-1} (0.31, 0.19, and 0.06 m^3 m^{-2} d^{-1}, respectively) to vegetated, and at 0.19 m^3 m^{-2} d^{-1} to bare soil lysimeters, during the summer months of 2002 to 2004. It was observed that in the vegetated lysimeters, the concentration of NH_4^+-N and TKN significantly decreased in the leachate and effluent, irrespective of the flow rates. This suggested that flow rates as high as 0.31 m^3 m^{-2} d^{-1} could be applied. The removal of TKN, NH_4^+-N, and COD from the wastewaters varied from 62 to 84%, 96 to 99%, and 6 to 67%, respectively in all the years. Most of the mineralization of NH_4^+-N and organic-N occurred in the top 0.1 m of soil, indicating substantial nitrification within this depth. The nitrification of organic and inorganic nitrogen in the influent increased nitrate levels in the leachate and effluent. The newly planted vegetation at the beginning of the experiment removed greater amounts of NH_4^+-N, TKN, NO_3^--N and COD from the wastewater compared to the bare soil. This suggests that well-developed vegetative cover in the floodplain area may remove appreciable amounts of nitrogen and organic matter from the wastewaters.

3.1 INTRODUCTION

Disposal of wastewater from industrial and domestic sectors contaminates our water resources, leading to fresh water shortages in many parts of the world. Nearly 7 billion people worldwide could be facing water scarcity by the middle of this century (Sahu, 2003). Even wastewater that is primarily and/or secondarily treated still contains contaminants at levels that can deteriorate the quality of water in rivers and lakes. This problem becomes more critical during drought periods. In rural areas of developing countries, 90~95% of domestic sewage and 75% of industrial wastewater are discharged into surface waters without any treatment (Allaoui, 1998; Carty, 1991). India's 14 largest rivers transport 5×10^7

m^3 yr^{-1} of untreated sewage into coastal waters (Harrison, 1992). Industries in China discharged 36 x 10^6 m^3 of untreated or partially treated effluents into rivers, streams and coastal waters in 1992 alone (WRI, 1992). In China, over three-quarters of the major rivers no longer support fish life, as the waters are highly tainted with pollutants and sediments (Abramovitz, 1996). The rivers in Thailand and Malaysia contain 30 times more pathogens, heavy metals and chemicals than the maximum allowable levels (Niemczynowicz, 1996). In Pakistan's largest city, Karachi, the sewage treatment plants are outdated and frequently function at less than 15% of their capacity. Due to frequent breakdowns and clogged pipes, sewage leaks out into the soil and contaminates surrounding drinking water wells (Rahman, 1995).

Different forms of nitrogen and organic matter are the main contaminants in the wastewaters. The presence of ammonium and nitrate in wastewater has adverse effects on human health and the environment. The maximum allowable levels of NO_3^--N and NO_2^--N in drinking water have been set to 10 mg L^{-1} and 1 mg L^{-1}, respectively (USEPA, 2003). Worldwide, the intake of drinking water with nitrate levels above the acceptable limit has resulted in nearly 3 million cases of blue baby syndrome (methaemoglobinaemia) in infants (Cunte, 1999; L'hirondel and L'hirondel, 2002). High levels of organic matter in the wastewater deplete dissolved oxygen content of the water bodies during its mineralization, thus adversely affecting aquatic life and causing environmental nuisance. The amount of organic matter in the wastewater can be estimated by measuring the chemical oxygen demand (COD), which measures the chemical oxidant required to break down the organics in the wastewaters (Living Machines, Inc., 2003). To reduce the COD of wastewater, its organic matter needs to be degraded or mineralized before it is discharged to water bodies.

Eighty percent of all diseases and more than one-third of all deaths in developing countries are water related (ICWQ, 2002). An appropriate treatment of wastewater, including primary, secondary and tertiary treatments, is therefore necessary. Existing tertiary level wastewater treatments, such as activated carbon, ion exchange, and reverse osmosis methods, unfortunately tend to be very costly. Therefore, there is a need to develop a low-cost treatment method for wastewaters.

Wetlands or biological filters provide protection against pollutants for surface water resources and ground water, however this technology is quite new. During the early 1950s, studies on wetland feasibility for wastewater treatment were initiated in Germany; and such studies began in the United States in the late 1960s (DeBusk, 1999). Its scope in wastewater treatment increased dramatically during the 1970s and thus gained popularity worldwide (DeBusk, 1999). However, only during the past few decades, has the use of wetlands for meeting wastewater treatment and water quality guidelines been seriously studied and implemented. Thus, the number of studies on natural or constructed wetlands for the removal of different pollutants in wastewater has shown a recent increase (Kadlec and Knight, 1996; Mitsch et al., 2000). Wastewater treatment by wetland (natural or constructed) is appropriate for the removal of nitrogen (Fennessey and Mitsch, 1991; Breaux and Day, 1994; Zhang et al., 2000), organic matter, and suspended sediments (Ewel and Odum, 1984; Kadlec and Knight, 1996; Boustany et al., 1997; Gemma et al., 2003; Day et al., 2003). Nitrogen levels were also found to decrease in riparian soils (Jacobs and Gilliam, 1985; Cooper, 1990; Magg et al., 1997; Grimaldi and Chaplot, 2000), shallow aquifers (DeSimone and Howes, 1998), estuarine headwaters (Thompson et al., 2000), and vegetated and forested filter strips (Groffman et al., 1991). These studies demonstrate the potential of using soils as an effective filtering media for the removal of nitrogenous compounds, thus indicating that soil filtration could be used as a tertiary wastewater treatment process.

A soil filter media with sufficient permeability for filtration should ideally be located near the wastewater disposal point for the wastewater land treatment. In many countries of south and southeast Asia, most of the rivers and streams, to which the wastewater is discharged directly, are bordered with wide floodplains that are inundated only during the rainy season. They are therefore available most of the year for soil filtration. Most parts of India receive 50~90% of the total annual precipitation during 2~3 months of the monsoon season (Kumar, 2003), causing widespread flooding. Similarly, two-thirds of the total annual precipitation in Korea is received during two months (Kim et al., 2003). This rainfall pattern results in narrow river channels and low water flows for more than 9 months. The wide fallow floodplains in such cases could be used as a soil filter media for wastewater treatment. These floodplains are predominantly made up of permeable alluvial materials that are best suited for filtration, and often support vegetation, which could enhance removal of N by plant uptake. Vegetation also increases microbial activity in the soil, which may help decompose and degrade the organic compounds. While the rate of oxygen diffusion into the soil is important for the decomposition of organic matter, which can be maintained by an appropriate water spray-rate to the soil (Collin and Rasmuson, 1988; Quyang and Boersma, 1992), the lower anoxic zones of soil could favor denitrification. In short, soil filtered waters could reduce the amount of contaminants that reach rivers, and thus improve river water quality.

In this study, tertiary treatment of municipal wastewater by a floodplain filtration technique was simulated using lysimeters filled with a field sandy soil (2002) and sand (2003 and 2004) having different organic matter and soil texture fractions. The study sought to determine (i) the effectiveness of sandy soils in removing nitrogen and organic matter from secondarily treated municipal wastewaters, (ii) the optimal wastewater application rate, (iii) the effect of soil depth on filtration, and (iv) to compare the relative effectiveness of vegetated and bare soil surfaces.

3.2 MATERIALS AND METHODS

The lysimeter study was carried out at the Macdonald Campus of McGill University (Ste-Anne-de-Bellevue, Quebec), from July to September, of 2002, 2003, and 2004. Each lysimeter was constructed from a PVC pipe (0.45 m I.D. × 1.0 m height) and equipped with a 50 mm drain pipe, and water sampling ports at 0.1, 0.2, 0.4, and 0.6 m depths (D1~D4) from the soil surface (Fig. 1). Ceramic filter probes were installed at these ports to collect leachate water samples. In 2002, the columns were packed with a field sandy soil (91:4:1 sand:silt:clay; OM: 3.5%) with a bulk density of 1400 kg m^{-3}, to a depth of 0.9 m. The porosity, saturated hydraulic conductivity and initial levels of available N, P, and K were 0.47 m^3 m^{-3}, 2.5 m d^{-1}, 13.3 mg kg^{-1}, 116.5 mg kg^{-1}, and 179.0 mg kg^{-1}, respectively. In 2003, the columns were packed with sand (96:2:2 sand:silt:clay, O.M: 0.5 %) with a bulk density of 1700 kg m^{-3}, to a total depth of 0.9 m. The porosity, saturated hydraulic conductivity, and initial levels of available N, P, and K, of the soil prior to any treatment were 0.26 m^3 m^{-3}, 15.0 m d^{-1}, 52 mg kg^{-1}, 14.4 mg kg^{-1}, and 92 mg kg^{-1}, respectively. These columns were reused in 2004. All lysimeters were sheltered with a rain cover to prevent the alteration of designed treatments. Wastewater was applied at the rate of 50 L d^{-1} (0.31 m^3 m^{-2} d^{-1}), 30 L d^{-1} (0.19 m^3 m^{-2} d^{-1}) and 10 L d^{-1} (0.06 m^3 m^{-2} d^{-1}) to vegetated lysimeters, and 30 L d^{-1} (0.19 m^3 m^{-2} d^{-1}) to bare soil lysimeters, in triplicate. At these flow rates, the soil-water flow conditions were unsaturated. The wastewater contact times with the soil in the column were 6.7, 2.2, and 1.3 days in sandy soil, and 4, 1.2, and 0.7 days in sand, respectively under the application rates of 0.06, 0.19 and 0.31 m^3 m^2 d^{-1}. Secondary treated wastewater obtained daily from Vaudreuil Wastewater Treatment Plant during 2002 and 2003, and from Pincourt Wastewater Treatment Plant during 2004 was used as the influent for the study.

Every day, overhead tanks were filled with the appropriate volumes of wastewater. An appropriate number of drippers regulated the flow of water to the lysimeters (0.06 m^3 m^{-2} d^{-1} dripper^{-1}). The wastewater application experiments were conducted over a 7-week period (weeks: T1 to T7, during 2002), 9-week period (weeks: T1 to T9, during 2003), and 6-week period (weeks: T1 to T6, during 2004). It was assumed that it would take 2~3 weeks to establish a steady state flow condition in the lysimeters, hence, from fourth weeks onward, water samples were taken of the influent (D0), the effluent (D5), and sampling ports (D1~ D4). Since the soil remained unsaturated under all three flow rates, a vacuum pump was used to collect water samples from depths D1~D4 through the ceramic filter probes.

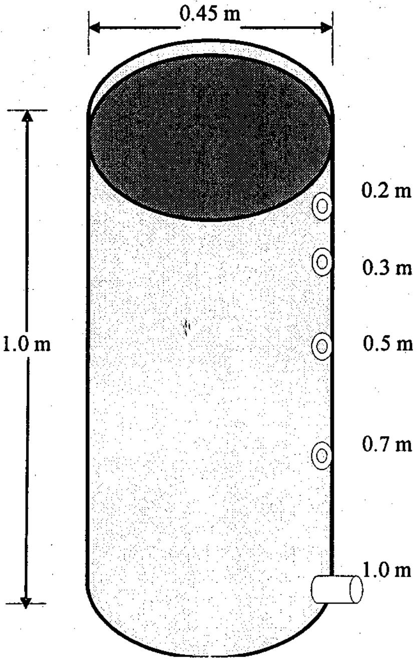


Figure 3.1 Schematic diagram of the lysimeter

3.2.1 Analytical methods

Immediately after the collection, the samples were analyzed for NH_4^+-N and NO_3^--N according to standard analytical methods using electrodes (APHA, 1998), during 2002, and with a flow injection type Lachat Instrument (Quick Chem Method, Lachat Instrument Division, Milwaukee, WI; Haris et al., 1999; Maynard, 1993; and Mulvaney, 1996) during 2003 and 2004. A colorimetric method for TKN and a closed reflux colorimetric method for COD were used for the analysis (APHA, 1998 and USEPPA, 1999). Data were analyzed to investigate the effect of various treatments on the concentrations of NH_4^+-N, NO_3^--N and COD at different depths over time using spatial-temporal repeated measure analysis of variance (SAS, 2001).

3.3 RESULTS AND DISCUSSION

3.3.1 Nitrogen reduction

The fate of nitrogen in NH_4^+-N, NO_3^-- N and organic-N forms is discussed in this section. The NH_4^+-N concentrations ([NH_4^+-N]) in the influent, leachate, and effluent over time are shown in figures 3.2, 3.3, 3.4 for the years 2002, 2003, and 2004, respectively. The summary of their concentrations in the influent, leachate at 0.1 m depth, and effluent are also given in table 3.1.

It is apparent from the figures that there was a significant (t-test, $P \leq 0.05$) reduction of [NH_4^+-N] in the leachate at D1 [treatment mean: 0.17, 0.18, and 0.02 mg L^{-1} for 2002, 2003, and 2004 respectively] as compared to the influent (D0) [mean: 4.34, 10.75, and 1.93 mg L^{-1} for 2002, 2003, and 2004, respectively] (Figs. 3.2, 3.3, and 3.4; Table 3.1). It is also evident that [NH_4^+-N] in the leachate at various depths (D1~D5) did not vary much, and there were no significant differences in its concentrations at these depths, in all three years ($P \leq 0.05$, Table 3.2; Figs. 3.2, 3.3, and 3.4). It seems that more than 94~99% of NH_4^+-N degraded in the upper 0.1m depth, and more than 96~99% of [NH_4^+-N] mineralized in the upper 0.1m soil depth. This suggests that most of the nitrification occurred at the upper 0.1 m soil depth. It appears that a sand filter of a smaller thickness of about 0.1 m would be enough to degrade most of the NH_4^+-N present in the wastewaters.

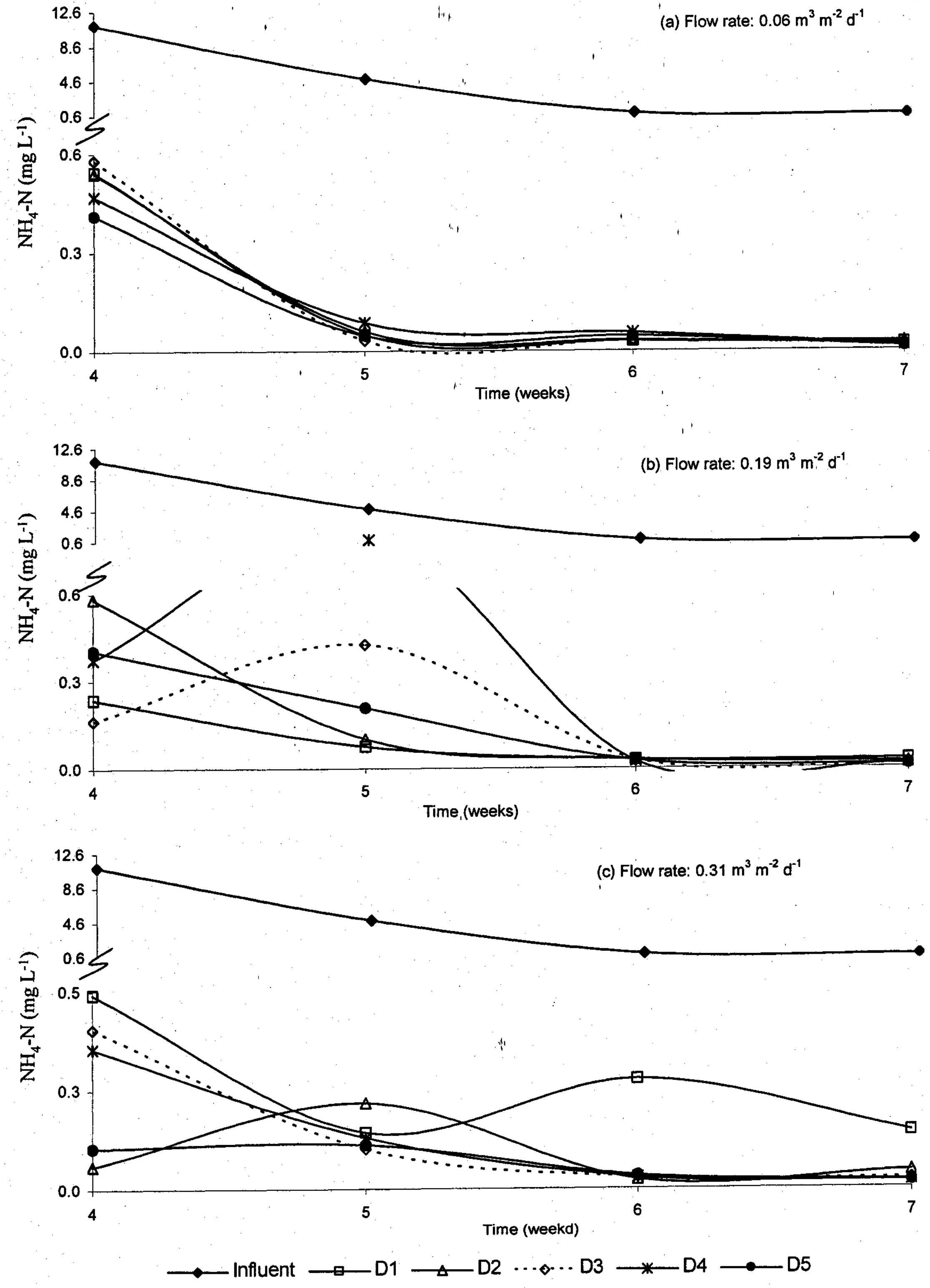


Figure 3.2: Concentration of ammonium-nitrogen at different depths over time (2002)

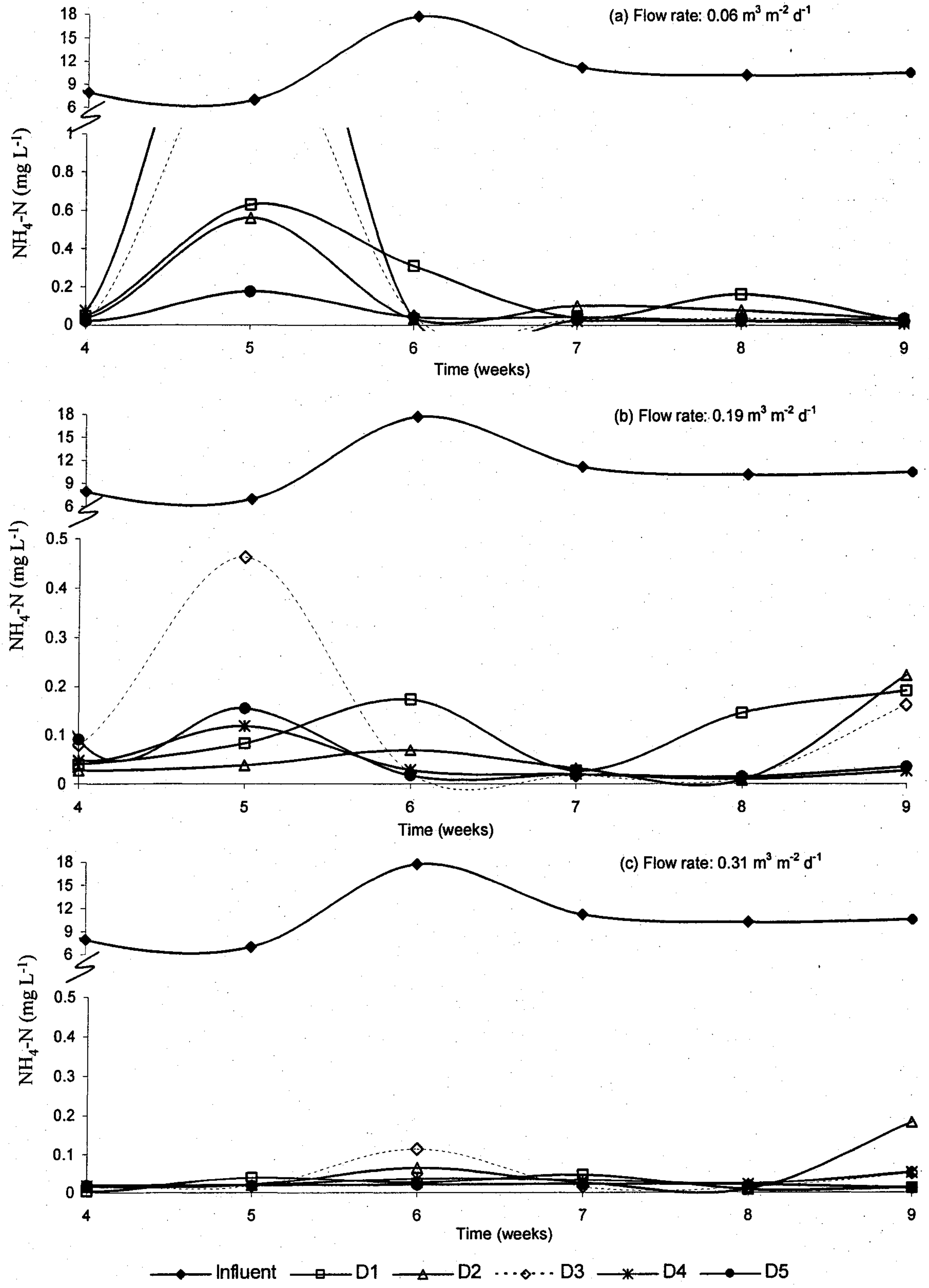


Figure 3.3: Concentration of ammonium-nitrogen at different depths over time (2003)

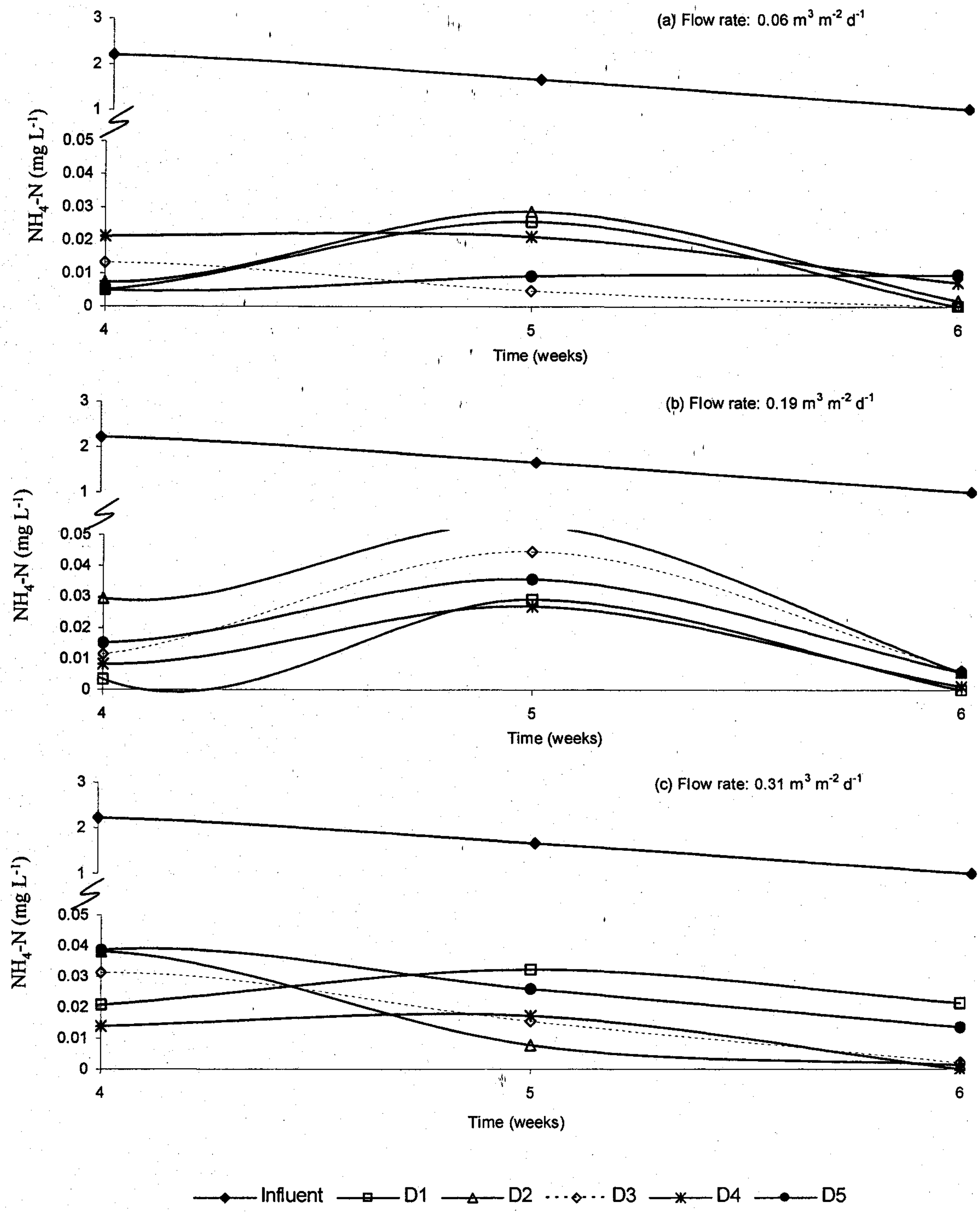


Figure 3.4: Concentration of ammonium-nitrogen at different depths over time (2004)

Table 3.1: Average removal rates of nitrate and ammonium-nitrogen and COD under different flow rates and years

Year	Parameter	Influent Conc. (mg L^{-1}) with Standard deviation	Flow rates (m^3 m^{-2} d^{-1})											
			0.31	0.19	0.06	0.31	0.19	0.06	0.31	0.19	0.06	0.31	0.19	0.06
			Leachate Concentration at D1 (mg L^{-1}) (with Standard deviation)			Effluent Concentration (mg L^{-1}) (with Standard deviation)			Removal through leachate at D1 in mg L^{-1} and [%]			Removal through effluent in mg L^{-1} and [%]		
2002	TKN	11.9 (± 4.80)	0.33 (± 0.18)	0.12 (± 0.10)	0.20 (± 0.25)	1.85 (± 1.5)	4.47 (± 1.35)	3.53 (± 1.69)	11.6 [97]	11.8 [99]	11.7 [98]	10.1 [84]	7.4 [62]	8.4 [70]
	NH_4^+-N	4.38 (± 4.84)	0.26 (± 0.16)	0.09 (± 0.10)	0.16 (± 0.26)	0.07 (± 1.70)	0.16 (± 1.48)	0.13 (± 1.71)	4.1 [94]	4.2 [98]	4.2 [96]	4.3 [98]	4.2 [96]	4.2 [97]
	NO_3^--N	4.77 (± 0.63)	19.24 (± 2.48)	18.62 (± 1.68)	18.07 (± 4.76)	16.24 (± 0.05)	16.29 (± 0.18)	15.49 (± 0.19)	-14.5 [NA]	-13.9 [NA]	-13.3 [NA]	-11.5 [NA]	-11.5 [NA]	-10.7 [NA]
	COD	25.85 (± 7.79)	22.99 (± 5.86)	22.88 (± 7.36)	25.86 (± 8.03)	24.20 (± 6.66)	23.17 (± 4.73)	23.23 (± 5.76)	2.9 [11]	3.0 [11]	0.0 [0]	1.7 [6]	2.7 [10]	2.6 [10]
2003	TKN	19.27(± 3.5	0.03 (± 0.02)	0.43 (± 0.40)	0.24 (± 0.21)	5.61 (± 0.00)	5.26 (± 0.04)	5.36 (± 0.04)	19.2 [99]	18.9 [98]	19.0 [99]	13.7 [71]	14.0 [73]	13.9 [72]
	NH_4^+-N	10.75 (± 3.78)	0.03 (± 0.02)	0.33 (± 0.43)	0.20 (± 0.24)	0.02 (± 0.00)	0.06 (± 0.06)	0.06 (± 0.06)	10.7 [99]	10.4 [97]	10.6 [98]	10.7 [99]	10.7 [99]	10.7[99]
	NO_3^--N	1.17 (± 0.72)	8.76 (± 1.87)	10.28 (± 2.61)	13.49 (± 2.07)	8.64 (± 2.41)	9.30 (± 2.17)	9.20 (± 3.25)	-7.6 [NA]	-9.1 [NA]	-12.3 [NA]	-7.5 [NA]	-8.1 [NA]	-8.0 [NA]
	COD	46.69 (± 15.9)	16.09 (± 8.38)	12.82 (± 1.46)	22.91 (± 13.33)	21.69 (± 10.27)	15.21 (± 5.67)	38.68 (± 16.61)	30.6 [66]	33.9 [73]	23.8 [51]	25.0 [54]	31.5 [67]	8.0 [17]
2004	TKN	5.72 (± 0.67)	0.03 (± 0.01)	0.04 (± 0.01)	0.02 (± 0.01)	2.07 (± 0.07)	1.45 (± 0.03)	1.30 (± 0.01)	5.7 [99]	5.7 [99]	5.7 [99]	3.7 [64]	4.3 [75]	4.4 [77]
	NH_4^+-N	1.93 (± 0.77)	0.02 (± 0.01)	0.03 (± 0.02)	0.01 (± 0.01)	0.05 (± 0.09)	0.04 (± 0.06)	0.02 (± 0.01)	1.9 [99]	1.9 [99]	1.9 [99]	1.9 [97]	1.9 [98]	1.9 [99]
	NO_3^--N	4.88 (± 0.87)	6.31 (± 1.14)	3.54 (± 1.19)	6.39 (± 1.34)	7.26 (± 1.11)	5.61 (± 0.78)	7.87 (± 1.60)	-1.4 [NA]	1.3 [27]	-1.5 [NA]	-2.4 [NA]	-0.7 [NA]	-3.0 [NA]
	COD	31.46 (± 25.39)	26.87 (± 3.21)	30.86 (± 3.70)	28.77 (± 9.61)	15.02 (± 6.21)	20.30 (±7.95)	22.21 (±5.30)	4.6 [15]	0.6 [2]	2.7 [9]	16.4 [52]	11.2 [35]	9.2 [29]

Table 3.2: Statistical analysis of NO_3^-- N, NH_4^+-N and COD in the leachate, and effluent waters for different years

Parameter	2002			2003			2004		
	NH_4-N	NO_3-N	COD	NH_4-N	NO_3-N	COD	NH_4-N	NO_3-N	COD
Flow rate	NS	NS	NS	S	S	S	NS	NS	S
T	S	S	S	S	S	S	S	S	S
D	NS	NS	S	NS	NS	NS	NS	NS	NS
Flow rate . T	NS	S	NS	S	S	NS	S	S	S
Flow rate . D	NS	NS	NS	NS	S	NS	NS	S	S
D . T	NS	S	NS	NS	NS	S	NS	S	S
Flow rate . D . T	NS	S	NS	NS	NS	NS	NS	S	NS

T, time; D, depth; S, Significant; and NS, non-significant at 0.05 probability level

The NO_3^-- N concentration ([NO_3^-- N]) in the influent, leachate, and effluent are shown in figures 3.5, 3.6, and 3.7 for 2002, 2003, and 2004, respectively. In contrast to [NH_4^+-N], there was a significant increase (t-test, $P \leq 0.05$) in the levels of [NO_3^-- N] at D1 (mean: 18.6, 10.84, and 5.42 mg L^{-1} for 2002, 2003, and 2004, respectively) compared to that in the influent (mean: 4.8, 1.17, and 4.88 mg L^{-1} for 2002, 2003, and 2004, respectively; Figs. 3.5, 3.6, and 3.7; Table 3.1). There were no significant differences in the [NO_3^-- N] at deeper depths (D1 ~ D5) for all the three years ($P \leq 0.05$; Table 3.2; Figs. 3.5, 3.6, and 3.7). This indicates that the increase of [NO_3^-- N] in lecahate and effluent was mostly due to the nitrification of organic matter occurring in the upper 0.1 m soil depth.

Irrespective of the flow rates, as most of the NH_4^+-N in the influent mineralized in the upper 0.1 m depth, only 0.14 ~ 0.18, 0.03 ~ 0.22, and 0.01 ~ 0.02 mg L^{-1} of NH_4^+-N were left in the deeper soil profile (D1 ~ D5), in 2002, 2003, and 2004, respectively. Thus, any noticeable effect of flow rates on further mineralization of such small quantities were not found in 2002 and 2004 ($P \leq 0.05$; Table 3.2; Fig. 3.3). In 2003, although the concentrations under the flow rate of 0.31 m^3 m^{-2} d^{-1}, numerically speaking, were significantly lower than the other flow rates, the differences have no practical value, as the concentration values are very low ($P \leq 0.05$; Table 3.1; Fig. 3.3).

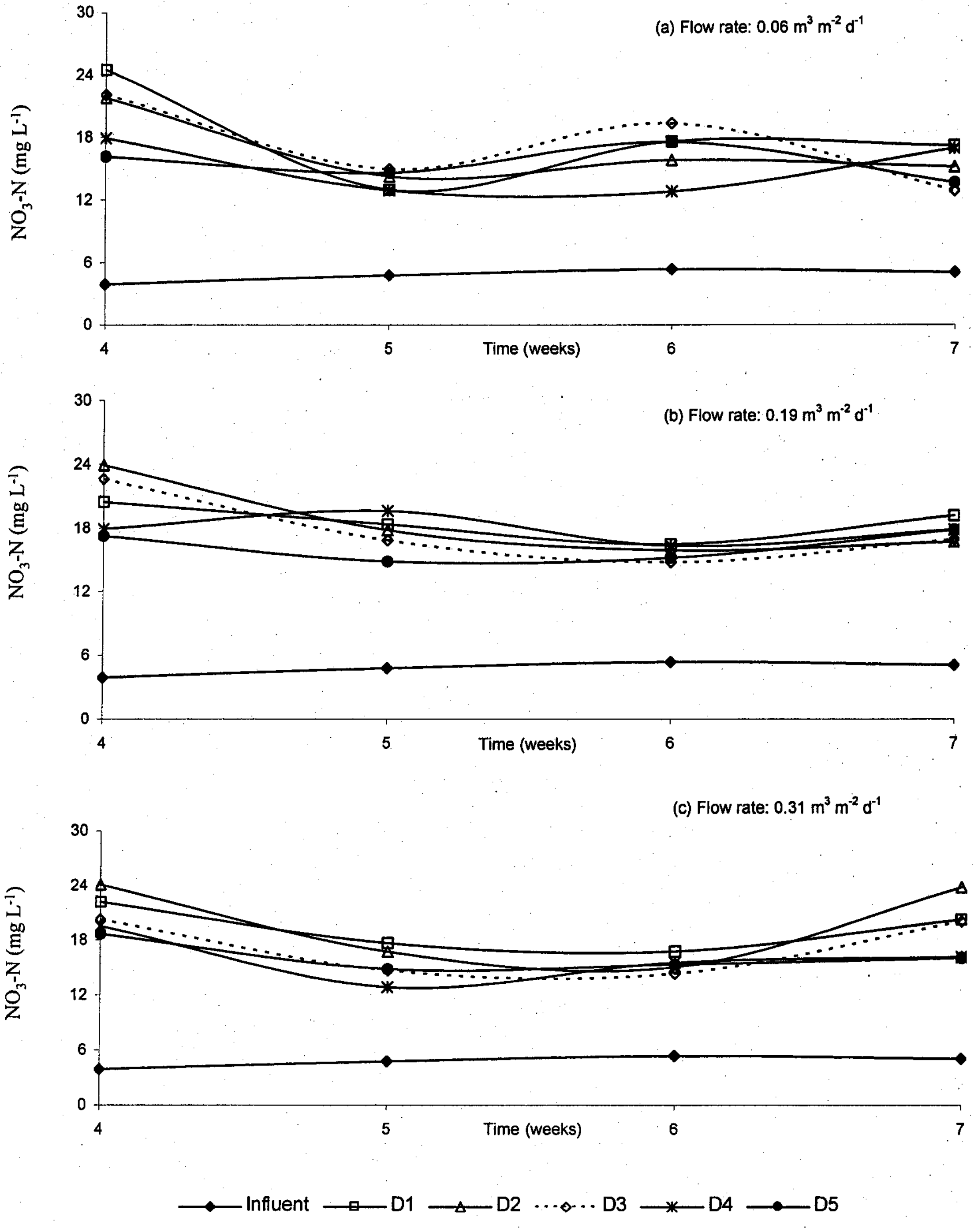


Figure 3. 5: Concentration of nitrate-nitrogen at different depths over time (2002)

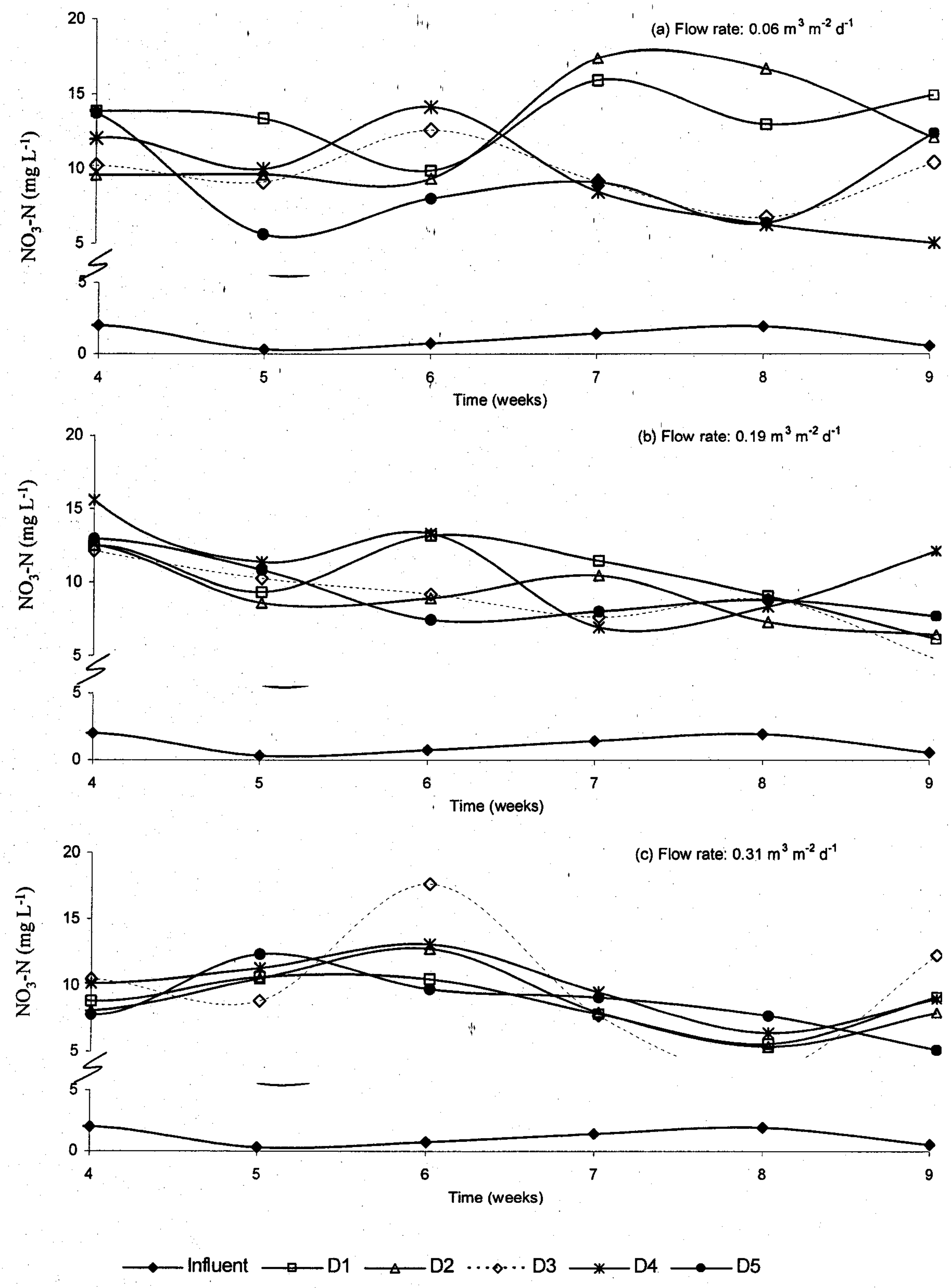


Figure 3. 6: Concentration of nitrate-nitrogen at different depths over time (2003)

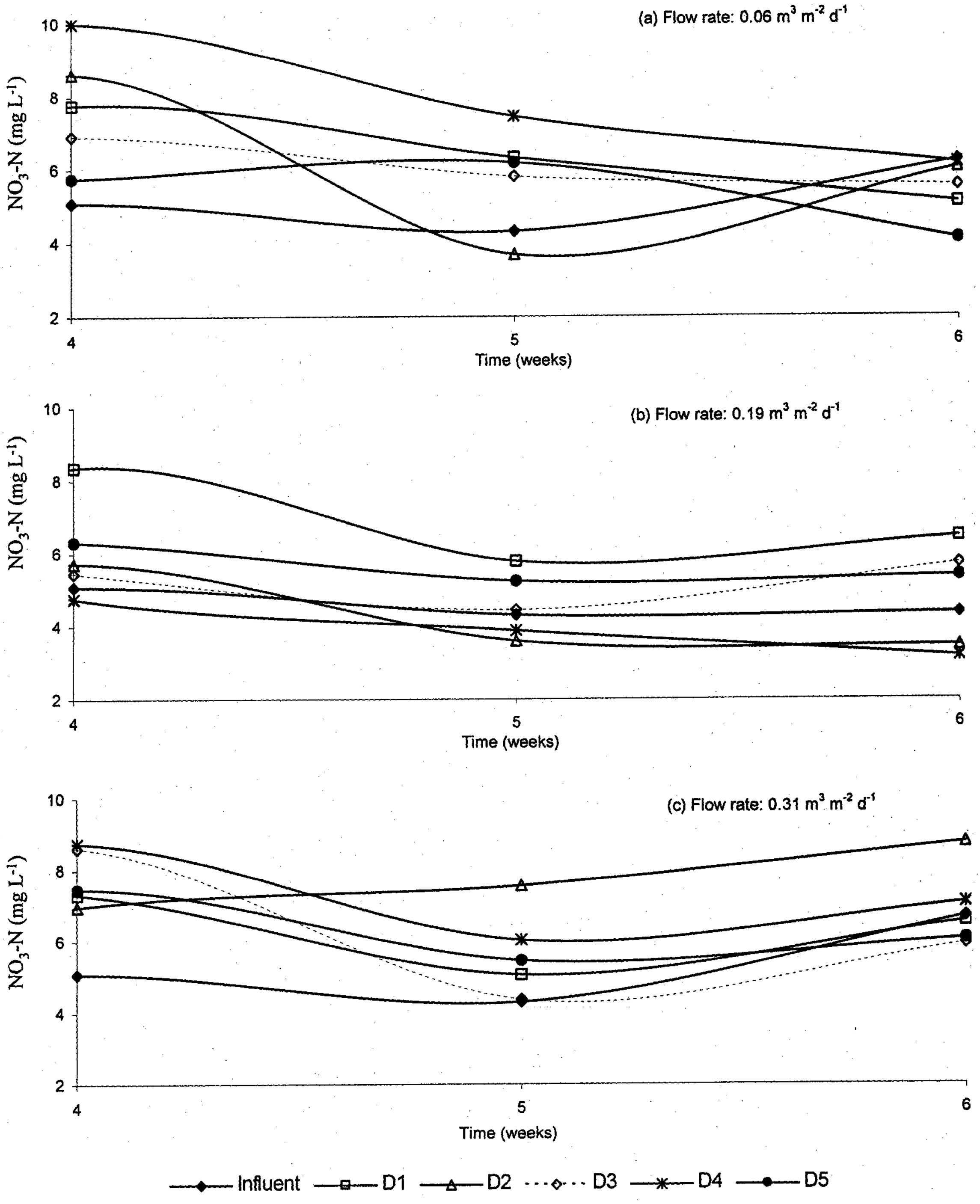


Figure 3.7: Concentration of nitrate-nitrogen at different depths over time (2004)

In the case of NO_3^-- N, the increase in its concentrations at D1 appears to be mainly due to the nitrification of the influent [NH_4^+-N] and other organic matter. Since there was no significant effect of flow rates on NH_4^+-N reduction, there were no significant effect of various flow rates on NO_3^-- N concentrations in the soil below 0.1 m depths in 2002 and 2004 ($P \leq 0.05$; Tables 3.1 and 3.2). In 2003 however, there were significantly higher nitrate concentrations at D1 under 0.06 m^3 m^{-2} d^{-1} (mean: 3.3 mg L^{-1}), as compared to that under the higher flow rates (mean: 2.4 and 2.1 mg L^{-1} under 0.19 and 0.31 m^3 m^{-2} d^{-1} flow rates, respectively; $P \leq 0.05$; Tables 3.1 and 3.2; Fig. 3.6). This might be due to the relatively low rate of denitrification in the soil under low flow rate (0.06 m^3 m^{-2} d^{-1}), resulting in low moisture content in the soil, compared to that in higher flow rates.

In 2003, although there were no significant differences in NO_3^-- N at different depths (D1 ~ D5), the significant effect of flow rates resulted in significant depth - flow rate interaction ($P \leq 0.05$; Table 3.2; Fig. 3.6). Similarly, in 2004, there were no effects of either depth or flow rates on NO_3^-- N concentrations. However, sufficient soil-water contact time for biochemical reactions of the incoming organic matter under 0.19 $m^3.m^2.d^{-1}$ resulted in lower NO_3^-- N concentrations at D1, as compared to that under other flow rates, thus showing a significant effect of depth-flow rate interaction ($P \leq 0.05$; Tables 3.1 and 3.2; Fig. 3.7). Nonetheless, such depth - flow rate interactions had minimal importance, as there were no significant differences in its concentrations at different depths in all three years, and under any flow rates in two out of the three years.

It is observed that, the [NH_4^+-N], and [NO_3^-- N] in the influent varied over time in all the years, as the wastewater was brought daily from a wastewater treatment plant (Figs. 3.2, 3.3, 3.4, 3.5, 3.6, and 3.7), and consequently significant time effect and interactions ($P \leq 0.05$; Table 3.2) on the concentrations of either NH_4^+-N or NO_3^-- N had no practical importance.

It is understood that NH_4^+-N nitrifies to NO_3^-- N, and therefore, the concentration of NO_3^-- N increases and NH_4^+-N decreases in the leachate and effluent. However, it was also observed that the increases of [NO_3^-- N] (Figs. 3.5. 3.6, and 3.7; Table 3.1) were greater than the decreases of [NH_4^+-N] in the leachate and the effluent (Figs. 3.2, 3.3, and 3.5; Table 3.1). In addition, both organic and inorganic nitrogen in the influent, other than NH_4^+-N, also undergo nitrification. Thus, not only the amount of NH_4^+-N present in the influent is converted into NO_3^--N, but the other forms of nitrogen as well, which could have contributed to the build-up of NO_3^-- N in the leachate and the effluent. This presumption is based on the fact that there was an appreciable amount of organic-N present in the wastewater (11.9, 19.27, and 5.72 mg L^{-1} in 2002, 2003, and 2004, respectively, Table 3.1), however, in the effluent, only 1.8~4.5, 5.3~5.6, and 1.3~2.1 mg L^{-1} of TKN was observed under various flow rates for 2002, 2003, and 2004, respectively (Table 3.1). Thus, the TKN decrease may be the result of nitrification, leading to increased [NO_3^-- N] in the effluent.

From table 3.1, it appears that, 14.4, 11.8, and 12.0 mg L^{-1} of TKN might have converted to NO_3^-- N under flow rates of 0.31, 0.19, and 00.06 m^3 m^{-2} d^{-1}, respectively, in 2002. Similarly, 3.0, 4.0, 3.8 mg L^{-1}, and 5.2, 4.2, and 6.6 mg L^{-1} of TKN might have converted in 2003 and 2004. However, the corresponding increases of NO_3^-- N in the effluents were only 11.5, 11.5, and 10.7 mg L^{-1} (2002), 7.5, 8.1, and 8.0 mg L-1 (2003), and 2.4, 0.7, and 3 mg L^{-1} (2004), under these flow rates (Table 3.1). Thus, 3.3, 0.7, and 2.4 mg L^{-1} of NO_3^-- N, under 0.31, 0.19 and 0.06 m^3 m^{-2} d^{-1} flow rates, might have been lost due to denitrification, volatilization, and plant uptake during 2002. Similarly, 7.4, 7.0, and 7.0 mg L^{-1} (2003), and 6.2, 8.4, and 6.3 mg L^{-1} (2004) of NO_3^-- N might have been lost under 0.31, 0.19 and 0.06 m^3 m^{-2} d^{-1} flow rates, respectively (Table 3.1).

The comparison of NO_3^-- N concentrations in the effluent in different years showed significantly high NO_3^-- N levels in 2003 ($P \leq 0.05$, t-test), and significantly low levels in 2004 ($P \leq 0.05$, t-test), resulting in significant differences in its concentrations within different years. This might be due to the high concentration of NH_4^+-N in the influent during 2003 (mean: 11 mg L^{-1}) as compared to that in 2002 and 2004 (mean: 4 and 2 mg L^{-1}) (Figs. 3.5, 3.6, and 3.7; Table 3.1).The comparison of year-wise NH_4^+-N mineralization was also done. It is observed that the influent NH_4^+-N was higher in 2003, as compared to that in 2002 (Figs. 3.2, and 3.4; Table 3.1). However, it was also observed that the mineralization rate in 2003 was significantly higher, as compared to that in 2002 (Table 3.2, $P \leq 0.05$). Therefore, the difference in the mineralization rate could be attributed to the different types of soil filter media used. It appears that the nitrification rate was higher in the pure sand filter used in 2003 as compared to that in the field sandy soil used in 2002. Generally, the biochemical reactions might be the same or better in sandy soil; however, the high soil organic matter might contribute some amount of nitrogen to water, thereby increasing its level in the leachate and effluent as compared to that in pure sand. In 2004, the same pure sand filter was used; however, the mineralization was not higher than that in 2002 because the NH_4^+-N concentration in the influent was quite low in 2004. It is also evident from table 3.1 that there was no effect of flow rates on the total organic matter removal, as the TKN removal appeared to have no significant differences under various flow rates.

3.3.2 Chemical oxygen demand (COD) reduction

The COD concentrations in the influent, leachate and effluent are shown in figures 3.8, 3.9, and 3.10 for 2002, 2003, and 2004, respectively. It was expected that soil filtration would significantly reduce COD in the leachate at 0.1 m depth. Even though more biochemical nitrification occurred in the first 0.1 m depth, the analysis showed that there was no significant difference between the COD levels ($P \leq 0.05$; Fig. 3.8) in the influent (D0) and the leachate at D1 during 2002. In contrast, the COD levels were significantly lower at D1 (mean: 17.2 mg L^{-1}) under all flow rates in 2003 and with 0.06 m^3 m^{-2} d^{-1} in 2004 (mean: 28.7 mg L^{-1}), as compared to their corresponding influent concentrations (mean: 46.7, and 31.5 mg L^{-1}, respectively in 2003 and 2004) (t-test, $P \leq 0.05$; Figs. 3.9 and 3.10). This might be due to the higher rate of biochemical reactions observed in the upper 0.1 m soil depth in sand (2003, and 2004; section: 3.3.1), as compared to that in the sandy soil (2002).

It is interesting to note that the amounts of NH_4^+-N and NO_3^-- N were also lower in sand as compared to that in the sandy soil. This supports the speculation that the sand could remove more organic matter and nitrogen forms, as compared to the sandy soil. This is because the relatively high soil organic matter in the sandy soil might have contributed some amount of organic matter during biochemical reactions, thus reducing overall mineralization of influent organic matter. Therefore, the floodplain soil filter with less organic matter content would have mineralized more influent organic matter and thereby, removed more nitrogen and organic matter from the wastewaters. The same soil in 2003 was used in 2004, which might have altered the biochemical reaction rates due to the added organic matter to the soil, and might have resulted in lower COD reduction in 2004, as compared to that in 2003. Therefore, the results indicate that the soil filtration can reduce COD levels in the leachate and effluent (mostly occurring in upper 0.1 m depth). The sand was found to be

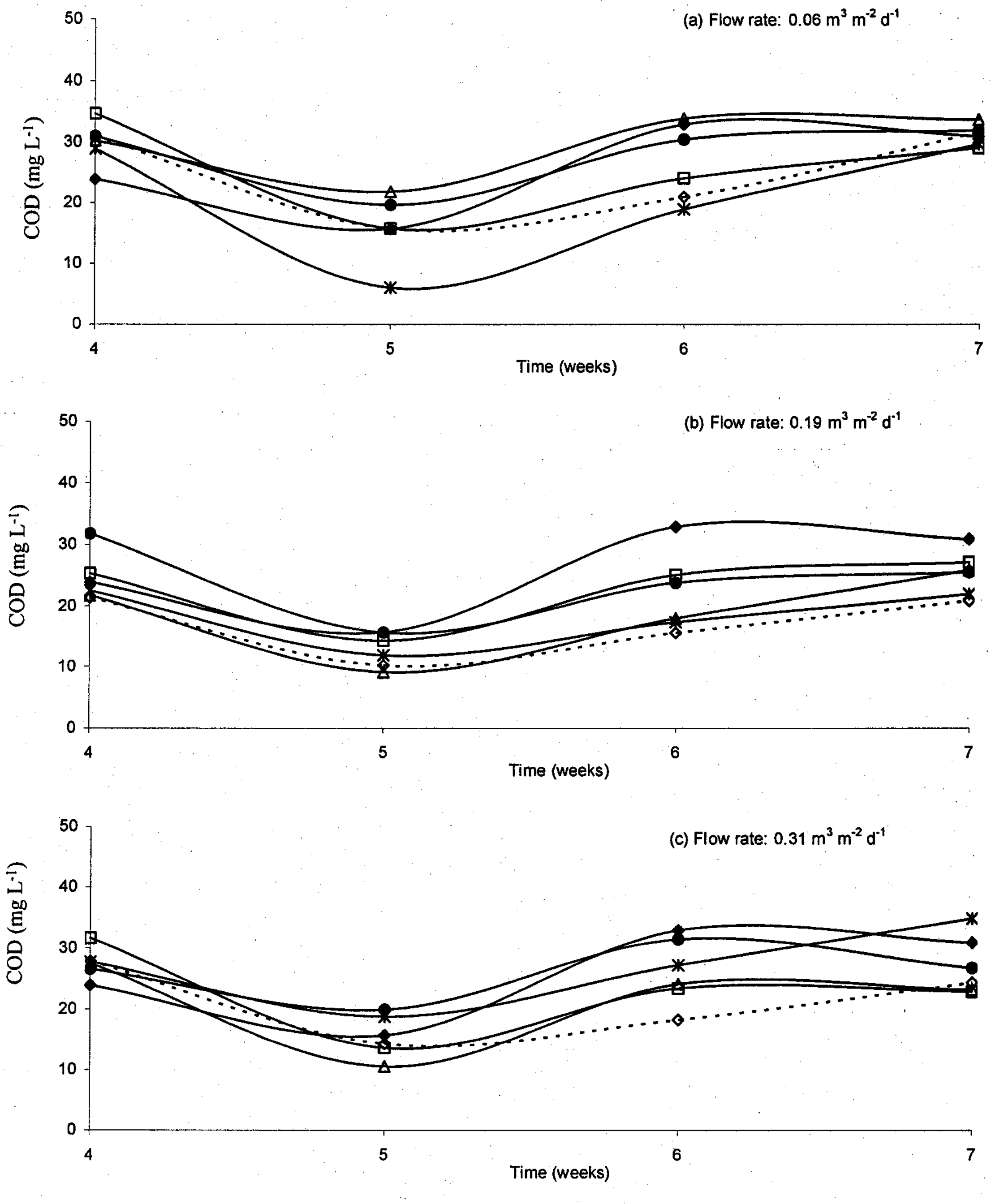


Figure 3.8: Concentration of chemical oxygen demand (COD) at different depths over time (2002)

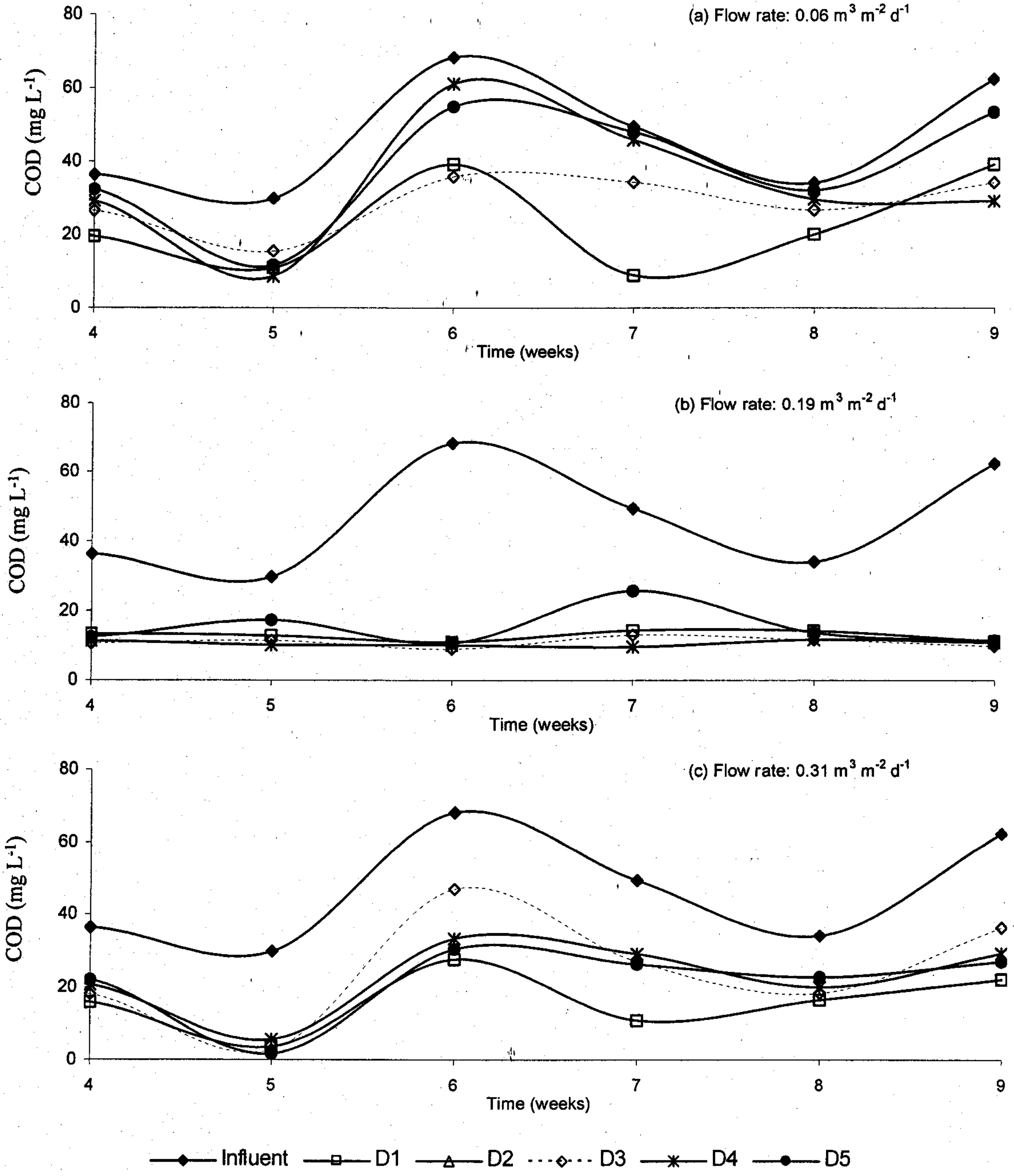


Figure 3.9: Concentration of chemical oxygen demand (COD) at different depths over time (2003)

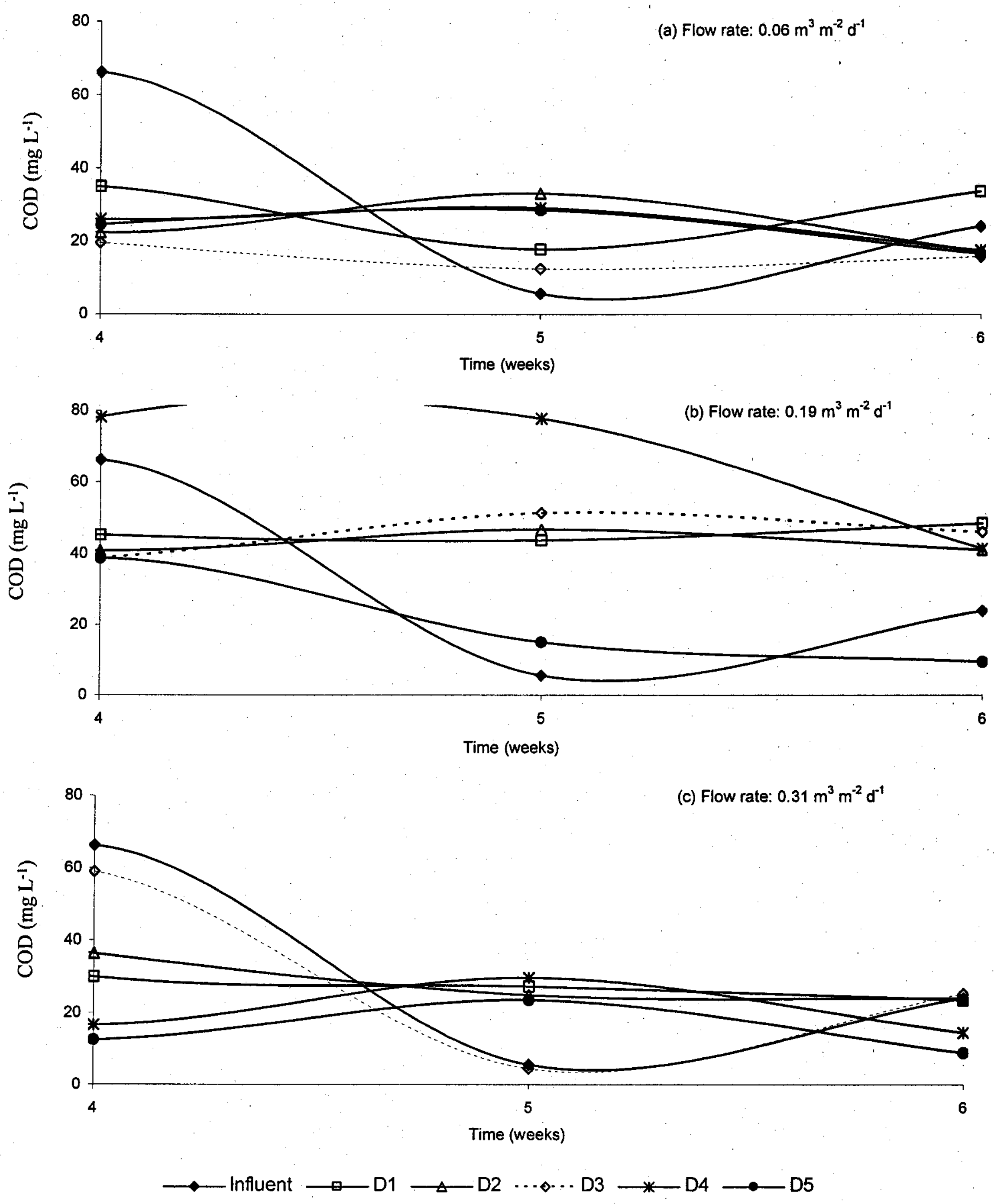


Figure 3.10: Concentration of chemical oxygen demand (COD) at different depths over time (2004)

quite effective in reducing COD levels, as compared to the sandy soil. However, continued application of wastewater might increase the organic matter content in the soil filter media, and hence, might reduce the effectiveness of the filter to remove the organic matter.

In 2002, it was observed that at the 0.6 m depth under 0.06 m^3m^{-2} d^{-1} flow rate, the COD level was relatively low (mean: 20.8 mg L^{-1}) compared to other depths (mean: 27.2 mg L^{-1}), which resulted in a significant depth effect ($P \leq 0.05$; Fig. 3.8; Table 3.2). However, there was no consistent reduction of COD along the depths, and therefore, any inferences on depth effect could not be drawn. In 2003 and 2004, there were no significant differences in COD levels along the depths ($P \leq 0.05$; Figs. 3.9 and 3.10; Table 3.2). The results showed that soil filtration removed more than 11 %, 51~7 %, and 54~77% of COD in the leachate at 0.1 m depth, and 6~10%, 17~ 7%, and 29~52% of COD in the effluent (D5) as compared to its influent level, under different flow rates in 2002, 2003, and 2004, respectively (Table 3.2). Therefore, a filter depth greater than 0.1 m not only has added benefits in terms of nitrogen removal but also in further removal of COD.

It is evident from figure 3.8 that there was no significant effect of different flow rates on the COD levels in the leachate and effluent during 2002 ($P \leq 0.05$; Table 3.2). However, in 2003, the COD levels in the leachate and effluent from 0.06 m^3 m^{-2} d^{-1} flow rate (mean: 38.7 mg L^{-1}) were significantly higher as compared to that from the flow rate of 0.31 m^3 m^{-2} d^{-1} (mean: 21.7 mg L^{-1}), which itself is significantly higher than 0.19 m^3 m^{-2} d^{-1} flow rate (mean: 15.2 mg L^{-1}) ($P \leq 0.05$; Table 3.2; Fig. 3.9). The lowest COD levels in the leachate and effluent under 0.19 m^3 m^{-2} d^{-1} might be due to more biochemical reactions in the incoming organic matter, with sufficient soil-water contact time. Whereas, in 2004, the COD levels were significantly higher under 0.19 m^3 m^{-2} d^{-1} flow rate (mean: 42.1 mg L^{-1}, Fig. 3.10; Table 3.1), as compared to 0.06 and 0.31 m^3 m^{-2} d^{-1} (mean: 24.6, and 25.3 mg L^{-1}) ($P \leq 0.05$, Tables 3.1 and 3.2; Fig.3.10). However, as both NH_4^+-N and NO_3^--N concentrations in the leachate and effluent, under 0.19 m^3 m^{-2} d^{-1} were found to be lower than that from other flow rates, the observed higher COD levels in 2004 might be due to the presence of other forms of non-nitrogenous organic and inorganic materials in the soil. In the case of the highest flow rate (0.31 m^3 m^{-2} d^{-1}), although other forms of non-nitrogenous organic and inorganic materials would be present in the soil, less soil-water contact time might have decelerated the biochemical reactions, and thereby contributing lower amounts of those materials from the soil to the leachate and effluent.

It was also observed that in all the three years, although the COD levels were appreciable in the leachate and effluents, their TKN levels were very low (Table 1). The average levels of COD in the leachate at D1, under all flow rates in 2002, 2003, and 2004 were 18.6, 10.8, and 5.4 mg L^{-1}, respectively, as opposed to their corresponding TKN levels of 0.21, 0.23, and 0.03 mg L^{-1} (Table 1). Similarly, their values in the effluents were respectively, 16.0, 9.0, and 6.9 mg L^{-1}, as opposed to their corresponding TKN levels of 3.3, 5.4, and 1.6 mg L^{-1} (Table 1). The root exudates [consists of water, sugars and amino acids, (Rovira, 1969)] produced by the vegetation might be the reason for high COD at these low TKN levels in the leachate at D1. However, the observed algae growth in the drainpipe during the wastewater application might be the reason for high COD in the effluent.

3.3.3 Effect of vegetation on nitrate-N, ammonium-N, and COD

Due to high hydraulic conductivity and wastewater application through one dripper point to the lysimeters, low soil moisture content and poor water distribution might have occurred under the 0.06 m^3 m^{-2} d^{-1} flow rate. Consequently, the available land area might not have been fully utilized for biochemical reactions. However, under the 0.19 m^3 m^{-2} d^{-1}flow rate, the soil moisture regime and distribution of water was efficient compared to other flow rates. Although the water distribution was better under the 0.31 m^3 m^{-2} d^{-1} flow rate, the moisture content was high, as compared to other flow rates. As a certain period of time is required for the vegetative cover to become effective in nutrient removal (Leeds-Harrison et al., 1996), the sod used as a vegetative cover in this study was planted at the start of the experiment; hence it would have little time to establish a rhizosphere. However, with a better soil moisture regime and proper water distribution, the vegetative growth under the intermediate flow rate of 0.19 m^3 m^{-2} d^{-1} was observed to be better, compared to that under other flow rates. Hence, a reasonable comparison of the NH_4^+-N, NO_3^--N or COD removal under vegetated *vs.* bare soil lysimeters under this flow rate could be made.

The [NH_4^+-N], [NO_3^--N] and COD levels in the lechate and effluent from the vegetated and bare soil lysimeters under the flow rate of 0.19 m^3 m^{-2} d^{-1} during 2002, 2003 and 2004 are shown in figures 3.11, 3.12, and 3.13, respectively. The concentrations of NH_4^+-N and COD significantly decreased and NO_3^--N significantly increased in the leachate at the 0.1 m depth, as compared to that in the influent in vegetated and bare soil (t-test; *$P \leq 0.05$;* Figs. 3.11 and 3.13). The differences in concentrations of these parameters were similar in vegetated and bare soils (Fig. 3.11, 3.12, and 3.13; t-test; *$P \leq 0.05$).* However, numerically, the reduction in NH_4^+-N and COD levels were higher, and the increase in NO_3^--N levels was lower, in the leachate and effluent in vegetated soil, as compared to that in bare soil. This indicated that there could be some positive impact of vegetation on biochemical reactions in the soil, and hence, could remove more nitrogen and organic matter. Consequently, with an active vegetative growth, it is quite likely that the vegetative filter would have been more effective in nitrogen and organic matter removal from wastewaters.

It is also evident from these figures that there were no significant differences among the [NH_4^+-N], [NO_3^--N] or COD levels in the leachate from different depths or effluents, collected from both vegetated and bare soil during all years of the study (Figs. 3.11, 3.12, and 3.13; *$P \leq 0.05$;* Table 3.3). This suggests that a filter thickness of 0.1 m is sufficient, irrespective of soil cover. However, some fluctuations in the NH_4^+-N, NO_3^--N, and COD concentrations over the profile depths were observed in 2002 and 2004, but the trends were not justifiable (Fig. 3.11, 3.12, and 3.13; Tables 3.3 and 3.4). Thus, it appears that a depth greater than 0.1 m of the sand filtering media had no additional advantage in NH_4^+-N, NO_3^--N or COD levels of lechate and effluent.

Table 3.3: Statistical analysis of NO_3^--N, NH_4^+-N and COD in the influent, leachate, and effluent waters (2002): comparison of Soil covers

Parameter	**2002**			**2003**			**2004**		
	NH_4-N	**NO_3-N**	**COD**	**NH_4-N**	**NO_3-N**	**COD**	**NH_4-N**	**NO_3-N**	**COD**
Soil cover	NS	NS	NS	NS	NS	NS	NS	NS	NS
T	S	NS	NS	NS	NS	S	S	S	S
D	NS	NS	NS	NS	NS	S	NS	S	S
Soil cover . T	S	S	S	NS	S	S	S	S	S
Soil cover . D	S	S	NS	NS	NS	S	S	S	NS
D . T	S	S	NS	NS	S	S	NS	S	NS
Soil cover . D . T	NS	NS	NS	NS	NS	S	S	S	NS

T, time; D, depth; S, Significant; and NS, non-significant at 0.05 probability level

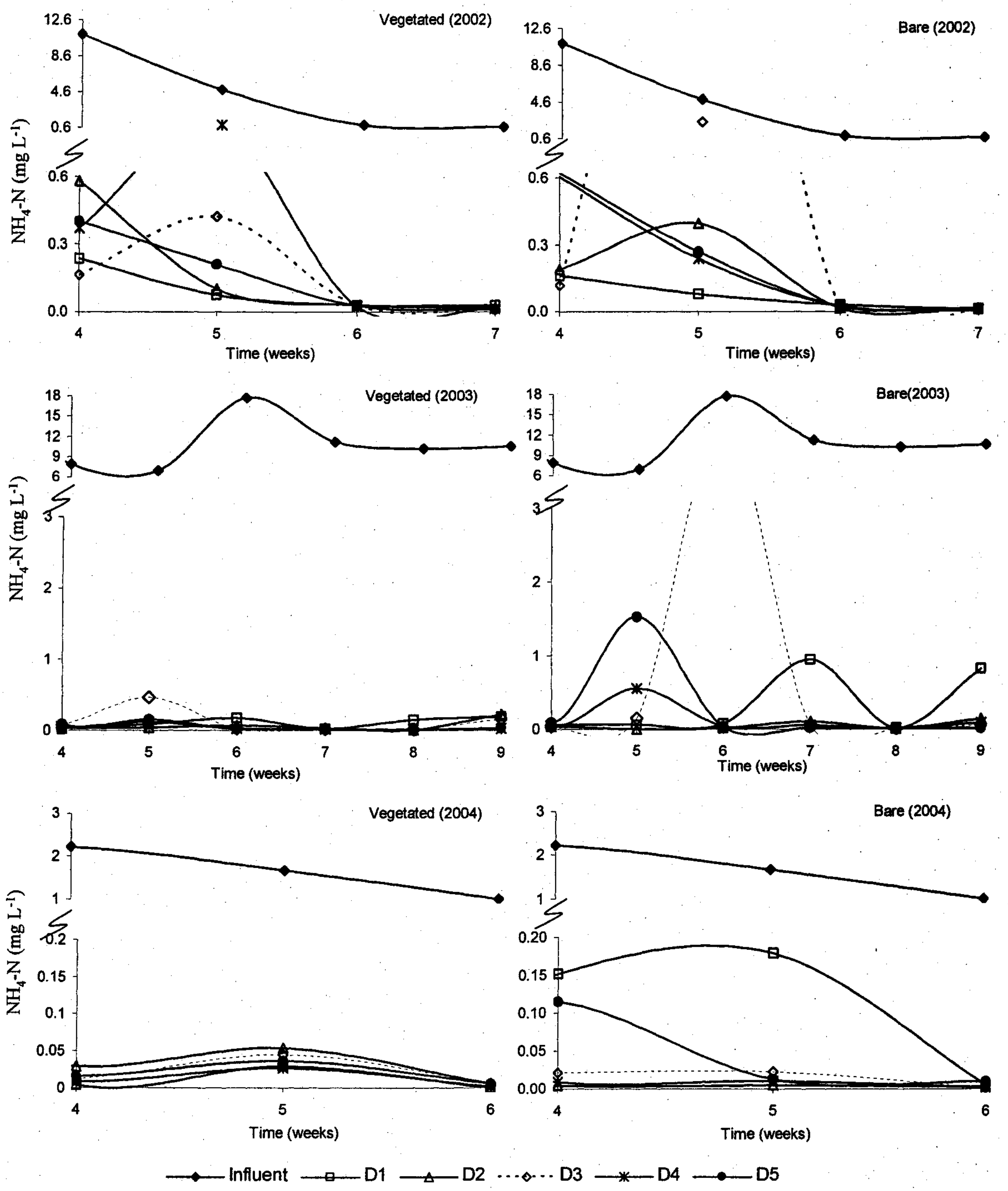


Figure 3.11: Comparison of the effects of vegetated vs. bare soil on the concentrations of NH_4^+-N at different depths over time under 0.19 m^3 m^{-2} d^{-1} flow rate (for different years)

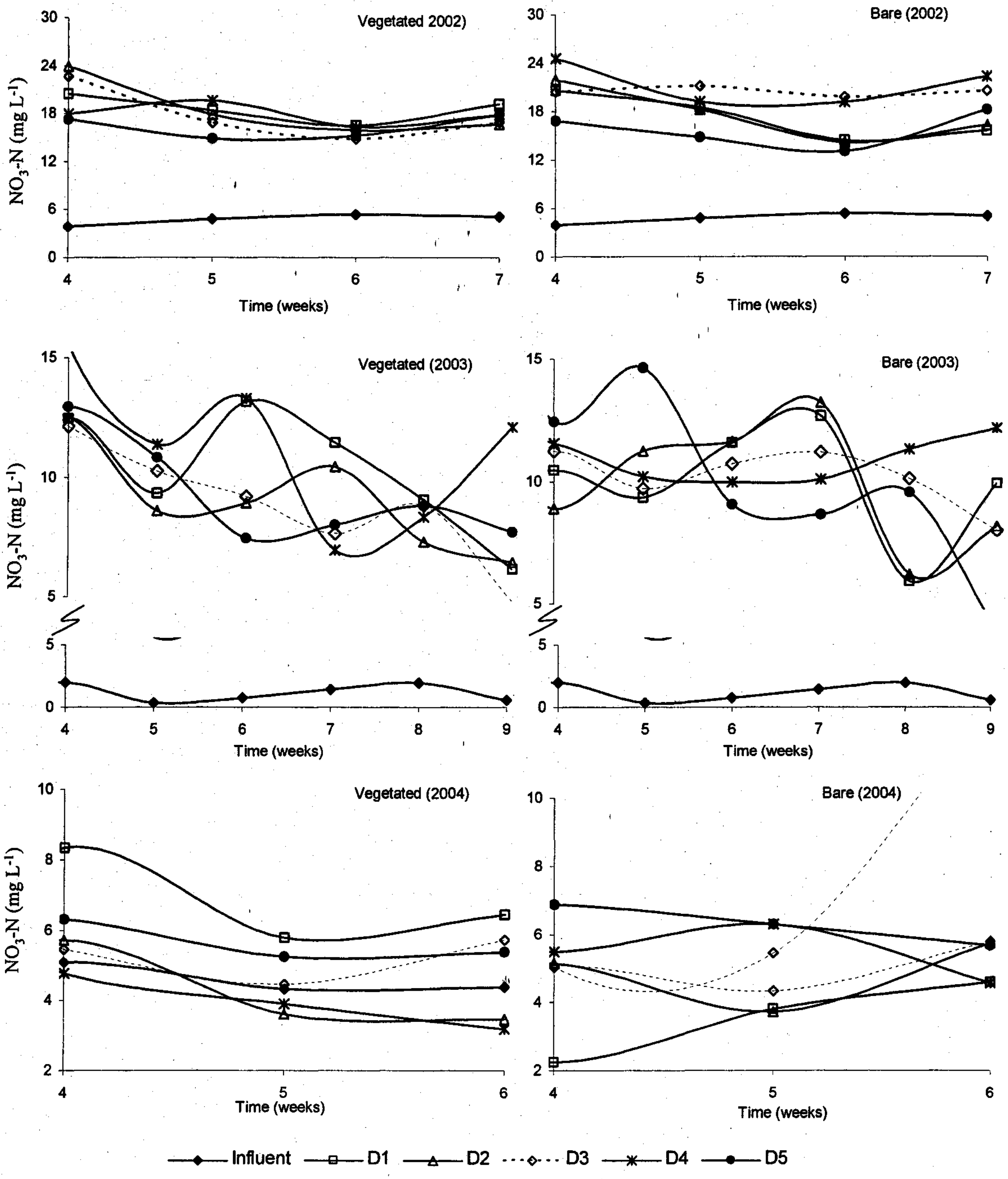


Figure 3.12: Comparison of the effects of vegetated vs. bare soil on the concentrations of NO_3^--N at different depths over time under 0.19 m^3 m^{-2} d^{-1} flow rate (for different years)

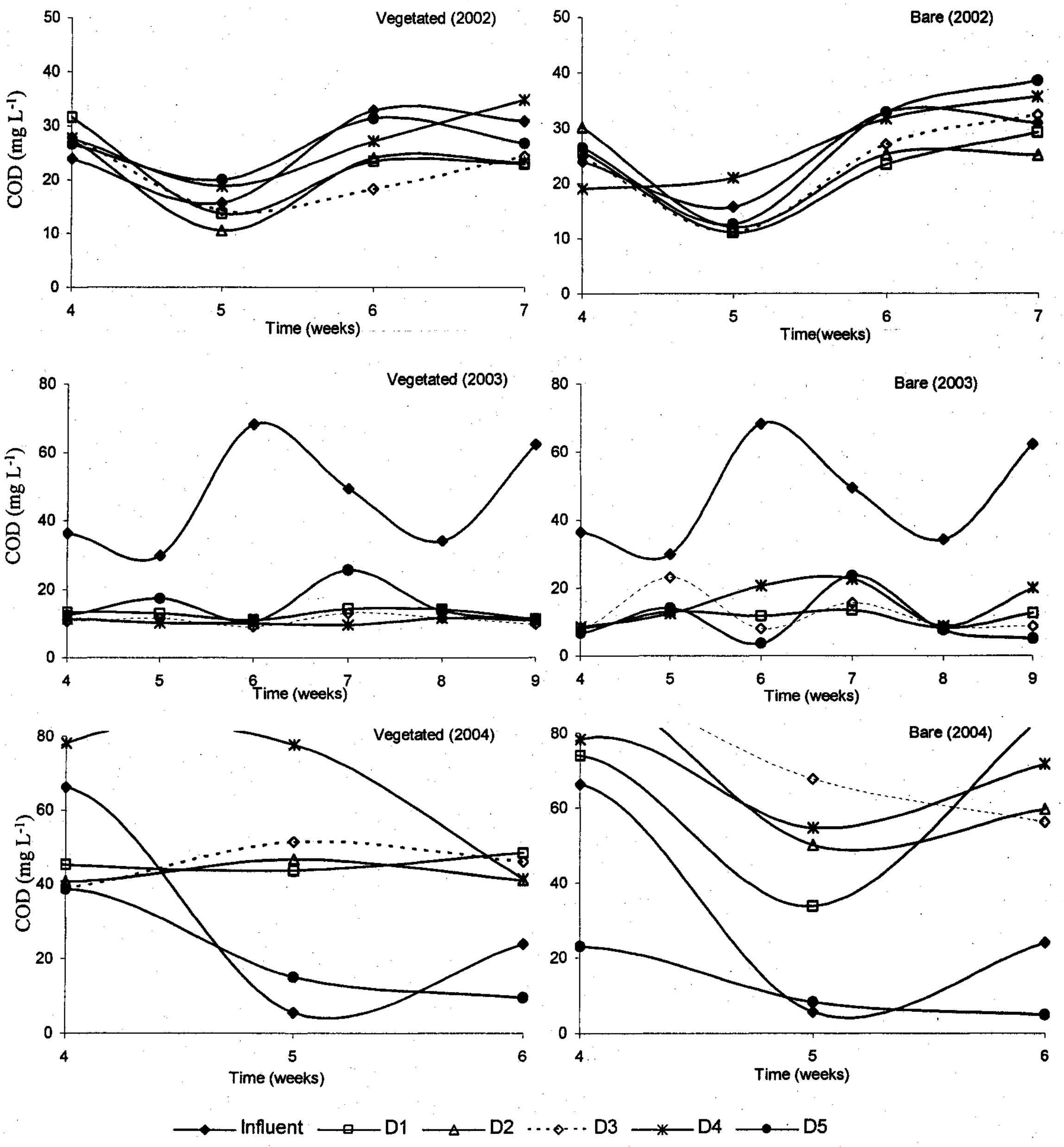


Figure 3.13: Comparison of the effects of vegetated vs. bare soil on the concentrations of COD at different depths over time under 0.19 m^3 m^{-2} d^{-1} flow rate (for different years)

Table 3.4: Variation in NH_4^+-N, NO_3^--N, and COD concentrations at different depths under different soil cover treatments

	NO_3-N (2004)		NH_4-N (2004)		COD (2004)		COD (2003)	
	Mean	SEM	Mean	SEM	Mean	SEM	Mean	SEM
D1	5.2624	0.5182	0.0615	0.0181	66.8528	8.9668	10.7962	0.8533
D2	4.5624	0.5519	0.0167	0.0052	62.8500	8.6346	13.1077	1.5847
D3	6.4741	0.7024	0.0179	0.0050	66.9360	6.7317	12.3346	1.6824
D4	4.6942	0.3374	0.0096	0.0031	66.9780	5.9515	12.8760	2.1369
D5	5.9602	0.1689	0.0324	0.0184	16.5820	3.9007	13.2200	1.8943

D1, D2. D3. D4. D5: Soil depths at 0.1. 0.2, 0.4, 0.6, and 0.9 m; SEM- Standard Error of Mean

3.4 CONCLUSIONS

Irrespective of the flow rates and soil cover, most of the nitrification of the organic and inorganic nitrogen in the influent wastewater occurred in the first 0.1 m soil depth. This indicated that a sand filter of 0.1 m depth would be sufficient for efficient removal of nitrogen and organic matter. The study also showed that 62~84 %, 71~73%, and 64~77% of TKN, 96~98%, 99%, and 97~99% of NH_4^+-N and 6~10%, 17~67%, and 29~52% of COD were removed from the municipal wastewaters by vegetated floodplain filtration in 2002, 2003, and 2004, respectively. However, the nitrification of organic and inorganic-N in the influent wastewater increased the NO_3^--N concentrations in the leachate and effluent. For the most part, different flow rates used in this experiment had no significant effect in the concentrations of NH_4^+-N, NO_3^--N, or COD in the leachate and effluent, which indicated that wastewater could be treated at application rates even higher than 0.31 m^3 m^{-2} d^{-1}, by a sand filter; however, further research is needed for confirmation.

A visible trend of lower concentrations in NH_4^+-N, NO_3^--N, and COD in the leachate and effluent were observed with the vegetated soil filter, compared to bare soil. Hence, a well-established vegetative soil filter could remove more nitrogen and organic matter from the wastewaters.

The floodplain filtration technique could be used during a good part of the year. It requires no chemical additives, and produces no sludge, making it an environment-friendly option. Its construction and operation costs would be much lower than those of the other conventional techniques. Thus, the floodplain filtration technique could prove to be the best option for wastewater treatment.

PREFACE TO CHAPTER IV

Although wastewater nitrogen inputs to lysimeters undergo different biochemical reactions, only effluent nitrogen and organic matter reduction by soil filtration was studied in chapter III. However, a nitrogen mass balance study could provide a better understanding of these biochemical processes and provide a basis for the selection of efficient nitrogen-management strategies to minimize water pollution. Hence, in this paper, in additions to N output from the lysimeters through effluent leaching, the amount of N retained in the soil, and emitted as N_2O from the soil surface were estimated to conduct a nitrogen mass balance study in the sand-filled lysimeters, under different flow rates and soil covers in 2003 and 2004. The N mass balance study in vegetated and bare lysimeters applied with the same flow rate of 0.19 m^3 m^{-2} d^-1, indicated the effect of vegetative cover on different biochemical reactions in the rhizosphere.

Research paper based on the chapter:

Kunjikutty S.P., S.O. Prasher, and S. Barrington. 2005. Nitrogen mass balance in a simulated floodplain filtration system for municipal wastewaters. *Canadian Biosystems Engineering Journal* (submitted for publication).

CHAPTER-IV

NITROGEN MASS BALANCE IN SIMULATED FLOODPLAIN FILTRATION SYSTEM FOR MUNICIPAL WASTEWATERS

ABSTRACT

The fate and mass transport of nitrogen compounds in municipal wastewater was studied in a floodplain filtration system simulated with sand-filled lysimeters, to understand various biochemical processes. Secondary treated municipal wastewater was applied at rates of 0.31, 0.19 and 0.06 m^3 m^2 d^{-1} to vegetated lysimeters, and 0.19 $m^3 m^2$ d^{-1} to bare lysimeters. Nitrogen inputs to the lysimeters through wastewater application, losses due to leaching, volatilization, and retention by soil were monitored. Nitrogen input to the lysimeters, and outputs through effluent, retention in soil, and volatilization as nitrous oxide (N_2O) were monitored to perform the mass balance. The levels of TKN decreased and NO_3^--N increased in the effluent as compared to the influent levels, due to the mineralization of organic and inorganic nitrogen compounds in the influent. In addition, the TKN and NO_3^--N contents in the soil and N_2O emissions from the soil surface increased with increases in the flow rates.

Nitrogen mass balance accounted for 98%, 85%, 91%, and 88% (2003), and 93%, 67%, 92%, and 96% (2004) of N under the flow rates of 0.06, 0.19, 0.31 m^3 m^2 d^{-1} to vegetated soil and 0.19 $m^3 m^2 d^{-1}$ to bare soil, respectively. The differences between vegetated and bare soils attributed to the presence of vegetation and volatilization losses of other non-N_2O-nitrogenous gases. Although the vegetation was not very well established in the lysimeters, it seems to have affected the nitrogen mass balance, thus, causing a net vegetative effect of 6% and 60% in the mass balance in 2003 and 2004, respectively. Based on the results obtained in this study, it can be concluded that a well-established vegetative floodplain filtration system can reduce NO_3^--N levels in the effluent, and thereby reduce water pollution.

4.1 INTRODUCTION

Municipal wastewater contains nutrients, organic matter, microorganisms, and heavy metals. The amount of nutrients in the wastewater varies based on the treatment process, the origin, and the type. However, a 0.065 m application of secondarily treated municipal wastewater could supply about 5 kg N ha^{-1}, 2 kg P ha^{-1}, and 1.8 kg K ha^{-1} (ACES, 2000). Even though nitrogen and phosphorus are beneficial to plants, their elevated concentrations in wastewater could lead to water quality deterioration due to eutrophication, which depletes the dissolved oxygen, thereby threatening aquatic life, and potentially causing groundwater pollution. Moreover, excess nitrogen in the water can cause health hazards to humans.

Generally, wastewater is discharged to water-bodies after primary and/or secondary treatment. However, it still contains many contaminants like nitrogen, phosphorus, partially decomposed organic matter, microorganisms and others. Land treatment of such wastewater prior to discharge could reduce its contaminant levels, and provide an added benefit of plant-nutrient supply to soil. This method is economically attractive for small rural communities (ACES, 2000), and is being practiced in many countries. Three types of wastewater land application methods exist: slow rate irrigation, overland flow and rapid infiltration. The slow rate irrigation is most widely used, and the rapid infiltration technique is also quite commonly used; the overland flow is rarely used. Other land application techniques such as subsurface absorption beds, deep-well injection, and evaporation ponds are limited in their application due to the associated cost of construction and maintenance (ACES, 2000).

Studies showed that the wastewater treated using land application meets aesthetic and irrigation standards (Bouwer, 1985). Such a soil treatment system implemented in the Dan region of Israel, was found to be a low cost and efficient method. The high quality of the reclaimed water made it suitable for a variety of non-potable uses such as agricultural, industrial, municipal (non-potable), and recreational usage (Kanarek and Michael, 1996). Australia opted in part for an artificial wetland wastewater treatment when they were faced with increased nutrient levels in their secondarily treated sewage effluent, which was predominantly discharged to waterways (Gardner et al., 2001). The groundwater quality at Sulaibiyah (Kuwait) showed the effectiveness of the soil filtration in water quality improvement of the groundwater, which receives recharges mostly from large wastewater storage ponds used for irrigation and other non-potable purposes (Viswanathan et al., 1999).

In land treatment of wastewater, the nutrient removal is enabled by biodegradation and adsorption processes in the soil-water system (Wilson et al., 1995). The decomposition of organic matter in the wastewater releases NH_4^+, which further degrades to nitrite and then to nitrate (nitrification). From nitrate, different gaseous forms of nitrogen evolve (denitrification). Nitrification of the organic and inorganic matter in the wastewater can increase the nitrate level in the soil-water. Generally, nitrogen, in the form of nitrate, does not adsorb in the soil, and hence leaches and pollutes the waterways and groundwater. Moreover, the continuous wastewater application to land can change the soil properties, and affect the retention of ammonium/nitrate in the soil. Ramirez-Fuentes et al. (2002) found that soil sodicity and salinity can increase even with treated wastewater application to land.

The denitrifiaction process associated with wastewater land application can increase the volatilization of nitrous oxide (N_2O), and can cause undesirable ground-level ozone (Masters, 1996). The main processes of N_2O emissions from the soil are the microbial nitrification and denitrification processes (Firestone and Davidson, 1989), which are commonly stimulated by fertilizer or wastewater application to the land (Clayton et al., 1994). Although no significant variations in N_2O emissions were observed from fine and medium-textured soils to which sewage sludge was applied, slight increased emissions were observed from the medium textured soil (Smith et al., 1996(a)). Moiser et al. (1982) found relatively low N_2O fluxes from a coarse textured soil. In contrast, EIA (2001) estimated that over one-half of the fertilizers applied to agricultural lands were being lost as N_2O.

The N_2O emissions may increase with the application of wastewater to land, and these effects can be mitigated by regulating wastewater loading rates and providing a vegetative cover to the land (EPM, 2004). The processes associated with nitrogen transformation, soil retention, plant uptake, volatilization, and leaching are complicated and interrelated.

A mass balance study of nitrogen in a soil-wastewater-plant system could provide a greater understanding of the processes and the basis for the selection of efficient nitrogen-management strategies that would minimize pollution threats. Therefore, a study was undertaken in a floodplain, simulated in field lysimeters, receiving secondarily treated wastewaters. The main objectives of this study were to investigate the nitrogen transformation processes in a soil-water system, and to conduct total nitrogen (TN) mass balance in lysimeters under different application rates of secondarily treated wastewater and surface soil covers.

4.2 MATERIALS AND METHODS

4.2.1 Experiment layout and sample collection

A floodplain simulated field lysimeter study was conducted on the Macdonald Campus of McGill University (Ste-Anne-de-Bellevue, Quebec, Canada) during the summer months of 2003 and 2004 (July to September). The experiment was done with three wastewater application rates (0.31, 0.19 and 0.06 m^3 m^{-2} d^{-1}, representing soil-water contact times of 0.7, 1.2, and 4 days) to vegetated lysimeters, and one rate of 0.19 m^3 m^{-2} d^{-1} to bare soil lysimeters; these were replicated three times. Each lysimeter was constructed of a PVC pipe (0.45 m I.D. × 1.0 m height) and was equipped with a 50 mm drain pipe at 0.9 m and rhisospheric ceramic probes at 0.1, 0.2, 0.4, and 0.6 m from the soil surface to collect water samples. The columns were packed with sand (96:2:2 sand:silt:clay; O.M: 0.5%) to a bulk density of 1700 kg m^{-3}, to a total depth of 0.9 m. With organic matter content less than 1%, the soil was representative of a floodplain soil. The porosity and initial levels of available N, P and K of the soil prior to any treatment were 0.33 m^3 m^{-3}, 52.0 mg kg^{-1}, 14.4 mg kg^{-1}, and 92.0 mg kg^{-1}, respectively. Sod was placed at the surface in the lysimeters subjected to vegetated treatment. Secondarily treated wastewater was obtained daily from the Vaudreuil and Pincourt Wastewater Treatment Plants during 2003 and 2004, respectively, and was used as the influent for the study.

Every day, overhead tanks were filled with the appropriate volumes of wastewater. Drippers were connected to the end loop of the pipe that was fixed to the overhead tanks. The number of drippers in the loop established the appropriate flow rate to each lysimeter (0.06 m^3 m^{-2} d^{-1} $dripper^{-1}$). The flow conditions were unsaturated under all the three flow rates; hence, a vacuum pump was used to collect water samples from sampling ports at 0.1, 0.2, 0.4 and 0.6 m depths through probes. The wastewater application experiment was conducted over 9 (weeks: T1~T9) and 6 (weeks: T1~T6) week periods in 2003 and 2004 respectively. Since, experiments in 2004 were carried out in the same soil columns that were used in 2003, the contaminants in the soil were assumed to be flushed out by 7 weeks of tap water application, prior to the establishment of the experiment. Influent (labeled D0) was collected daily, and leachate from the four probes (0.1, 0.2, 0.4, and 0.6 m) and the effluent (0.9 m) were taken weekly and labeled respectively as D1, D2, D3, D4, and D5. Soil samples were collected during the column packing process, and from different soil profile depths at the end of the wastewater application in each year (week T9 in 2003, and week T6 in 2004).

Gas samples were collected weekly by chamber method. In each lysimeter, circular bases were inserted into the soil to fix the sampling chamber for gas collection. Eighteen-liter plastic sampling chambers, equipped with a septum and a stopcock, were set on the circular bases for 20 minutes. This time was chosen to ensure minimal changes in incoming radiation, soil temperature and gas concentration gradients within the soil (Andrade et al., 1999). Before sampling, the gases in the chamber were mixed five times with a 60 cm^{-3} syringe, and then the gas samples were taken. The samples were analyzed for N_2O.

4.2.2 Nitrogen mass balance

The nitrogen mass balancing procedure used in this study is shown in figure 4.1. The incoming nitrogen (mainly nitrate nitrogen (NO_3^--N) and total kjeldahl nitrogen (TKN)) to the lysimeters was through the influent wastewater. The outgoing nitrogen was through leaching and soil retention, and volatilization of N_2O from the soil surface. The TKN and NO_3^--N concentrations in the influent were multiplied with the corresponding flow rates and period of application, to get the total inputs to the lysimeters over time under different flow rates. Similarly, their concentration in the effluents under different flow rates was calculated, and accounted for the total amount of N leached over time under different flow rates. Since, the gas emissions from each lysimeter were measured over time during the experiment, the gas samples analyzed for N_2O, which were obtained in ppm or mg g^{-1}, were converted into mg of N emission from the lysimeter over time. The TKN and NO_3^--N levels in the soil at different depths under different flow rates were analyzed, and the average values corresponding to two subsequent depths were multiplied with the soil volume within that segment, to get the total TKN/ NO_3^--N in that soil segment. Likewise, the TKN/ NO_3^--N amounts were calculated per depth-segments, and added together to get the total soil content per lysimeter under different flow rates. Thus, the input of N through the influent, and output through leaching, soil retention, and N_2O gas emissions were calculated in milligrams over time per lysimeter under different flow rates. The same N mass balance procedure was used in the vegetative lysimeters.

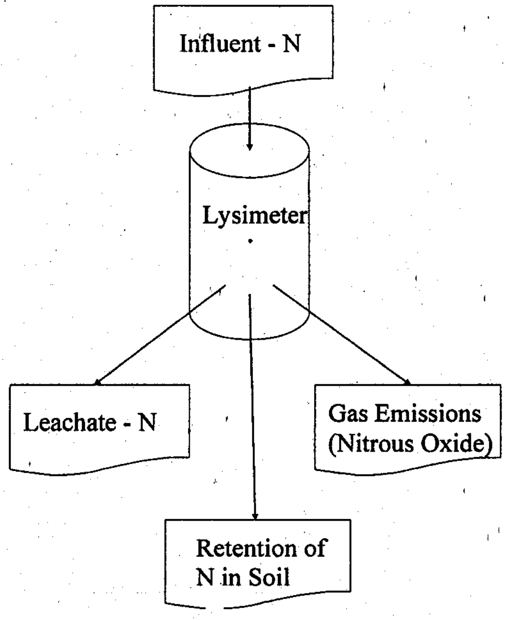


Fig.4.1 Schematic representation of nitrogen mass balance in lysimeter

4.2.3 Analytical methods

Water samples were analyzed for the concentration of NO_3^--N ([NO_3^--N]) using standard analytical methods with a flow-injection lachat instrument (Quick Chem Method, Lachat Instrument Division, Milwaukee, WI; Maynard, 1993; and Mulvaney, 1996; Haris et al., 1999). Samples were digested with sulfuric acid and a digestion catalyst (standard kjeldahl procedure), and the TKN was measured using an ammonia sensitive electrode (Carlson, 1978; APHA, 1999). Analysis was either done immediately after sample collection, or samples were refrigerated at 4^0C till the analysis.

The soil sample extraction was done with 2 M KCl (5 g of soil to 50 mL), and was analyzed for [NO_3^--N] using a flow injection type lachat instrument. The soil TKN was determined using the same procedure used in the water sample analysis. The gas samples that evolved from the soil surface collected weekly, were analyzed for nitrous oxide using a gas chromatograph equipped with an electron capture detector (Hewlett-5890 series), and were considered as an average emission rate for the week. The daily concentrations of influent TKN and NO_3^--N averaged over a week, and the concentrations determined in the effluent, representing the average weekly concentrations, were used to study the N mass balance.

4.2.4 Data analysis

The TKN and NO_3^--N concentrations in the influent and effluent water samples, in soil at different profile depths, and emissions of nitrous oxide from the soil surface, under different flow rates and soil covers, were analyzed using the t-test to examine differences in their concentrations in the influents and effluents, among effluents under different flow rates, initial soil-N contents versus the ones at the end of wastewater application, and N_2O emissions from different flow rates and soil covers. The percent differences in input and output nitrogen to the lysimeters under different flow rates and soil covers were calculated to estimate the unaccounted portion of nitrogen in its mass balance in the soil-wastewater-plant system.

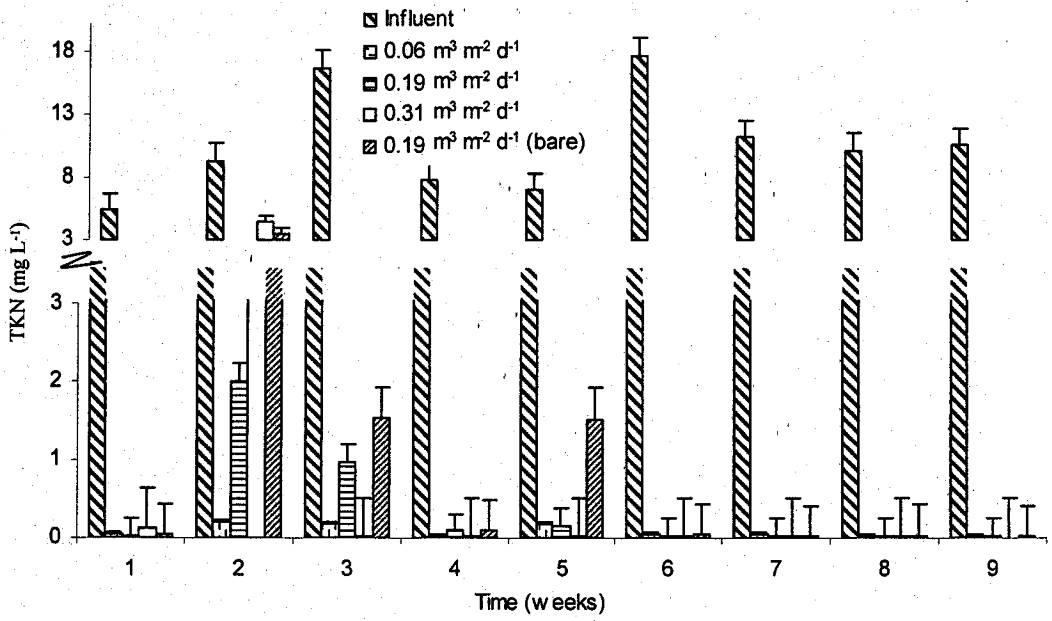
4.3 RESULTS AND DISCUSSION

The experiments were conducted in the summer months of 2003 and 2004. Hence, the data were analyzed separately for the nitrogen mass balance in the lysimeters under different flow rates and soil covers for each year. The results are discussed in the following sections.

4.3.1 Nitrogen mass balance in 2003

4.3.1.1 TKN and nitrate-N in the influent and effluent waters

The weekly average of TKN in the influent and effluent under different flow rates and soil cover are shown in figure 4.2. It is observed from figure 4.2 that TKN concentration in the influent varied over time (6.7~21.9 mg L^{-1}, mean: 13.2 mg L^{-1}), as the wastewater collected from the treatment plant was used as the influent. The TKN in the effluents under different flow rates were in the range of 0.02~5.5 mg L^{-1} (mean: 0.4 mg L^{-1}). The mean TKN concentrations in the effluent were 0.1, 0.46, and 0.65 mg L^{-1} under flow rates of 0.06, 0.19, and 0.31 $m^3\,m^{-2}\,d^{-1}$, respectively; these were statistically indifferent from each other ($P \leq 0.05$, t-test). The TKN concentrations in the effluents were significantly low, as compared to that in the influent ($P \leq 0.05$, paired t-test). Hence, the observed rates of TKN mineralization in the soil-water system were similar, irrespective of the flow rates (Fig. 4.2).

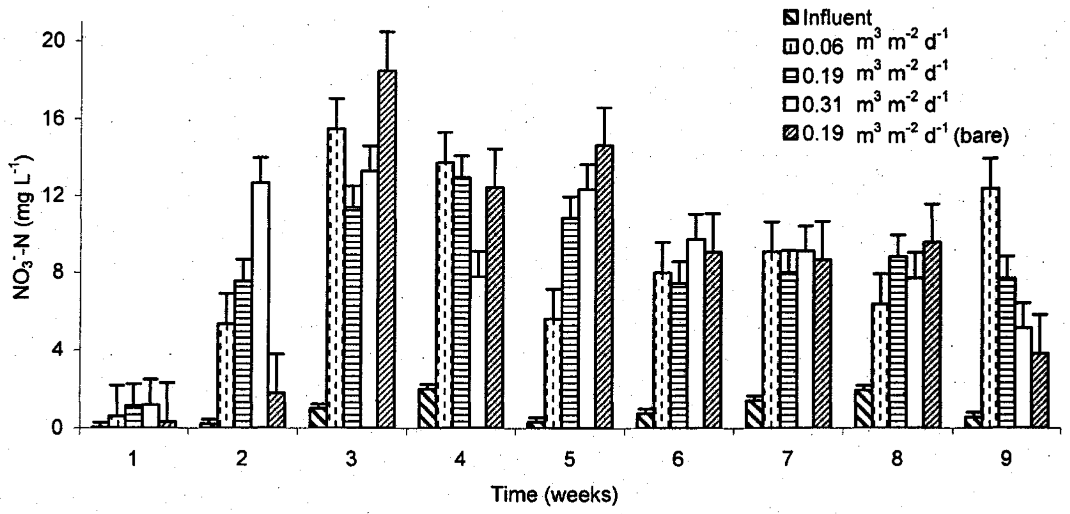


(Error bars show Standard Error)

Fig.4.2 Concentration of TKN in influent and effluent under different flow rates and soil covers (2003)

The concentrations of NO$_3^-$-N in the influent (0.04~2 mg L^{-1}) also varied over time. However, in contrast to TKN, there was a significant increase in NO$_3^-$-N concentrations in the effluents under all three flow rates (mean: 8.6 mg L^{-1}, Fig. 4.3), as compared to that in the influent (mean: 0.9 mg L^{-1}) ($P \leq 0.05$, paired t-test). The increase was due to the nitrification of organic and inorganic nitrogen in the influent wastewater. Similar to TKN concentrations, there were no significant differences in NO$_3^-$-N concentrations of the effluents under different flow rates (mean: 8.5, 8.4, and 8.8 mg L^{-1} under 0.06, 0.19, and 0.31 m^3 m^{-2} d^{-1}, respectively; $P \leq 0.05$, t-test).

To investigate the effect of vegetation, the TKN and NO$_3^-$-N concentrations in the influent and effluent under vegetated and bare lysimeters with the same flow rate of 0.19 m^3 m^{-2} d^{-1} were compared. It was observed that the concentration of TKN as well as NO$_3^-$-N in the effluents from bare and vegetated lysimeters were similar (respective TKN concentration: 0.93 and 0.46 mg L^{-1}; NO$_3^-$-N concentration: 8.75, and 8.43 mg L^{-1}; $P \leq 0.05$, t-test; Figs. 4.2 and 4.3). Although these concentrations were statistically similar due to higher standard error (SE) resulting from fewer data, numerically their concentrations were reasonably low in the vegetated lysimeters, as compared to in the bare soil. Thus, although not very conclusive, certain amounts of N must have been used up by the vegetation. The portion of N taken up by the vegetation is not considered in the mass balance; therefore, it is likely that there could be a greater percentage of unaccounted-N in the vegetated lysimeters, as compared to the bare lysimeters.

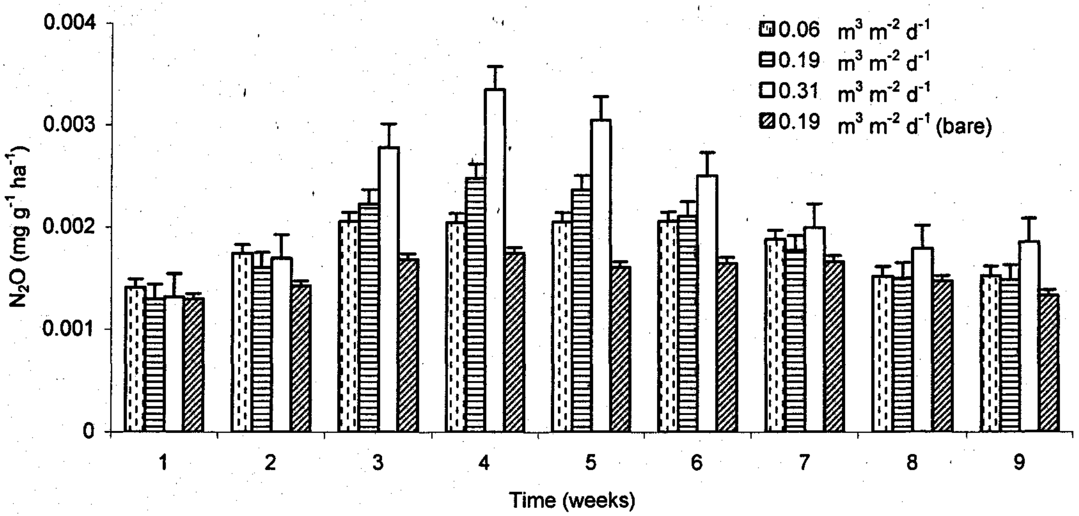


(Error bars show Standard Error)

Fig.4.3 Concentration of NO_3^--N in influent and effluent under different flow rates and soil covers (2003)

4.3.1.2 Nitrous oxide emission

Nitrous oxide is the prominent greenhouse gas emitting from the soil surface due to denitrification in the soil; therefore, its emission rates under different flow rates over time were estimated, and included in the N mass balance in the soil-wastewater system. It was observed that initially the emission of N_2O was low and then gradually increased up to the 5th week (Fig. 4.4). This initial increase in N_2O emission over time might be caused by the increase in the rate of biochemical reactions, due to the gradual establishment of active rhizosphere in the soil and also due to the increase in the influent TKN levels during these weeks. The observed decreases in the N_2O emissions after the 5th week might be due to low amounts of TKN and NO_3^--N available for denitrification in the soil profile, with low levels of TKN and NO_3^--N in the influent during these weeks (total TKN and NO_3^--N: 13~15 mg L^{-1} during 6~9 weeks as compared to total TKN and NO_3^--N: 7~23 mg L^{-1} during 1~5 weeks; Figs. 4.2, 4.3, and 4.4).



(Error bars show Standard Error)

Fig. 4.4 Emission of N_2O from soil surface under different treatments

It was observed that the N_2O emission from the lysimeters under the highest flow rate of 0.31 $m^3 m^{-2}$ d^{-1} was significantly higher (mean: 0.0023 mg g^{-1} ha^{-1}) ($P \leq 0.05$, t-test) compared to that from other flow rates (mean: 1.8 x 10^{-3} and 1.9 x 10^{-3} g g^{-1} ha^{-1}, respectively, under 0.06 and 0.19 $m^3 m^{-2}$ d^{-1} flow rates; Fig. 4.4). The differences in the amount of organic matter inputs and their subsequent mineralization in the lysimeters under different wastewater application rates might have caused these dissimilarities.

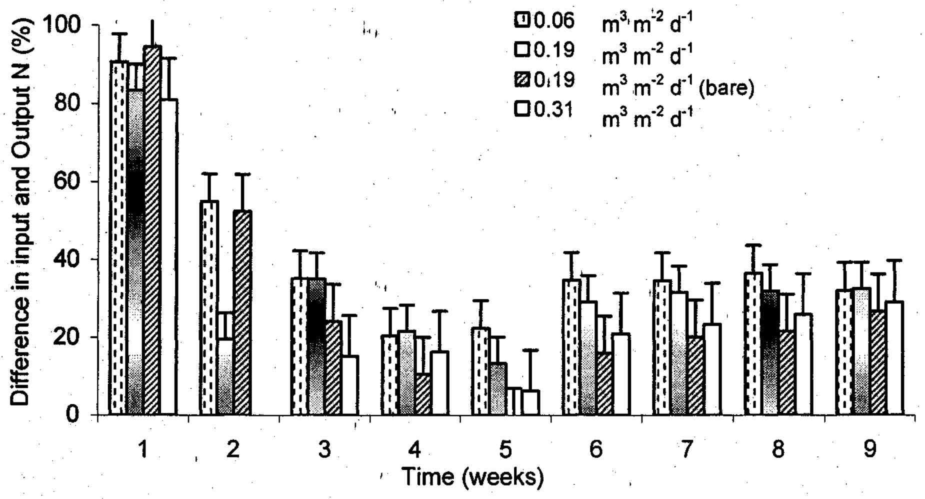
The comparison of N_2O emissions from bare and vegetated soil under the same flow rate indicated that there was significantly less emission from bare soil ($P \leq 0.05$, t-test). This might be due to less microbial activity and fewer biochemical reactions under bare soil. Moreover, the carbon content also might be less in the bare soil, which could have resulted in the reduced N_2O emissions (EPA, 2004).

It is known that the N_2O emission from the soil surface decreases with increases in soil pH (Foundation Magazine, 1991). Even so, generally N volatilization is not expected at a pH below 7 (Wild, 1988); however, when the soil solution exceeds NH_4^+ solubility as a result of ammonification of organic nitrogen, NH_3 can volatilize from the soil surface. In this study, the pH of the influent and effluents were in the range of 6~6.5, hence a small amount of N_2O emission is possible. The amount of N_2O emissions under different flow rates and soil covers were less than 3% of the total N input to the system through the influent. Thus, although there was an impact of flow rates and vegetation on the emission of N_2O from the soil surface, its effect on nitrogen mass balance was minimal.

4.3.1.3 Nitrogen mass balance over time

It was presumed that, although there would be certain a amount of N adsorbed or desorbed in the sand filter media, these amounts might be a nominal fraction of the total N input to the soil-water system. Therefore, in order to study the effectiveness of the soil filtration system over time in nitrogen transformation processes and removal, a weekly nitrogen mass balance was conducted, excluding the soil component. The percentage differences in the nitrogen input and output in the lysimeters under different flow rates and soil covers over time are shown in figure 4.5. It is clear that the difference between input and output nitrogen in the system decreased over time (Fig. 4.5; Table 4.1). This might be due to enhanced biochemical reactions over time in the rhizosphere, which might increase the nitrification of organic-N present in the influent, thereby reducing the unaccounted portion of N in the mass balance.

As discussed earlier, the NO_3^--N and TKN levels in the effluents during later weeks (T6~T9) were in a similar range among different flow rates (Figs. 4.2 and 4.3). Hence, the differences in input and output nitrogen were also observed to be in a similar range during these weeks (Fig. 4.5; Table 4.1; 32~37%, 29~33%, 21~29%, and 16~27%, under the flow rates of 0.06, 0.19, and 0.31 $m^3 m^{-2} d^{-1}$ with sod and 0.19 $m^3 m^{-2} d^{-1}$ with bare soil, respectively). The low amounts of unaccounted-N observed in the first 3~5 weeks might be due to high levels of NO_3^--N that leached through their effluents during these weeks (8.4~13.4 mg L^{-1}), as compared to other weeks (mean: 7.5~11.4 mg L^{-1}; Figs. 4.2, 4.3, and 4.5).



(Error bars show Standard Error)

Fig. 4.5 Difference in input and output nitrogen on weekly nitrogen mass balance in lysimeters under different treatments (2003)

Although the N content of the soil was assumed to be less, there could be some adsorption of N to the soil particles. Moreover, there could be volatilization of nitrogenous gases other than N_2O (e.g. inert nitrogen, ammonia and other forms of nitrogen oxides), and some amount of N might be taken up by the plant. Therefore, these amounts of N could be attributed to the unaccounted-N portion in the mass balance over time. Given the relatively small amount of N_2O emission, there are fair chances that soil adsorption and plant uptake might have relatively greater shares in unaccounted-N, as compared to the emission of other forms of N-gases. Therefore, the amounts of TKN and NO_3^--N retained in the soil were analyzed at the end of the experimental period (week 9), and the data were incorporated in the N mass balance.

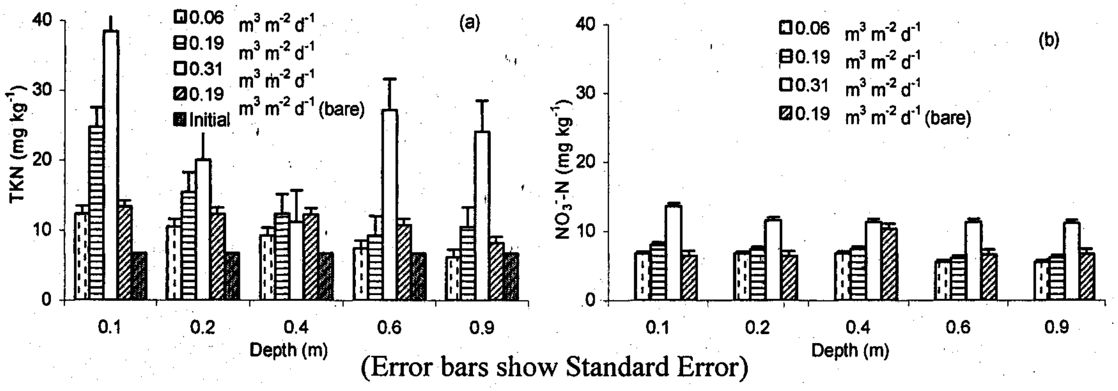
4.3.1.4 TKN and nitrate-N in soil

The TKN contents in soil at different depths and under different treatments (flow rates and soil covers) are shown in figure 4.6 (a). It is observed that wastewater application increased TKN levels in the soil under all flow rates (mean: 16 mg kg^{-1}), and were significantly higher ($P \leq 0.05$, t-test) with respect to its initial level (6.8 mg kg^{-1}). The average TKN levels in the soil were 9.2, 14.5, and 24.2 mg kg^{-1}, under 0.06, 0.19, 0.31 $m^3\ m^{-2}\ d^{-1}$ flow rates, respectively. Therefore, the increase in the TKN levels in the soil were observed

Table 4.1: Nitrogen mass balance in lysimeters under different wastewater application rates and soil covers over time (2003)

	Flow rate ($m^3 m^{-2} d^{-1}$)	Total Input (mg)	Outputs (mg)		Total Output (mg)	Input/Output Difference (%)
Week			Leaching	N2O		
T1	0.06	218	20	0.1	20	91
	0.19	655	108	0.4	108	84
	0.31	1092	206	0.6	207	81
	0.19 (bare)	655	34	0.4	35	95
T2	0.06	672	301	0.9	302	55
	0.19	2015	1616	2.4	1618	20
	0.31	3359	4773	4.1	4777	42
	0.19 (bare)	2015	956	2.3	958	52
T3	0.06	2392	1543	6.3	1550	35
	0.19	7177	4639	19.4	4658	35
	0.31	11962	10099	38.1	10137	15
	0.19 (bare)	7177	5420	15.9	5436	24
T4	0.06	2999	2369	15.9	2385	20
	0.19	8997	6991	50.2	7041	22
	0.31	14995	12442	101.6	12543	16
	0.19 (bare)	8997	8001	39.9	8041	11
T5	0.06	3627	2777	34.8	2812	22
	0.19	10882	9308	112.7	9421	13
	0.31	18136	16771	232.3	17003	6
	0.19 (bare)	10882	11078	86.5	11164	3
T6	0.06	5218	3341	62.2	3404	35
	0.19	15653	10878	202.3	11080	29
	0.31	26088	20189	418.5	20608	21
	0.19 (bare)	15653	12987	153.7	13141	16
T7	0.06	6289	3981	127.7	4109	35
	0.19	18868	12567	321.5	12889	32
	0.31	31446	23389	663.6	24053	24
	0.19 (bare)	18868	14809	245.4	15055	20
T8	0.06	7308	4429	207.9	4637	37
	0.19	21925	14423	472.2	14895	32
	0.31	36542	26100	972.4	27073	26
	0.19 (bare)	21925	16819	363.8	17183	22
T9	0.06	8261	5299	304.0	5603	32
	0.19	24784	15947	657.5	16604	33
	0.31	41307	27723	1352.5	29076	30
	0.19 (bare)	24784	17603	510.9	18114	27

to be in accordance with the increase in the flow rates, as the input of N increased with increases in flow rates. Therefore, the TKN levels in the soil under low flow rates are significantly lower ($P \leq 0.05$, t-test), as compared to higher flow rates.



(Error bars show Standard Error)

Fig. 4.6 Concentrations of TKN and NO_3^--N in soil at different depths under different treatments (2003): (a) TKN, (b) NO_3^--N

Initially there was no NO_3^--N in the soil, but wastewater application increased its levels in the soil. However, most of the NO_3^--N in influent leached out through the effluent, and hence, the increase in NO_3^--N levels in the soil was low, as compared to the amount of total-N that entered the soil (Fig. 4.6 (a) and (b)). As was the case for TKN, NO_3^--N levels in soil also increased with increases in flow rates (6.3, 7, and 11.8 mg kg^{-1} under 0.06, 0.19, and 0.31 m^3 m^{-2} d^{-1}, respectively); hence, its level under higher flow rates was significantly higher as compared to the lower flow rates ($P \leq 0.05$, t-test).

The TKN and NO_3^--N levels in the bare and vegetated lysimeters under the same flow rate of 0.19 m^3 m^{-2} d^{-1} were similar (Fig. 6 (a) and (b); $P \leq 0.05$, t-test). However, it is noticeable from figure 4.6 (a) that TKN levels in the lysimeter under the bare soil were lower as compared to the vegetated lysimeter. The smaller amount of N observed under the bare soil may perhaps be due to relatively high amounts of NO_3^--N leaching out through the effluent, as compared to that from the vegetated lysimeter (Figs. 4.2 and 4.3).

The soil TKN and NO_3^--N levels under the higher flow rate (0.31 m^3 m^{-2} d^{-1}) are significantly higher, as compared to that under 0.06 and 0.19 m^3 m^{-2} d^{-1}; therefore, total N accumulated was, respectively five and two times more than in the soil under the highest flow rate. If the filtration process were continued for an extended period, there would be further increased differences in the total N in the soil under various flow rates, and this might alter the filtration process. This implies that selection of an appropriate wastewater application rate based on soil properties is an important factor to be considered in soil filtration/land treatment of wastewater. Even though the soil N content showed 20~24% of the total N input, the increase in soil N content due to wastewater application was only 14~20% of the total N input through the wastewater under different flow rates, which corroborates 10~16% of soil nitrogen content found by Thonguekhang and Puetpaiboon (2004) in a land treatment study.

4.3.1.5 Nitrogen mass balance incorporating soil retention for the year 2003

The nitrogen mass balance in the lysimeter under different treatments (flow rate and soil cover) is presented in table 4.2. The total nitrogen (TN) entering the lysimeters was compared with the sum of total nitrogen in the effluent, in the soil, and that which was lost as N_2O from the soil surface. It is evident that about 52~66% of the nitrogen leached through the effluent, 20~24% in the soil, and about 3% was lost as N_2O, as compared to the total N input (Table 4.2). Thus, the nitrogen mass balance for the entire study period showed 2%, 15%, 9%, and 12% differences between total input and output of nitrogen under 0.06, 0.19, 0.31 m^3 m^{-2} d^{-1} with sod, and 0.19 m^3 m^{-2} d^{-1} with bare soil, respectively. As the input N was different under different flow rates, the unaccounted amounts of N under different flow rates (162, 3920, and 3775 mg under 0.06, 0.19. and 0.31 m^3 m^{-2} d^{-1}, respectively) were significantly different among themselves ($P \leq 0.05$, t-test). However, the percent of unaccounted-N amounts under these flow rates were not significantly different, beyond that it was lowest in the case of the lowest flow rate ($P \leq 0.05$, t-test).

Although statistically non-significant, there was a 3% higher unaccounted portion of nitrogen in vegetated soil, as compared to bare soil under 0.19 m^3 m^{-2} d^{-1}. This could be due to vegetative uptake. However, the study also indicated that there were some vegetative effects on leaching, soil retention and volatilization. Therefore, detailed analysis of the data showed that the TN which leached through the effluent under vegetated lysimteter was lower (7%; Table 4.2) than that under bare soil. There was a 1% increase in N_2O emission, and 3%

more N retention in the soil under vegetated soil, as compared to the bare soil. Hence, there was 3% of unaccounted N under the vegetated soil.

Table 4.2: Nitrogen mass balance in lysimeters at the end of 2003 under different wastewater application rates

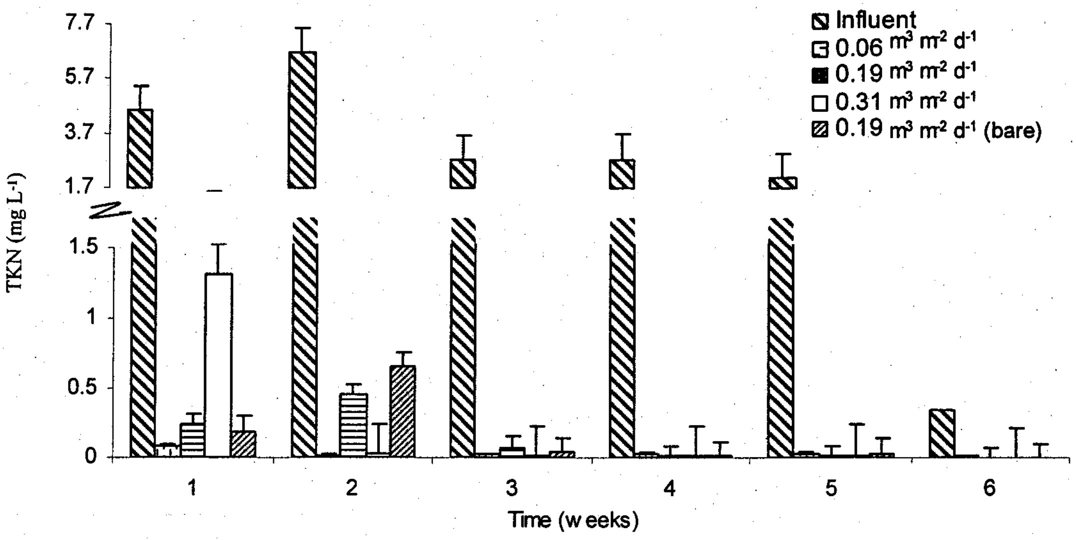
Flow Rates (m^3 m^{-2} d^{-1})		0.06	0.19	0.31	0.19 (bare)
	Inputs				
Nitrate Nitrogen (mg)		7698	23094	38490	23094
TKN (mg)		563	1690	2817	1690
Soil Content (mg)		1998	1998	1998	1998
	Total (mg)	10259	26782	43305	26782
	Outputs				
Leaching					
	Nitrate Nitrogen (mg)	5251	15198	26249	16554
	TKN (mg)	47	749	1474	1049
	Total (mg)	*5299*	*15947*	*27723*	*17603*
Soil Content					
	Nitrate Nitrogen (mg)	1834	2050	3427	2129
	TKN (mg)	2661	4207	7027	3308
	Total (mg)	4495	6257	10454	5437
Volatilization (N_2O gas, mg)		304	657	1353	511
	Total (mg)	10098	22862	39530	23551
Difference (mg)		162	3920	3775	3231
Percentage Difference (%)		*2*	*15*	*9*	*12*

It should be note that this 3% vegetative N uptake is applicable only to the flow rate of 0.19 m^3 m^{-2} d^{-1}. This same amount of vegetative effect cannot be applied to other flow rates (0.06 and 0.31 m^3 m^{-2} d^{-1}), as the vegetative growths were different under different flow rates. However, a certain percentage of vegetative effects might be associated with the biochemical reactions under these flow rates too; hence, the unaccounted N in mass balance would reduce by incorporating the vegetative effects. Thus, a well-established vegetative soil filter would further reduce the nitrogen levels in the effluent. It also would reduce the amount of unaccounted N in the mass balance.

4.3.2 Nitrogen mass balance in 2004

4.3.2.1 TKN and nitrate-N in the influent and effluent waters

The weekly average TKN and NO_3^--N concentrations in the influent and effluent under different flow rates and soil covers are shown in figures 4.7 and 4.8, respectively. It is observed from figure 7 that the mean TKN concentrations in the effluents were 0.03, 0.13, and 0.23 mg L^{-1}, respectively, under flow rates of 0.06, 0.19, and 0.31 $m^3 m^{-2} d^{-1}$, and were statistically indifferent (*$P \leq 0.05$*, t-test). However, the average TKN concentrations of the effluents under different treatments (0.14 mg L^{-1}) were significantly lower, as compared to that in the influent (mean: 3.17 mg L^{-1}; *$P \leq 0.05$*, t- test). These trends were similar to those observed in 2003.

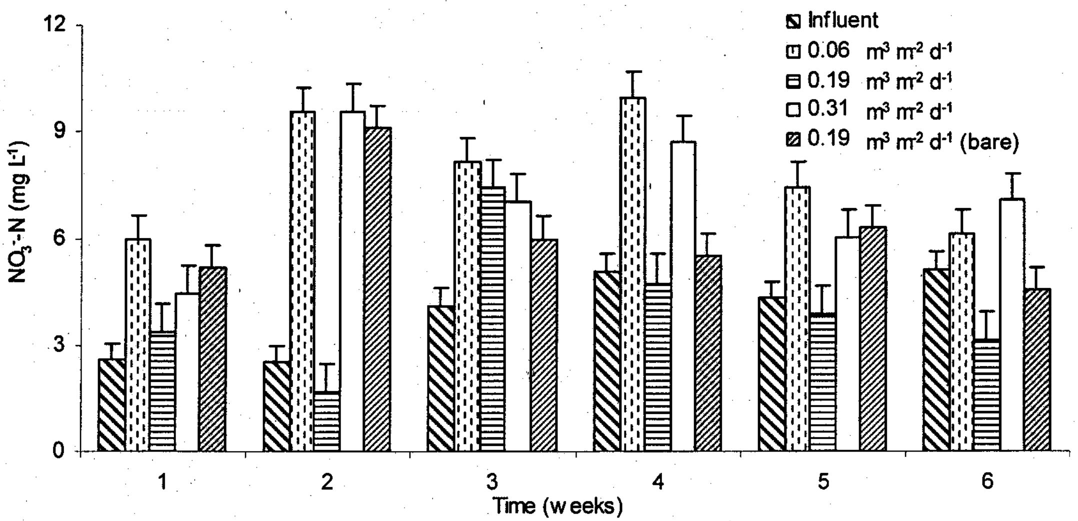


(Error bars show Standard Error)

Fig.4.7 Concentration of TKN in the influent and effluent under different flow rates and soil covers (2004)

Due to the mineralization of the influent TKN, a significant increase in NO_3^--N concentration was observed in the effluents under different flow rates (Fig. 4.8, mean: 5.83 mg L^{-1}), as compared to that in the influent (mean: 3.9 mg L^{-1}; *$P \leq 0.05$*, t-test). Significantly lower NO_3^--N concentrations were observed in the effluents under the flow rate of 0.19 $m^3 m^{-2} d^{-1}$ (mean: 4.0 mg L^{-1}), as compared to other flow rates (mean: 7.9 and

7.2 mg L^{-1} under 0.06 and 0.31 m^3 m^{-2} d^{-1}, respectively; $P \leq 0.05$, t-test). The average total N (TKN and NO$_3^-$-N) in the influent was 7.1 mg L^{-1}. Thus, there were 0.8 and 0.1 mg L^{-1} of observed NO$_3^-$-N level increases in the effluent under the flow rates of 0.06 and 0.31 m^3 m^{-2} d^{-1}, respectively. In contrast, reductions in NO$_3^-$-N levels were observed under the 0.19 m^3 m^{-2} d^{-1} flow rate (3.1 and 1 mg L^{-1}, respectively in vegetated and bare soil), which indicates that there might be higher vegetative N uptake and greater denitrification occurring due to increased biochemical reactions in the soil caused by adequate soil-water contact time under this flow rate (0.19 m^3 m^{-2} d^{-1}), as compared to that under other flow rates. However, although the total N in the influent, under the 0.06 m^3 m^{-2} d^{-1} flow rate was low, the observed poor vegetative growth due to lack of adequate water might have resulted in low N uptake. In addition, microbial populations under this flow rate might be low, which could affect the biochemical reactions, and hence result in higher NO$_3^-$-N in the effluent. On the other hand, under the 0.31 m^3 m^{-2} d^{-1} flow rate, high nitrogen input through the influent and poor vegetative growth (pale yellow/decay) due to excess water might have also resulted in high NO$_3^-$-N in the effluent.



(Error bars show Standard Error)

Fig.4.8 Concentration of NO$_3^-$-N in the influent and effluent under different flow rates and soil covers (2004)

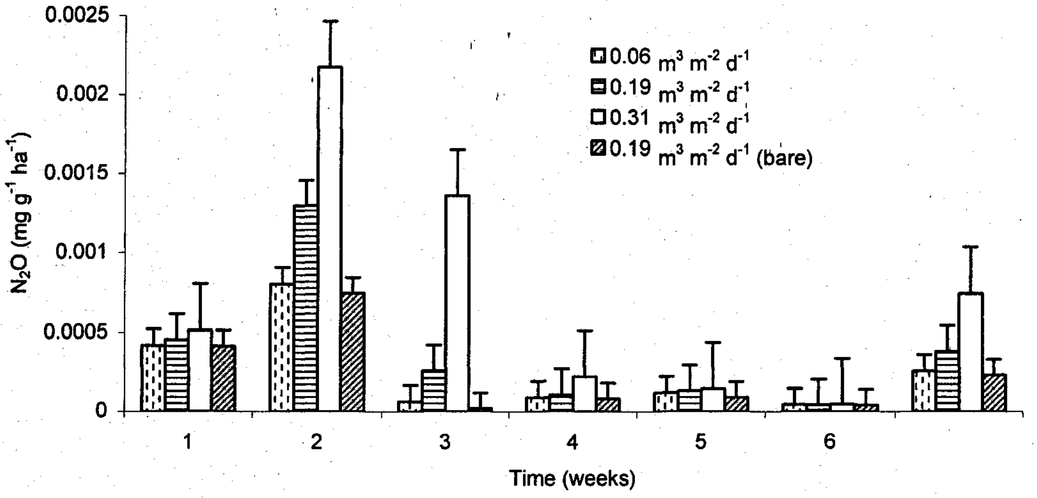
The comparison of 2003 and 2004 data analysis showed almost the same amount of denitrification under the flow rate of 0.19 m^3 m^{-2} d^{-1}, in both the years (reductions of 4.9 mg L^{-1} in 2003 vs. 3.1 mg L^{-1} in 2004). However, in 2004, the amount of total N (TKN and NO_3^--N) in the influent was relatively low, as compared to that in 2003 (14 mg L^{-1} in 2003 vs. 7.1 mg L^{-1} in 2004). Thus, the relatively low concentrations of NO_3^--N of the effluent in 2004 might be due to the low amounts of TKN and NO_3^--N inputs through the influent. Hence, although there might be differences in the amounts of unaccounted-N in the mass balance under different flow rates, the significantly low levels of NO_3^--N under 0.19 m^3 m^{-2} d^{-1} flow rate might result in a high percentage difference in unaccounted-N under this flow rate, as compared to other flow rates.

There were no apparent differences in the TKN as well as NO_3^--N levels in the effluents from bare (0.23 and 7.1 mg L^{-1}, respectively) and vegetated lysimeters (0.13 and 4 mg L^{-1}, respectively) under the same flow rate of 0.19 m^3 m^{-2} d^{-1} (Figs. 4.7 and 4.8). Like in 2003, although it is not possible to derive any conclusive inferences on the effect of vegetation on TKN or NO_3^--N levels, numerically low levels of TKN and NO_3^--N were observed in the effluent from vegetated soil, as compared to those from the bare soil (Figs. 4.7 and 4.8). Hence, it corroborates the presumption of some vegetative effects on biochemical reactions in the rhizosphere. As a result, there might be higher unaccounted-N in mass balance under vegetated, as compared to bare lysimeters. The data showed that there was greater removal of N in 2004 under vegetated soil, as compared to that in 2003 (difference in the reduction of NO_3^--N in the effluent under vegetated and bare soil: 0.4 and 2.1 mg L^{-1}, respectively in 2003 and 2004). Thus, the vegetative effect is clearer with the 2004 data.

4.3.2.2 Nitrous oxide emission

The N_2O emissions from the soil surface during the wastewater application period are shown in figure 9. Since TKN and NO_3^--N in the influent varied over time, the N_2O emission significantly varied during different measurements times ($P \leq 0.05$, t-test). However, there were no significant differences in its amounts under different flow rates ($P \leq 0.05$, t-test; the mean amounts of N_2O emission were 0.26 x 10^{-3}, 0.38 x 10^{-3}, and 0.75 x 10^{-3} mg g^{-1} ha^{-1} under 0.06, 0.19, and 0.31 m^3 m^{-2} d^{-1} flow rates, respectively).

Comparing with the total input nitrogen, the amount of N_2O emissions were less than 3% under different flow rates and soil covers (2, 2, and 3% under flow rates of 0.06, 0.19, and 0.31 $m^3 m^{-2} d^{-1}$, respectively, and 1% under 0.19 $m^3 m^{-2} d^{-1}$ bare soil). Hence, the amount of N_2O emissions had only minimal impact on N mass balance under different flow rates and soil covers. The flow rate and soil cover effect on N_2O emissions were similar in both the years, irrespective of the influent concentration.

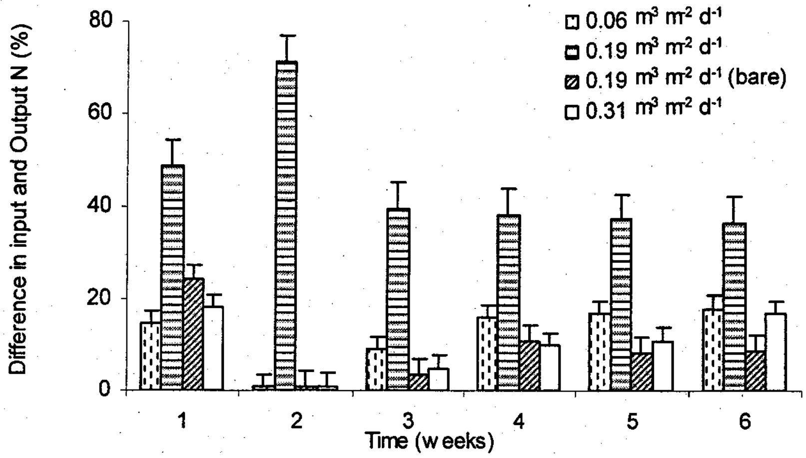


(Error bars show Standard Error)

Fig. 4.9 Emission of N_2O from soil surface under different treatments

4.3.2.3 Nitrogen mass balance over time

The unaccounted portion of nitrogen in mass balance in the lysimeters under different flow rates and soil covers over time is shown in figure 4.10. It is clear from the figure that during the weeks T3~T6, the unaccounted portions of nitrogen in the mass balance under all treatments, except 0.19 m^3 m^{-2} d^{-1} under vegetated soil, were in the range of 21~24%. The unaccounted N was relatively high in the first week (27%) due to fewer biochemical reactions, and low in the second week due to the low amount of NO_3^--N in the influent during this week (2.5 mg L^{-1}), as compared to other weeks (mean: 4 mg L^{-1}; Figs. 4.7, 4.8, and 4.10; Table 4.3). As in 2003, in the later weeks (T4~T6), the unaccounted-N was similar because an active rhizosphere system might have been established in the soil, and hence, similar levels of TKN and NO_3^--N were observed in the effluents during these weeks (Figs. 4.7, 4.8, and 4.10; Table 4.3).



(Error bars show Standard Error)

Fig. 4.10 Difference in the input and output Nitrogen mass balance in the lysimeters over time under different flow rates and soil covers (2004)

It is clearly observed from the figure that the percentage of unaccounted-N portion under 0.19 m^3 m^{-2} d^{-1} was relatively higher (mean for all weeks: 40%) compared to that under other flow rates (19% and 17%, under 0.06 and 0.31 m^3 m^{-2} d^{-1}, respectively). This high percent difference under the flow rate of 0.19 m^3 m^{-2} d^{-1} is due to low levels of NO_3^--N in the effluent, which might be due to better biochemical reactions with sufficient soil-water contact time; this may have enhanced vegetative effects in various soil-water-plant interactions. The unaccounted-N portion in the vegetated soil (mean: 40%) was observed to be significantly high, as compared to that under the bare soil (14%) with same flow rate, which showed that there was vegetative uptake of N (Fig. 4.10; Table 4.3). In order to minimize the unaccounted-N in mass balance, and to examine the N content in the soil with wastewater application, the soil was analyzed at the end of the experiment and the results were incorporated into the mass balance.

4.3.1.4 TKN and nitrate-N in soil

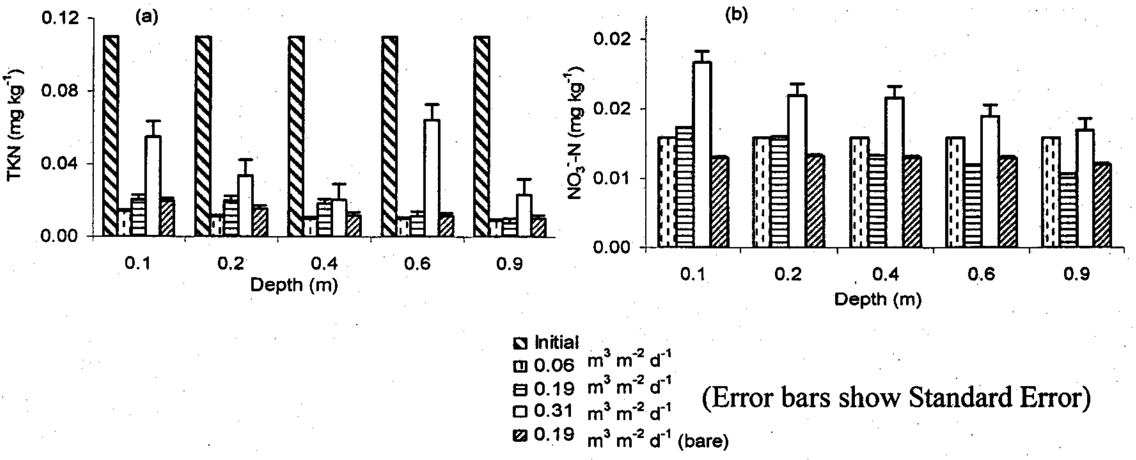
The same sets of lysimeters were also used in the year 2004. It is likely that the wastewater application of 2003 might have modified the initial concentrations of nitrogen

Table 4.3: Nitrogen mass balance in lysimeters under different wastewater application rates and soil covers over time (2004)

Week	Flow rate (m^3 m^{-2} d^{-1})	Total Input (mg)	Outputs (mg)		Total Output (mg)	Input/Output Difference (%)
			Leaching	N2O		
T1	0.06	142	121	0.2	121	15
	0.19	427	217	1.3	219	49
	0.31	711	578	2.5	581	18
	0.19 (bare)	427	322	1.2	323	24
T2	0.06	787	791	5.4	797	1
	0.19	2362	664	13.0	677	71
	0.31	3937	3946	31.8	3978	1
	0.19 (bare)	2362	2371	9.1	2380	1
T3	0.06	1265	1366	15.8	1381	9
	0.19	3796	2238	51.6	2290	40
	0.31	6326	6425	222.6	6648	5
	0.19 (bare)	3796	3637	26.2	3663	4
T4	0.06	1813	2067	31.8	2099	16
	0.19	5440	3240	107.9	3348	38
	0.31	9066	9489	496.2	9985	10
	0.19 (bare)	5440	4793	52.1	4845	11
T5	0.06	2259	2591	56.5	2647	17
	0.19	6778	4058	194.5	4253	37
	0.31	11297	11610	879.4	12490	11
	0.19 (bare)	6778	6122	94.7	6216	8
T6	0.06	2643	3022	87.9	3110	18
	0.19	7930	4725	304.6	5029	37
	0.31	13216	14090	1359.6	15450	17
	0.19 (bare)	7930	7079	150.0	7229	9

and other contaminants in the soil. Therefore, all lysimeters were flushed with tap water for about ten weeks prior to the beginning of the 2004 experiment. The average total N (TKN and NO_3^--N) concentrations of the flushed water were 0.88, 0.42, 0.42, and 0.37 mg L^{-1} under 0.06, 0.19, 0.31 m^3 m^{-2} d^{-1} flow rates with sod, and 0.19 m^3 m^{-2} d^{-1} with bare soil, respectively. Hence, 4133, 5966, 9809, and 5162 mg of total N were leached out respectively, under different flow rates. Therefore, the levels of total N in the soil at the beginning of the 2004 experiment were 362, 291, 646, and 275 mg per lysimeters under

0.06,0.19, 0.31 m^3 m^{-2} d^{-1} flow rates with sod, and 0.19 m^3 m^{-2} d^{-1} with bare soil, respectively. Thus, the TKN and NO_3^--N contents in the soil at different depths after six weeks of wastewater application were analyzed and the results are shown in figure 4.11 (a) and (b), respectively.



(Error bars show Standard Error)

Fig. 4.11 Concentrations of TKN and NO_3^--N in soil at different depths under different treatments: (a) TKN, (b) NO_3^--N (2004)

The TKN and NO_3^--N levels are significantly less in the soil at the end of the year 2004, as compared to the levels at the end of the experiment in 2003 ($P \leq 0.05$, t-test; Figs. 4.6 (a) and 4.11 (a)). This decrease is most likely due to an overall lower concentration of nitrogenous compounds in the influent applied in 2004 (mean total N: 7 mg L^{-1}, Figs. 7 and 8), as compared to that in 2003 (14.1mg L^{-1}, Figs. 4.2 and 4.3). However, like in the year 2003, both TKN and NO_3^--N levels in the soil were in accordance with the amount of wastewater application rate, hence, their levels observed under different flow rates were significantly different ($P \leq 0.05$, t-test; Figs. 4.6 (a), 4.6 (b), 4.11 (a), and 4.11 (b)).

Although, there were no significant differences in the TKN as well as NO_3^--N levels of bare and vegetated soil treatments under the flow rate of 0.19 m^3 m^{-2} d^{-1}, their levels were numerically low in the bare lysimeters, as compared to that in the vegetated lysimeters ($P \leq 0.05$, t-test). This trend is same as that observed in 2003, and thus corroborates that high amount of N losses through the effluent from bare soil, as compared to the vegetated soil (Figs. 4.2, 4.3, 4.7, and 4.8).

4.3.2.5 Nitrogen mass balance incorporating soil retention for the year 2004

The nitrogen mass balance at the end of the experiment period (week T6) is presented in table 4.4. It is evident that about 60~84% "nitrogen" leached through the effluent, 6~15% was retained in the soil and nearly 1~5% was lost as N_2O (Table 4.4) with respect to the total N input. Thus, the nitrogen mass balance for the entire study period showed 7%, 33%, 8%, and 4% differences in the input and output of nitrogen under the flow rates of 0.06, 0.19, 0.31 m^3 m^{-2} d^{-1} with sod, and 0.19 m^3 m^{-2} d^{-1} with bare soil, respectively. It is evident from the results that for both years, unaccounted-N under 0.19 m^3 m^{-2} d^{-1} was higher, as compared to that under other flow rates ($P \leq 0.05$, t-test). Hence, it appears that this flow rate might be adequate for better biochemical reactions under the vegetated condition (Tables 4.2 and 4.4). Like in case of 2003, although the amount of TKN in the effluent or N content in the soil or N_2O volatilizations were not significantly different under vegetated and bare soil ($P \leq 0.05$, t-test), the significantly lower NO_3^--N levels in the effluent under the flow rate of 0.19 m^3 m^{-2} d^{-1} resulted in significantly higher unaccounted N (33%) in the vegetated lysimeters, as compared to other flow rates ($P \leq 0.05$, t-test).

Table 4.4: Nitrogen mass balance in lysimeters at the end of 2004 under different wastewater application rates

Flow Rates (m^3 m^{-2} d^{-1})		0.06	0.19	0.31	0.19 (bare)
	Inputs				
Nitrate Nitrogen (mg)		1536	4607	7679	4607
TKN (mg)		1108	3323	5538	3323
Soil Content (mg)		362	291	646	275
	Total (mg)	3006	8221	13862	8205
	Outputs				
Leaching					
	Nitrate Nitrogen (mg)	2213	4592	10930	6912
	TKN (mg)	9	133	160	167
	Total (mg)	*2222*	*4725*	*11090*	*7079*
Soil Content					
	Nitrate Nitrogen (mg)	214	187	286	464
	TKN (mg)	195	281	708	247
	Total (mg)	*409*	*468*	*994*	*711*
Volatilization (N_2O gas, mg)		150	305	657	88
	Total (mg)	2781	5497	12741	7879
Difference (mg)		224	2724	1121	326
Percentage Difference (%)		*7*	*33*	*8*	*4*

Although amounts of N output through leaching, soil content, or N_2O emission were not significantly different in bare or vegetated soil, significantly higher unaccounted-N was observed under vegetated soil, as compared to that in the bare soil ($P \leq 0.05$, t-test). This significant difference might due to the relatively low nitrate-N in the effluent from vegetated soil, as compared to the bare soil (4 vs. 7.1 mg L^{-1}). Hence, as the study revealed, there were some vegetative effects on biochemical reactions (e.g. leaching, soil retention and volatilization). It was found that there was 29% less nitrogen leaching from vegetated soil, as compared to the one from the bare soil (Table 4.4). However, 3% lower soil retention and 3% higher N_2O emissions occurred under the vegetated soil (Table 4), and thus, a net 29% greater unaccounted-N was observed under the vegetated soil.

Although in both the years, the soil retention and N_2O volatilization were in a similar range under vegetated and bare soils, the N-leaching through the effluent was high from the bare soil, as compared to the vegetated soil (53% vs. 33% of TN input in 2004, 66% vs. 60% of TN in 2003). The observed low percentage of N leaching through the effluent from vegetated lysimeters in 2004 might be due to more vegetative N uptake, as vegetative growth was better in 2004 than that in 2003, and also might be due to the input of low concentration influent wastewater in 2004, as compared to that in 2003. Although 41% of vegetative effects (including 20% reduction in N leaching through the effluent) were observed in the vegetated lysimeter, it should be noted that the vegetative growth during this study was not satisfactory, therefore, a well-established vegetation might further reduce the nitrogen levels in the effluent. In this study, under different flow rates and soil cover treatments, the unaccounted portion of N were in the range of 2~15% and 4~33%, during 2003 and 2004, respectively, which is reasonable. In a study with agricultural drainage water, using an Algal-Bacterial Selenium Removal (ABSR) technique, John et al. (2002) had accounted for only 69% of N in the mass balance.

4.4 CONCLUSIONS

The soil filtration of the secondarily treated municipal wastewater reduced TKN levels from the influent. The high rate of mineralization of TKN and other inorganic nitrogen in the influent resulted in an increase of NO_3^--N levels in the effluent. Although NO_3^--N generally does not accumulate in the soil, the study showed a little increase of NO_3^--N and

TKN levels in soil with increases in the wastewater application rates. Likewise, N_2O emissions from the system increased with increases in the flow rates. Thus, the wastewater should be applied to the soil at an appropriate rate, and effluent water quality and N_2O emissions should be monitored regularly.

This nitrogen mass balance study was focused on the determination of the amount of nitrogen that leached through the soil, retained in the soil, or lost as N_2O. This study showed that 85~98% and 67~96% of the input nitrogen was accounted for in 2003 and 2004, respectively. The remaining portion could be attributed to vegetative effects and volatilization of non-N_2O nitrogenous gases. It was also observed that even poorly established vegetation reduced the nitrogen leaching through soil, and showed 3% and 29% vegetative effects on nitrogen transformations during 2003 and 2004, respectively. Thus, a well-established vegetative floodplain filtration system could reduce NO_3^--N levels in the wastewater effluent to a greater extent, and hence reduce water pollution.

PREFACE TO CHAPTER V

As municipal wastewater may receive some industrial wastewater, certain amounts of heavy metals and/or synthetic organic compounds may be present in it. Hence, potentially toxic heavy metals, present in industrial wastewater (Cd, Cr, Pb, and Zn), are often present in municipal wastewaters as well. Floodplain filtration might remove some heavy metals from the wastewaters; however, continuous application of the wastewater may lead to accumulation of heavy metals in the soil. Therefore, in this paper, the effectiveness of the floodplain filtration in heavy metals reduction in the effluents, the accumulation of heavy metals in the soil, and times to reach maximum permissible limit (MPLP) of heavy metals in the soil were estimated in the sand filtration system under different wastewater application rates, in both 2003 and 2004.

Research paper based on the chapter:

Kunjikutty S.P. and S.O. Prasher. 2005. Removal of heavy metals from wastewater and their accumulation in soil under floodplain soil filtration of municipal wastewater (under preparation).

CHAPTER-V

REMOVAL OF HEAVY METALS FROM WASTEWATERS WITH A SOIL FILTRATION SYSTEM

ABSTRACT

The accumulation and movement of heavy metals such as Al, Ca, Cr, Cu, Fe, Mn, Mg, Na, Ni, and Zn in the soil, applied with secondarily treated municipal wastewater, were evaluated with floodplain simulated field lysimeters. Wastewater was applied at 0.06, 0.19, and 0.31 m^3 m^2 d^{-1} flow rates to sand filled, vegetated lysimeters, and at a flow rate of 0.19 $m^3 m^2$ d^{-1} to bare lysimeters. The effluent (at 0.9 m depth) from the lysimeters, which was collected weekly, and the influent, which was collected daily, were analyzed. The study showed a 58%, 9%, 3%, 37%, 63%, and 52% reductions of As (non-metal), Cd, Cu, Ni, Pb, and Zn (heavy metals) [in 2003], and a 20%, 63%, 5%, 23%,18%, 57%, and 79% reduction of As, Cd, Cr, Cu, Ni, Pb, and Zn [in 2004], relative to their levels in the influent.

The soil samples collected at the end of the wastewater application in each year from different soil depths (0.1, 0.2, 0.4, 0.6, and 0.9 m) were subjected to a MEHLICH III extraction procedure to determine the accumulation of available heavy metals. It was observed that the heavy metals, such as Al, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, and Zn, accumulated in the soil, whereas, although As, Cd and Pb were present in the influent, they were absent in the soil. Although there were no significant effects of flow rate on heavy metal accumulation, relatively low amounts were observed with the intermediate flow rate of 0.19 m^3 m^{-2} d^{-1}, due to better biochemical reactions of the incoming organic matter with sufficient soil-water contact time. There were no vegetative effects observed on heavy metal accumulations in the soil. The sodium absorption ratio (SAR) of the soil decreased with wastewater application. The quantity of the influent required to accumulate pollutants in the soil to reach maximum permissible limit of pollutants (MPLP) were evaluated. Even with the highest application rate of 0.31 m^3 m^2 d^{-1}, the annual accumulation of Cd, Cu, Ni, Pb and Zn in the soil were below 0.5%, 1.7%, 6.6%, 1.8% and 23% respectively, of the USEPA recommended annual maximum pollution loading (in 2003). According to AAFC limits, their accumulations were below 7.4%, 18.2%, 38.4%, 6.4%, and 19.6%, respectively and a similar

trend was observed in 2004. The wastewater application in the preceding year further increased the heavy metal levels in the soil, irrespective of the low concentrations of the pollutants in the influent. Hence, although the observed time to reach MPLP was longer, continuous monitoring and evaluation of the wastewater land-treatment system is necessary under varied heavy metal concentrations in the influent over time.

5.1 INTRODUCTION

Generally, wastewater is discharged to water-bodies after primary and/or secondary treatment. Unfortunately, this wastewater still contains different heavy metals, which stem from sewage sludge and various industries such as battery recycling, and electronic and ceramic manufacturing (Alloway and Ayres, 1993). The discharge of such untreated or partially treated wastewater to water-bodies deteriorates water quality; however, its quality can be improved by soil treatment.

In a natural soil environment, dissolved organic carbon is observed at a typical concentration of 0.1~200 mg L^{-1} (Kinniburgh et al., 1996). However, generally, wastewater contains a high amount of organic matter having a large portion of humic substances. Although humic substances in soil can enhance the microbial activity, these anionic humic substances react with heavy metal ions and other pollutants in wastewater (Lenhart and Honeyman, 1999; LeBoeuf and Weber, 2000). Even low concentrations of humic substances can affect heavy metal concentrations in the soil by affecting adsorption/binding and leaching of heavy metal ions from the soil (Buffle, 1988)

The organic matter entering the soil through wastewater is decomposed to carbon dioxide, soluble organic acids, residual organic matter and inorganic constituents, and releases heavy metals into the soil solution (Boyd et al., 1980). However, due to the low solubility and limited plant uptake, heavy metals tend to accumulate in the soil (McGrath et al., 1994). Such soil contamination with heavy metals is generally permanent in nature due to their non-biodegradable, non-thermo-degradable and non-leachable characteristics, hence, eventually becoming a part of the soil matrix (Mulchi et al., 1991; Nriagu and Pacyna, 1988). Although small amounts of B, Cu, Ni and Zn are essential for plant growth, higher concentrations of these heavy metals can be toxic, can hinder root growth and plant uptake of macronutrients, and, as a result, can decrease plant productivity [Burton et al., 1983; Chang et al., 1992; Breckle and Kahle, 1992; and Smith et al., 1996 (a)].

During wastewater irrigation and/or land application for treatment, due to their immobile nature, heavy metals may adsorb, and hence retain in soil. The change in pH due to continuous wastewater application, or the reduction in soil capacity to retain the heavy metals, can release heavy metals into the soil solution; consequently these may be taken up by plants or leach to groundwater. As a result, the heavy metal concentration in the effluent could be even higher than that in the influent wastewater. Although clay content, pH, organic matter, and cation exchange capacity (CEC) are the main factors affecting the adsorption and mobilization of most of the heavy metals in soil (Kimberly and William, 1999), generally soil pH has the greatest single-factor effect on the solubility or retention of heavy metals in the soils, with high soil pH resulting in greater retention and lower solubility of heavy metal cations in the soil (Stahl and James, 1991; Basta and Pantone, 1993; and Martinez and Motto, 2000, Apak, 2002). Moreover, due to precipitation reactions, the mobility of most of the heavy metals decreases with increases in soil pH (Smith, 1996).

However, insoluble complex compounds of heavy metals are also formed with organic matter in soil (Sauve et al., 2000). The heavy metal concentration, its species, chemical behavior, and availability in soil and sediments are controlled by the reactions in the soil-water interface. Heavy metal sorption in the soil is an ion transfer (soil-solid-solution) and dispersion mechanism with clay, oxides, hydroxides, carbonates, and phosphates of heavy metals, organic matter, and microorganisms (Apak, 2002). Moreover, hydrous Fe and Mn oxides are the important natural particles that control the soil-water-sediment reactions with nutrients and heavy metals (Dixon and Weed, 1989; Benjamin and Leckie, 1981; Wu et al., 1990). Moreover, CEC, an index of soil's capacity to exchange cations with the soil solution, also affects the ability of the soil to adsorb and retain cations and heavy metals.

The continuous application of wastewater to land can also change the soil chemical and physical properties. For example, elevated concentrations of sodium in soil could increase salinity and cause adverse physico-chemical changes in the soil. This could reduce water uptake by plant roots and could affect soil structure. The sodium absorption ratio (SAR= $[Na^+/(Ca^{2+}+Mg^{2+})/2]^{0.5}$), is an index to estimate adverse levels of Na in irrigation waters and soil. Irrigation water, with a SAR value greater than 15, could adversely increase soil sodicity (Peterson, 1999). The recommended limits of SAR for irrigation water and wastewater for irrigation are less than 13 and 6, respectively (EPA, 1999). As land application of wastewater could contaminate soil with heavy metals and could change soil physical and chemical properties, the water has to be treated to a further level before it is applied to land or discharged to water bodies.

The conventional tertiary level treatment methods are activated carbon, reverse osmosis, and ion exchange. These methods require high inputs of energy and chemicals (Tchnobanoglous, 1990), and thus are too costly for many countries. The use of land filtration for wastewater treatment appears to be a low-cost alternative that could be technologically and environmentally acceptable. One of the land filtration methods, natural or constructed wetlands, has been proven to be well suited for treating municipal, agricultural, and industrial wastewaters (DeBusk, 2001). According to Tam and Wong (1994), and Eger (1994), both natural and artificially constructed wetlands represent an alternative to chemical-based methods. In addition, wetlands are flexible, less susceptible to loading problems, and can be established at the site of the release of wastewaters (Brix and Schierup, 1989). However, in many highly populated developing countries, scarcity of land and high initial costs of construction limit the use of wetlands. On the other hand, the floodplains, bordering rivers and streams, are usually available for most of the year. This is because in most of the South-Asian developing countries, floodplains are inundated during one-third of the year (monsoon season), and remain unused for the rest of the period. Hence, these floodplains could be used for wastewater treatment. However, the effectiveness of floodplains in removing heavy metals from the wastewater needs to be evaluated.

The main objectives of this study were to compare the heavy metal levels in the influent wastewater to those of the effluent from the soil filtration system, and to estimate the amounts of accumulation of certain heavy metals in the soil by wastewater application. The effects of water application rates and vegetation on the accumulation of heavy metals in the soil were evaluated. The annual loading and time required to reach MPLP were also estimated to provide insight for the planning and implementation of floodplain filtration systems.

5.2 MATERIALS AND METHODS

The experiments were conducted in field lysimeters located at the Macdonald Campus of McGill University (Ste-Anne-de-Bellevue, QC) during the June–September period, 2003 and 2004. Secondarily treated wastewater, obtained daily from the Vaudreuil and Pincourt wastewater treatment plants during 2003 and 2004, respectively, was applied to the lysimeters at three different application rates (0.06, 0.19, and 0.31 m^3 m^2 d^{-1}, representing soil-water contact times of 4, 1.2, and 0.7 days, respectively), and replicated three times. The lysimeters were constructed of PVC pipe (0.45 m I.D. x 1.0 m height), and were fitted with a 50 mm drain, as well as water sampling ports at 0.1, 0.2, 0.4, and 0.6 m from the soil surface. The lysimeters were packed with sand (96:2:2 sand:silt:clay; O.M 0.5%) to a depth of 0.9 m, and sodded with grass for vegetated lysimeters. The bulk density, porosity, total N, P, and K contents of the soil prior to any treatment were 1700 kg m^{-3}, 0.33 $m^3 m^{-3}$, 52.0 mg kg^{-1}, 14.4 mg kg^{-1} and 92.0 mg kg^{-1}. The lysimeters were protected using a rain cover.

The lysimeters were covered during the off-months between the experiments in 2003 and 2004. Prior to the wastewater application in 2004, tap water was applied over ten weeks to the lysimeters at the same flow rate as that of the wastewater application to flush out the contaminants from the soil. Each day, wastewater or tap water was filled in overhead tanks, and was evenly distributed to each lysimeter through drippers connected in a loop at the end of the pipe from an overhead tank. The number of drippers in the loop regulated the appropriate water flow to each lysimeter (i.e. 10 L or 0.06 m d^{-1} $dripper^{-1}$). Water samples were collected from the sampling ports and from the drain at weekly intervals, whereas, the influent samples were collected daily. Soil samples were collected initially during the column packing process and from different soil depths at the end of the experiment in each year.

5.2.1 Analytical Methods

The effective cation exchange capacity (CEC) of the soil was measured with the barium chloride method (Martin, 1993), and soil pH was measured with a standard pH meter. The soil samples were subjected to Mehlich III soil extraction to determine the concentrations of available Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, and Zn in it (Tran et al., 1993). For this purpose, the soil samples (2.5 g) were equilibrated with 25.0 ml of

Mehlich III solution (pH: 2.45-2.55) at 120 oscillations per minute for 5 minutes in a shaker. The resulting suspension was filtered with Whatman No. 40 or Fisherbrand Q5 filter paper. The concentrations of heavy metals in each soil sample extract and leachate water sample were determined by inductively coupled plasma mass spectrometry (ICP-MS). The data were analyzed using SAS (SAS, 2001).

5.3 RESULTS AND DISCUSSION

The concentrations of Cd, Cr, Cu, Ni, Pb, Zn (heavy metals) and As (non-metal) in the influent and effluents from the lysimeters under different flow rates (0.06, 0.19, and 0.31 m^3 m^2 d^{-1}) and soil covers in 2003 and 2004 are shown in Table 5.1. It is observed from Table 5.1 that the concentrations of these heavy metals in the effluents from vegetated lysimeters under different flow rates are lower than that in the influent; however, the levels of most of these heavy metals in the effluents were significantly (t-test, $P \leq 0.05$) not lower, except in the case of Pb (mean: 0.0015 mg L^{-1}) and Zn (0.0266 mg L^{-1}) compared to their influent levels (Table 5.1). On an average for different flow rates, 58%, 9%, 3%, 37%, 63%, and 52% of As, Cd, Cu, Ni, Pb, and Zn, respectively were removed from the influent during 2003. In 2004 also, significant (t-test, $P \leq 0.05$) decreases in As, Pb and Zn levels were observed in the effluents, as compared to their levels in the influent. Cadmium, Cu, and Ni levels in the effluents also decreased, but their removal rates were not conclusive. In addition to the above-mentioned heavy metals, Cr was also present in the influent during 2004, and thus, 20%, 63%, 5%, 23%, 18%, 57%, and 79% of As, Cd, Cr, Cu, Ni, Pb, and Zn, respectively, were removed from the influent. All the heavy metals' levels in the effluent from the bare soil also decreased with respect to their influent levels, except in the case of Cu in 2004 (11% increase). However, this increase of Cu in the effluent was non-significant (t-test, $P \leq 0.05$). Therefore, it can be concluded from both years' results that soil filtration can effectively reduce the amounts of certain heavy metals from wastewaters.

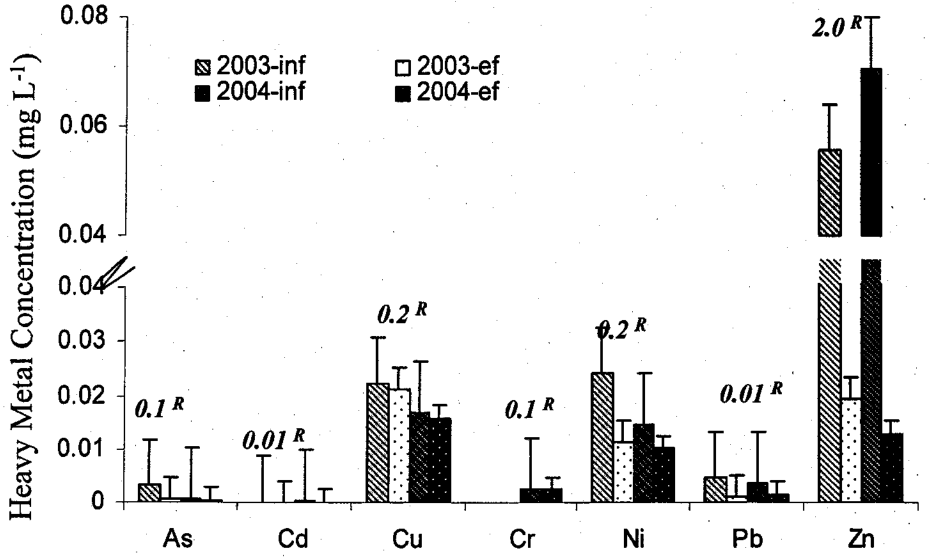
Although the heavy metals' levels were reduced in the effluents by soil filtration, its levels in the influent should be compared to the recommended levels in irrigation water to assess the susceptibility of soil filtration of the wastewaters. Since the heavy metals' levels in the effluents under different flow rates were similar, the concentrations of heavy metals in the effluent under the intermediate flow rate of 0.19 m^3 m^{-2} d^{-1} and that in the influents

Table 5.1: Influent and effluent concentrations of heavy metals under different flow rates during 2003 and 2004

Heavymetal /non-metal	Influent Concentration (mg L^{-1})		Effluent concentration (mg L^{-1}) under different flow rates (m^3 m^{-2} d^{-1})							
	2003	2004	2003				2004			
			0.06	0.19	0.31	0.19 (bare)	0.06	0.19	0.31	0.19 (bare)
As	0.00315	0.00063	0.00153	0.00078	0.00166	0.00093	0.00052	0.00041	0.00059	0.00095
Cd	0.00017	0.00029	0.00016	0.00013	0.00016	0.00030	0.00026	0.00003	0.00004	0.00027
Cu	0.02222	0.01686	0.02120	0.02145	0.02214	0.02122	0.01592	0.01594	0.01598	0.01869
Cr	—	0.00270	—	—	—	—	0.00118	0.00246	0.00258	0.00081
Ni	0.02407	0.01486	0.01004	0.01152	0.02371	0.01141	0.01477	0.01016	0.01175	0.01214
Pb	0.00481	0.00372	0.00118	0.00117	0.00304	0.00120	0.00167	0.00162	0.00146	0.00202
Zn	0.05556	0.07046	0.01487	0.01947	0.04542	0.01610	0.01111	0.01289	0.02098	0.01344

(during 2003 and 2004) were compared with their respective permissible limits in irrigation water (AAFC, 1999; Fig. 5.1). It is observed from figure 5.1 that the heavy metal concentrations in the influents were well below the recommended permissible limits for irrigation water, and hence in the effluents. The study showed that soil filtration can reduce certain amounts of heavy metals from the wastewaters, even at reasonably low concentrations of heavy metals in the influent, and thus, would reduce the risk of surface and groundwater pollution.

Even though the heavy metal concentrations in the influent were lower than the permissible limits for irrigation water (Fig. 5.1; Table 5.1), application of such wastewater to land over prolonged periods could affect the physiochemical properties of the soil. Therefore, the effects of continuous wastewater application to the soil for the experimental periods of 9 weeks (2003) and 6 weeks (2004) were examined. In both the years, although As, Cd, and Pb were present in the influent wastewater, they were absent in the soil after wastewater application, which might be due to the observed leaching of these heavy metals through the effluent, (42~80%, 37~90%, and 37~43% leach out of As, Cd, and Pb, respectively; Table 5.1), rather than their adsorption. The accumulated amounts of available Al, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, and Zn in the soil at the end of 2003, determined by MEHLICH III extraction, are presented in figure 5.2. Since, the heavy metal concentrations in the soil-extract is high and is more important, as compared to the small portion which assimilated with microorganisms and that was retained in the filter paper (in the filter paper used for filtration of the soil extract), only the soil-extracts were analyzed for the available heavy metal concentrations.



^{R} Recommended levels in irrigation water (AAFA)

Figure 5.1: Concentration of heavy metals and non-metal in influent, effluent, and permissible levels in irrigation water

The concentrations of the above-mentioned heavy metals in the soil increased after wastewater application, which is likely due to the different metal sorption processes that occurred in the soil (Fig. 5.2). All the heavy metal levels in the soil under different flow rates in 2003 were significantly higher, as compared to their initial levels, except in the case of Cr, Ni, and Zn (t-test, $P \leq 0.05$; Fig. 5.2; Table 5.2). The concentrations of Cr, Ni, and Zn in the soil were relatively low (mean concentrations: 0.03, 0.016, and 0.027 mg L^{-1}, respectively; Fig. 5.2), and hence resulted in relatively small variations with their initial levels (0.024, 0.024, and 0.06 mg L^{-1}, respectively; Fig. 5.2). Thus, Cr, Ni, and Zn levels in the soil showed non-significant differences with their initial levels (t-test, $P \leq 0.05$; Fig. 5.2; Table 5.2).

As heavy metals are non-leachable, the adsorbed heavy metals in the soil with wastewater application in 2003 are assumed to have remained in the soil. Hence, the heavy metal levels in the soil at the end of the 2003 experiment were considered as the initial levels of the heavy metals in the soil at the beginning of the experiment in 2004. Therefore, the

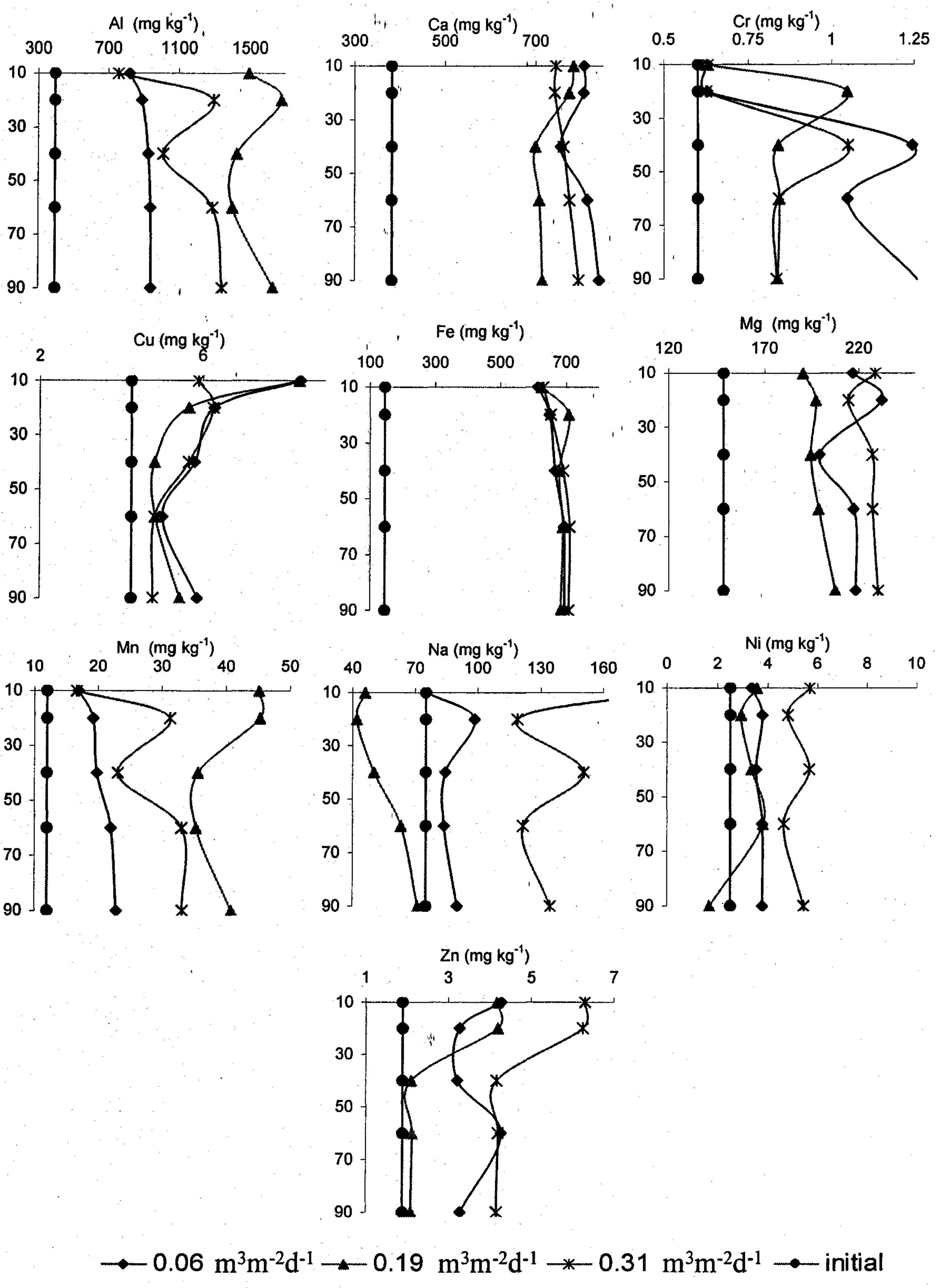


Figure 5.2: Heavy metal Concentrations in soil solution at different depths under different wastewater application rates (2003)

Table 5.2: Statistical results of comparison of initial and final heavy metal concentration in the soil under different wastewater application rates (2003)

Parameter	Al	Ca	Cr	Cu	Fe	Mg	Mn	Na	Ni	Zn
IN vs. 0.31	*	*	NS	*	*	*	*	*	NS	NS
IN vs. 0.19	*	*	NS	*	*	*	*	*	NS	NS
IN vs. 0.06	*	*	NS	*	*	*	*	*	NS	NS
0.31 vs. 0.19	*	NS	NS	NS	NS	*	*	*	*	*
0.31 vs. 0.06	NS	*	NS	NS	*	NS	*	*	*	NS
0.19 vs. 0.06	*	*	NS	NS	NS	*	*	*	NS	NS

IN, Initial; 0.31, 0.31 m^3 m^2 d^{-1}; 0.19, 0.19 m^3 m^2 d^{-1}; 0.06, 0.06 m^3 m^2 d^{-1}; *, Significant; NS, Non-significant

levels of the heavy metals in the soil at the end of the experiment in 2004 (after 6 weeks of wastewater application) under different flow rates were analyzed and are shown in figure 5.3. It is evident that the levels of heavy metals in the soil in 2004 were higher, as compared to their corresponding levels in 2003 (Figs: 5.2 and 5.3). It should be noted that all the heavy metal levels in the influent in 2004 were lower, as compared to their levels in the influent in 2003 (Table 5.1). Therefore, it can be concluded that irrespective of high or low concentrations of heavy metals in the influent, continuous wastewater application could increase their levels in the soil (Table 5.1; Figs. 5.2 and 5.3). A similar study, where wastewater was used to irrigate a tree plantation for about 5~17 years, also showed accumulations of Cr, Pb, Cu, Ni, Zn and Cd in the soil (Smith et al., 1996 (b)). The high adsorption ability and formation of stable organo-metallic complex in the soil can lead to relatively low mobility of heavy metals in the soil (Ram and Verloo, 1985). Moreover, according to Eriksson (1988), organic matter addition to the soil reduces plant uptake in sand, as compared to that in clay soil, thus, our study results with sand corroborate previous findings of increases in heavy metal accumulation in soil with wastewater application.

The heavy metal accumulations in the soil, as shown in figures 5.2 (2003) and 5.3 (2004), can be categorized into transition (Cr, Cu, Fe, Mn, Ni, and Zn), alkali (Na), alkaline-earth (Mg and Ca), and others (Al). Aluminum accumulation in the soil might be due to its least order of replaceability by cations in the soil. The commonly quoted relative order of replaceability on the cation exchange complex of heavy metal cations is

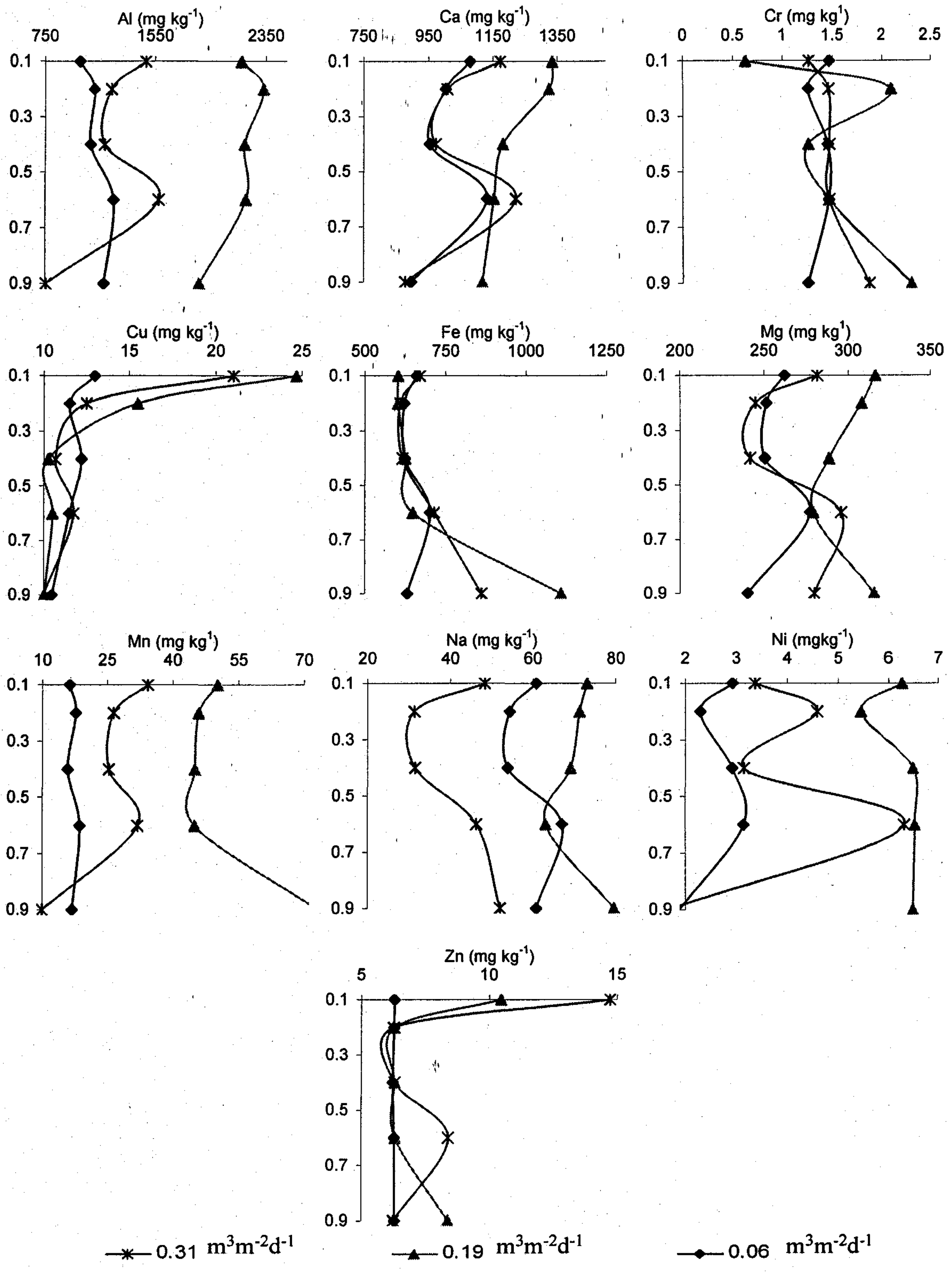


Figure 5.3: Heavy metal Concentrations in soil solution at different depths under different wastewater application rates (2004)

$Mg^{2+} > Ca^{2+} > Al^{3+}$ (Matagi et al., 1998). The increase in soil organic matter decreases the amount of exchangeable-Mn by forming its complexes, thus favoring its accumulation in the soil. Due to lower replaceabilty, Fe, Al, and Mn could form their oxides with the available cations in the soil. Although sand with lower oxides and organic matter content is expected to have lower metal sorption capacities and greater heavy metal availabilities, the continuous organic matter addition to soil by wastewater application might increase the formation of metal-oxides in the soil, and thereby the adsorption of heavy metals (Batsa et al., 2005; Spartks, 2003; Stumm, 1992). As the oxides of these metals in the soil could increase the heavy metal sorption, the observed increase in their concentrations in the soil with wastewater application might increase the sorption of other heavy metals (e.g. Cr, Cu, and Zn). Copper can also form the most stable complexes with organic matter (Elliott et al., 1986), and thus, exists in organically-bound forms of the heavy metals in the soil, and hence showed increased levels in the soil. Nickel accumulation in soil is mainly influenced by the amount of the soil organic matter content, and hence, accumulates in the soil with wastewater application.

It is well known that metal-oxides, as well as soil organic matter, are the main soil constituents which most significantly affect retention, mobility, and bioavailability of heavy metals in the soil (Martinez and Mc Bride, 1988). However, the heavy metal exchange between soil and water also depends on type, pH, and CEC of the soil, as well as speciation and concentration of the heavy metals and residence time of wastewater in the soil.

The soil pH values at different depths during 2003 and 2004 are given in Table 5.3. It is observed that soil pH increased with wastewater application. The initial soil pH of 5.2 increased to a range of 6~6.5 during 2003, and remained roughly in the same range in the following year. Depth-wise, variations in soil pH under different flow rates were relatively small (non-significant, $P \leq 0.05$) and in the same range of 6~6.5, in both years. As the soil pH is not high (nearly neutral), the retention of heavy metals in soil might be lower; regardless, the organic matter addition through wastewater might have increased the heavy metal retention in the soil (Eriksson, 1988), and consequently increased heavy metal levels in the soil.

The CEC of the initial soil, and after wastewater application in 2003 and 2004, were analyzed and the results are shown in figure 5.3. The CEC along the soil profile depth increased from the initial level of 0.65 cmole kg^{-1} to a range of 0.56~1.06 cmole kg^{-1} in the soil profile in 2003, and to 0.68~1.63 cmole kg^{-1} in 2004 (Fig. 5.4 (a) and (b)). This increase in soil CEC indicates the increase of exchangeable cations in the soil with increases in organic matter input through wastewater application. As soils with high CEC and organic matter content can exchange and retain large amounts of cations, the observed increase in CEC and organic matter input to soil through wastewater application might increase the heavy metal accumulation in the soil. In both years, under all the flow rates, the CEC of the soil at deeper depths of the lysimeter were low. This might be due to the high occupancy of the anions in the wastewater with the available soil cations due to higher moisture content at the bottom of the lysimeters.

Table 5.3: Soil pH under different flow rates for 2003 and 2004

	2003	2004
Initial Soil	5.2	
Soil treated with 0.06 m^3 m^2 d^{-1}	6.30 - 6.45	6.30 - 6.5
Soil treated with 0.19 m^3 m^2 d^{-1}	6.02 - 6.18	6.01 - 6.17
Soil treated with 0.31 m^3 m^2 d^{-1}	6.01 - 6.18	6.01 - 6.17

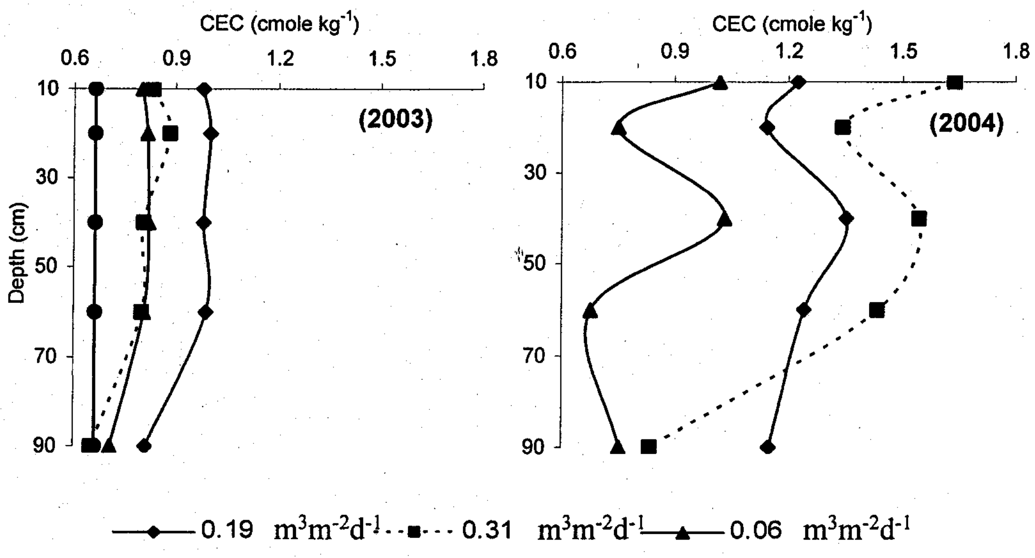


Figure 5.4: Cation exchange capacity (CEC) of soil at different soil depths under different treatments during 2003 and 2004

The alkali heavy metal, Na, causes soil sodicity at its higher concentrations in soil and thereby affects soil physical properties. The Na hazard in soil can be tested based on the sodium absorption ratio (SAR, used to represent Na ratio of soil-solution) or exchangeable sodium percent (ESP, used to represent Na ratio of soil). The SAR/ESP depends on the concentrations of Na, Ca, and Mg. The SAR of the soil-solution can be used as a surrogate of ESP of the soil, and can be related as 0.8 times soil ESP to SAR value (Krista Pearson, 2005). There were no significant differences in the SAR values at different depths of the soil under any flow rates (t-test, $P \leq 0.05$). Hence, the average SAR values of the soil-solution under different flow rates in 2003 and 2004 are shown in Table 5.4. The SAR values of the soil-solutions, collected at the end of the experiment in 2003 and 2004, were decreased, as compared to their levels in the soil collected in the beginning of the experiments in the corresponding years. This decrease is mainly due to low Na, and high Ca and Mg levels in 2003, and low levels of Na and high levels of Ca in 2004 (Table 5.4). In both years, high and low SAR values were observed with the highest (0.31 $m^3 m^2 d^{-1}$) and intermediate (0.19 $m^3 m^2 d^{-1}$) flow rates, respectively (Table 5.4). The lowest SAR value observed under 0.19 $m^3 m^2 d^{-1}$ flow rate might be due to low levels of Na, Ca, and Mg in the soil under this flow rate, compared to other flow rates (Fig.5.2; Table 5.4). The highest SAR value observed under the highest application rate (0.31 $m^3 m^2 d^{-1}$) was also within the recommended typical municipal effluent range (5~8; EPA, 1990).

Table 5.4: Soil Sodium Absorption Ratio (SAR)

Soil applied under flow rates ($m^3 m^{-2} d^{-1}$)	Ca ($mg L^{-1}$)	Mg ($mg L^{-1}$)	Na ($mg L^{-1}$)	SAR
Initial	12.85	5.05	3.90	7.12
2003				
0.06	15.97	5.32	3.18	5.28
0.19	14.85	5.00	2.67	4.59
0.31	15.29	5.45	4.07	6.87
2004				
0.06	12.83	3.46	1.38	2.60
0.19	11.71	3.14	0.87	1.71
0.31	12.15	3.59	2.27	4.36

As the input of heavy metals through the wastewater is in the order of the flow rates, and their levels in the soil increase with respect to their input levels, all the heavy metals showed significantly different concentrations under different flow rates in 2003 and 2004 (t-test, *$P \leq 0.05$*, Tables 5.2 and 5.5), except in the case of Cr and Cu in 2003 and 2004 (t-test, *$P \leq 0.5$*, Table 5.2) and Fe and Zn in 2004 (t-test, *$P \leq 0.5$*, Table 5.3). Even though there were no observed conclusive relations in soil heavy metal adsorption under different application rates in 2003 and 2004 (Figs. 5.2 and 5.5), relatively low accumulation of Ca, Cr, Cu, Fe, Mg, Na, Ni, and Zn in 2003 (Fig. 5.2) and Cu, Fe, and Zn in 2004 (Fig. 5.3) were observed under the intermediate application rate of 0.19 m^3 m^{-2} d^{-1}. Therefore, it can be assumed that more biochemical reactions might have occurred to the incoming organic matter under the intermediate flow rate of 0.19 $m^3 m^2 d^{-1}$. There might be a higher microbial population under this flow rate due to favorable conditions, and as a result, there might be an enhanced assimilation of some amount of heavy metals.

Table 5.5: Statistical results of comparison of final heavy metal concentration in the soil under different wastewater application rates (2004)

Interactions	Al	Ca	Cr	Cu	Fe	Mg	Mn	Na	Ni	Zn
0.31 vs. 0.19	*	NS	NS	NS	NS	NS	*	*	*	NS
0.31 vs. 0.06	*	NS	NS	NS	NS	NS	NS	*	NS	NS
0.19 vs. 0.06	*	*	NS	NS	NS	*	*	*	*	NS

0.31, 0.31 m^3 m^2 d^{-1}; 0.19, 0.19 m^3 m^2 d^{-1}; 0.06, 0.06 m^3 m^2 d^{-1}; *, Significant; NS, Non-significant

To examine the effect of vegetation on heavy metal accumulations in the soil, the metal levels in the soil under vegetated and bare lysimeters, applied with the same flow rate of 0.19 m^3 m^{-2} d^{-1}, were analyzed. In 2003, all the heavy metal levels in both vegetated and bare soil were similar (t-test, *$P \leq 0.05$*; Fig. 5.5), except in the case of Cu. In 2004, the levels of most of the heavy metals (Al, Ca, Fe, Mg, Mn, Na, and Ni) in the bare soil were lower, as compared to their levels in the vegetated soil (Fig. 5.6). However, Cr, Cu, and Zn levels in the soil were not significantly (t-test, *$P \leq 0.05$*) different from their levels in the vegetated soil

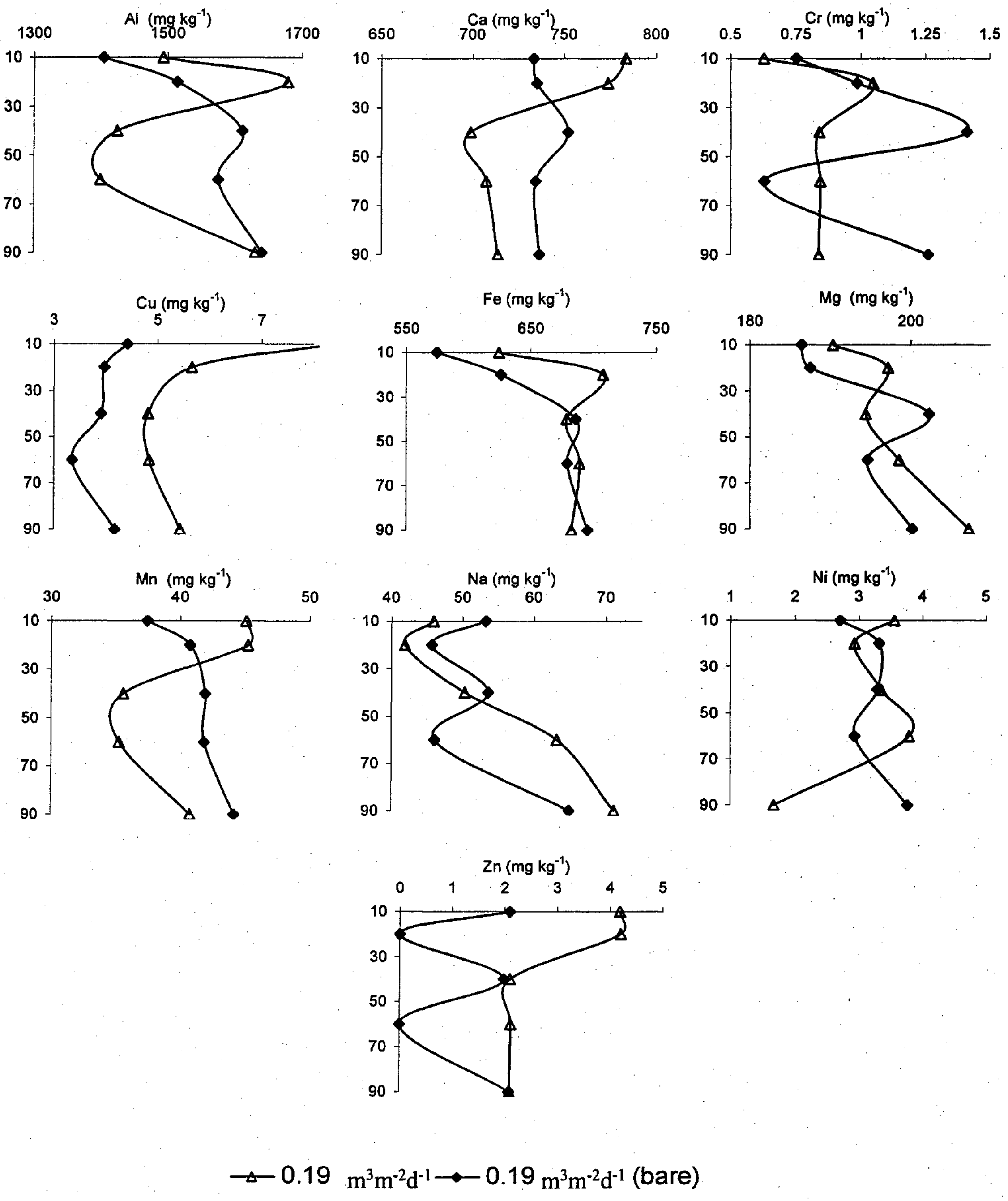


Figure 5.5: Heavy metal Concentrations in the soil solution at different depths under vegetated and bare lysimeters under 0.19 m3 m^{-2} d^{-1} flow rate (2003)

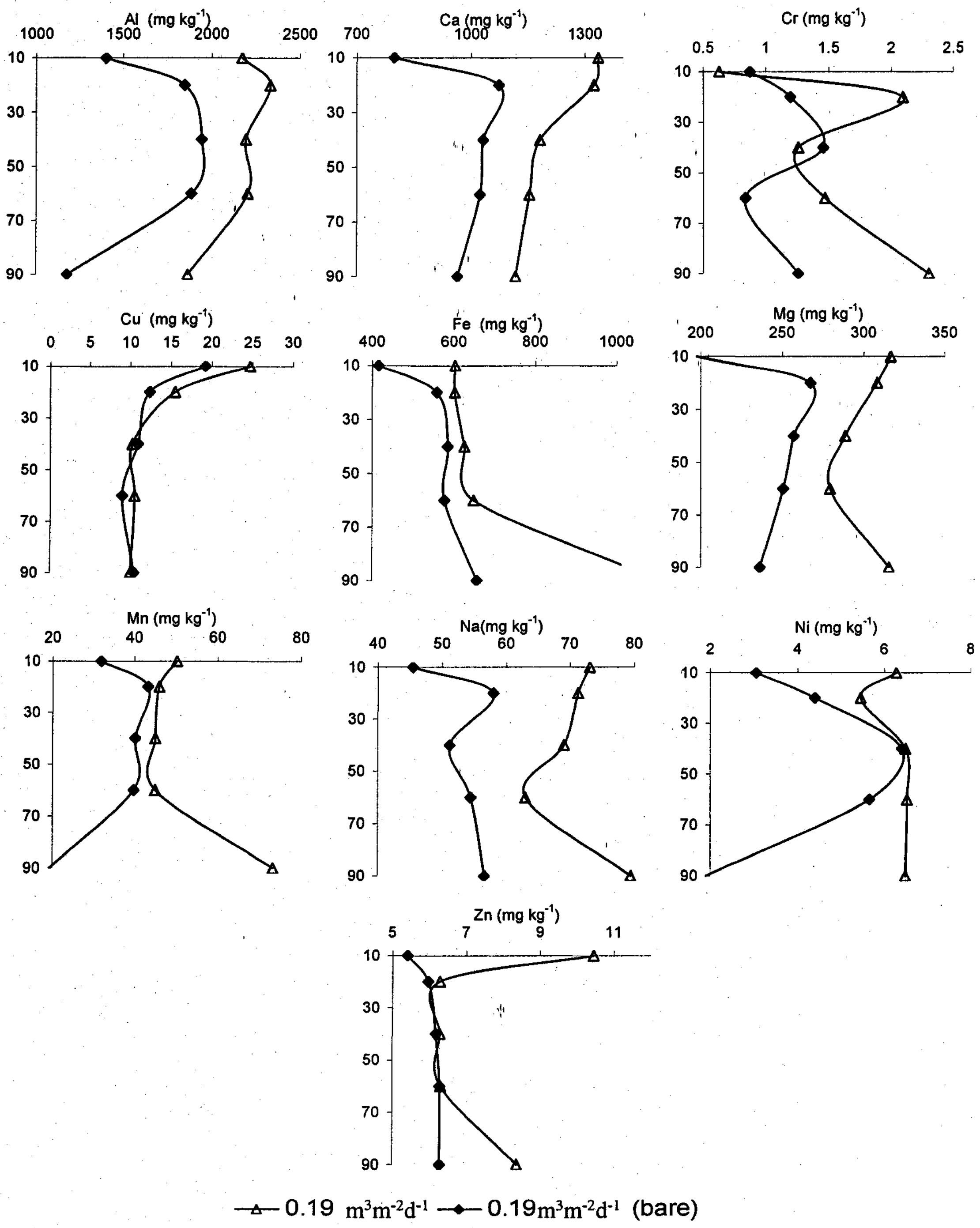


Figure 5.6: Heavy metal Concentrations in the soil solution at different depths under vegetated and bare lysimeters under 0.19 m^3 m^{-2} d^{-1} flow rate (2004)

(Fig. 5.6). It should be noted that the vegetative growth was comparatively better in 2004, as compared to that in 2003. Hence, in 2004 under vegetated soil, a better rate of biochemical reactions including adsorption reactions and increased microbial populations for assimilation might have occurred, and thereby increased heavy metal accumulations. Therefore, although statistically not different, the vegetated soil numerically increased certain amounts of heavy metal accumulations in the soil, as compared to that in the bare soil.

It can be seen from figures 5.2 and 5.3 that the amounts of all heavy metals in the soil increased from 2003 to 2004. To illustrate heavy metal accumulation in the soil with prolonged wastewater land application, the amount of heavy metals in the soil at different depths under the 0.19 $m^3 m^2 d^{-1}$ flow rate during 2003 and 2004 are depicted in figure 5.7. Although most of the heavy metal concentrations in the influent during 2004 were lower, as compared to those in 2003 (Fig. 5.1), there were noticeable increases in the concentrations of all the heavy metals in the soil under different flow rates (Table 5.6) in 2004, as compared to their 2003 levels. As additional increases in the organic matter input to the soil might have affected various soil bio-chemical reactions, an appreciable increase in the soil CEC (from 2003 to 2004) was observed (Figs. 5.4 (a) and (b)). The increase in the soil CEC in 2004 was in accordance with the increase in the flow rates with the increase in the organic matter input through the influent ((Fig. 5.4 (b)). Hence, with increased CEC and organic matter content of the soil, the heavy metal adsorption in the soil might have further increased in 2004 from 2003 levels (Figs. 5.2, 5.3, and 5.7). The average percent increase of heavy metal accumulations in the soil from 2003 to 2004 were 42%, 66%, 80%, 137%, 6%, 53%, 29%, 36%, 123%, 59%, and 179% for Al, Ca, Cr, Cu, Fe, Mg, Mn, Na, Ni, P, and Zn, respectively. Therefore, the study showed that irrespective of the concentrations of the heavy metals in the influent wastewater, its continuous application to the soil would increase their accumulation in the soil. Hence, a close monitoring of the heavy metal levels in the soil and investigations on time to reach the maximum permissible limit of pollutants (MPLP) in the soil are needed.

5.3.1 Time to reach maximum permissible limit of pollutants (MPLP)

The times to reach the recommended maximum permissible limit (USEPA, 1995; AAFC, 1999) for heavy metals in soil applied with secondarily treated wastewater were estimated from the data collected in 2003 and 2004 (Table 5.7). The continuous application

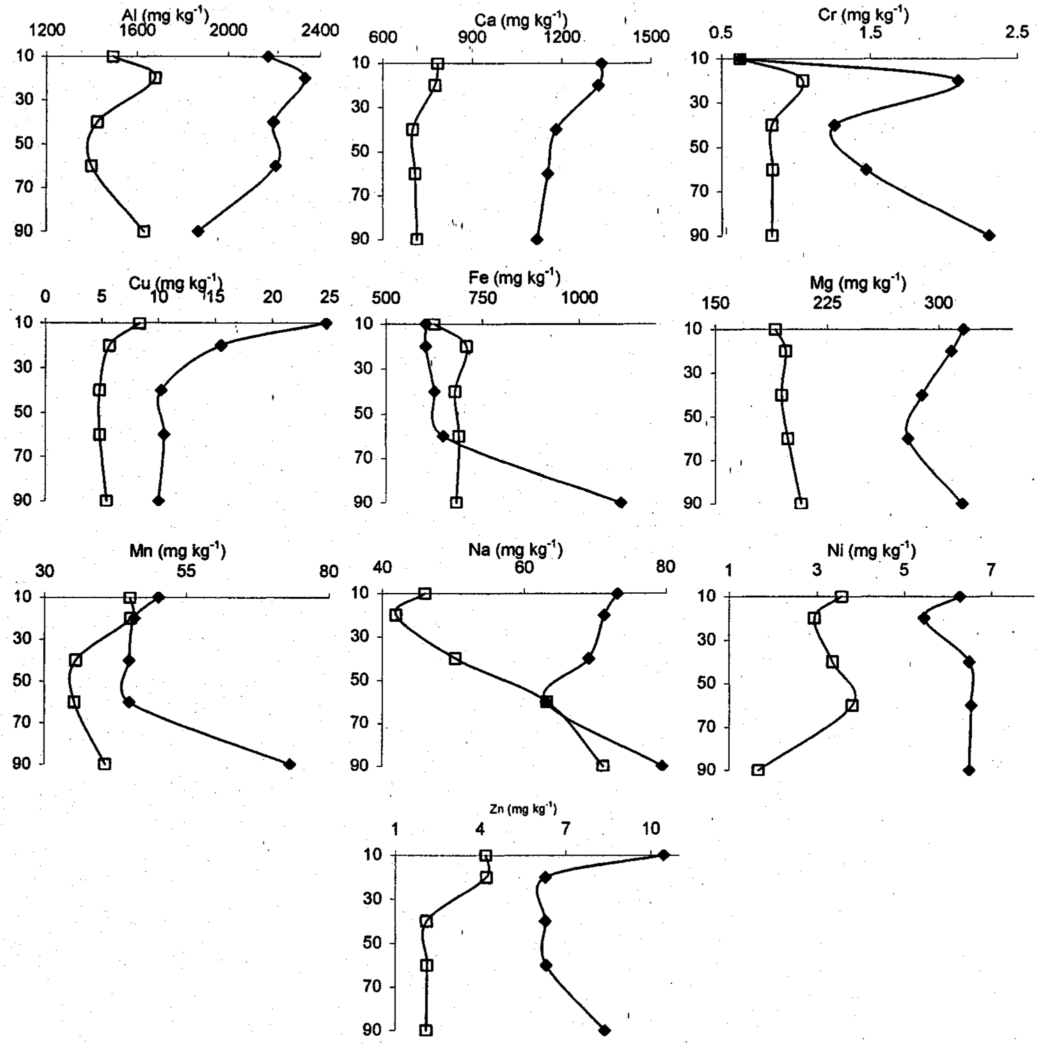


Figure 5.7: Comparison c —◆— 2004 —□— 2003 ulation of Heavy metals in Soil for 2003 and 2004 years under the flow rate of 0.19 m^3 m^{-2} d^{-1}

of wastewater at the highest rate of 0.31 m^3 m^2 d^{-1} (in 2003) showed annual loading of 0.5%, 1.7%, 6.6%, 1.8% and 23% of USEPA limits for Cd, Cu, Ni, Pb and Zn, respectively, in the soil. According to Canadian guidelines (AAFC, 1999), the annual loading rate of these heavy metals are very low, and hence, annually 7.4%, 18.2%, 38.4%, 6.4%, and 19.6% of Cd, Cu, Ni, Pb and Zn, respectively were accumulated in the soil with the wastewater application at 0.31 m^3 m^2 d^{-1} flow rate (in 2003). Thus, the time to reach the maximum permissible limit (MPLP) for these heavy metals in the soil were estimated. As expected, the estimated times

Table 5.6: Heavy metal concentrations in soil: Initial and after wastewater application under different rates

Metal	Initial concentration in soil (mg kg^{-1})	Final concentrations (mg kg^{-1}) in soil under different flow rates (m^3 m^{-2} d^{-1})							
		2003				2004			
		0.06	0.19	0.31	0.19 (bare)	0.06	0.19	0.31	0.19 (bare)
Al	83.47	190.11 [128]	321.32 [285]	239.72 [187]	326.34 [291]	237.17 [25]	453.77 [41]	304.74 [27]	347.87 [7]
Ca	80.31	169.31 [111]	154.90 [93]	160.66 [100]	155.49 [94]	213.18 [26]	257.29 [66]	221.17 [38]	205.91 [32]
Cr	0.13	0.20 [60]	0.17 [40]	0.17 [33]	0.49 [289]	0.29 [44]	0.32 [85]	0.32 [89]	0.23 [-52]
Cu	0.90	1.32 [47]	1.23 [37]	1.15 [29]	0.21 [-76]	2.47 [87]	2.99 [144]	2.78 [141]	2.60 [1130]
Fe	30.52	139.52 [357]	142.43 [367]	142.67 [367]	0.83 [-97]	140.30 [1]	151.02 [6]	146.13 [2]	117.61 [13973]
Mg	31.28	45.63 [46]	41.60 [33]	47.49 [52]	137.32 [339]	53.97 [18]	63.51 [53]	56.58 [19]	50.88 [-62]
Mn	2.52	4.25 [68]	8.51 [238]	5.78 [129]	40.89 [1522]	4.59 [8]	10.92 [28]	6.39 [11]	7.34 [-82]
Na	15.80	18.20 [15]	11.48 [-27]	30.00 [90]	8.68 [-45]	18.49 [2]	14.99 [31]	30.82 [3]	11.19 [28]
Ni	0.53	0.77 [45]	0.64 [22]	1.10 [109]	11.09 [2007]	0.85 [12]	1.31 [104]	1.80 [64]	0.90 [-91]
Zn	0.40	0.77 [94]	0.62 [55]	1.05 [166]	0.26 [-34]	1.32 [71]	1.58 [157]	1.76 67]	1.26 [389]

Percentage increase in heavy metal accumulations in the soil in each year are given in brackets

Table 5.7: Time to Reach Maximum Permissible Limit of Pollutants (MPLP) for Heavy metals in Soil Irrigated with Secondarily Treated Wastewater

Element	Flow rate (m^3 m^2 d^{-1})	Annual Input (kg ha^{-1})	Max. Pollution loading (kg ha^{-1})[a]		Time to reach MPLP (yrs)	
			United States[b]	Canada[c]	United States	Canada
Cd	0.06	0.04 [0.07]	39	2.6	1019 [584]	68 [39]
	0.19	0.11 [0.2]	39	2.6	340 [195]	23 [13]
	0.31	0.19 [0.33]	39	2.6	204 [117]	14 [8]
Cu	0.06	5.1 [3.89]	1500	140	294 [387]	27 [36]
	0.19	15.31 [11.61]	1500	140	98 [129]	9 [12]
	0.31	25.51 [19.36]	1500	140	59 [77]	5 [7]
Ni	0.06	5.53 [3.41]	420	72	76 [123]	13 [21]
	0.19	16.58 [10.24]	420	72	25 [41]	4 [7]
	0.31	27.64 [17.06]	420	72	15 [25]	3 [4]
Pb	0.06	1.11 [0.85]	300	86	271 [351]	78 [101]
	0.19	3.32 [2.56]	300	86	90 [117]	26 [34]
	0.32	5.53 [4.27]	300	86	54 [70]	16 [20]
Zn	0.06	12.76 [16.18]	2800	326	219 [173]	26 [20]
	0.19	38.27 [48.54]	2800	326	73 [58]	9 [7]
	0.31	63.78 [80.89]	2800	326	44 [35]	5 [4]

[a]Chang et al., 2002; [b]U.S. Environmental Protection Agency 1995; [c]Page et al., 1988; Meijer, 1989; and McGrath et al., 1994; Numbers in bracket are the results for 2004

to reach MPLP of heavy metals' level were decreased with an increase in application rate. Thus, the time to reach the MPLP levels for different heavy metals in the soil increased 5, 3 and 1.7 times while comparing the flow rates of 0.06 with 0.31, 0.06 with 0.19, and 0.19 with 0.06 m^3 m^2 d^{-1}, respectively (2003). The observed decreases in time to reach MPLP with increases in the wastewater application rate necessitate regulating the water application rate to a filter area based on its soil properties. In 2003, the time to reach MPLP for Cd with an influent concentration of 0.29 x 10^{-3} mg L^{-1} and annual input of 0.04 ka ha^{-1}, was estimated to be 1019 years. A similar study with the same annual input, and 0.006 mg L^{-1} of influent concentration reported 975 years to reach MPLP, while applied to 4.5 ha of land (Smith et al., 1996(b)).

The results of time to reach MPLP obtained with 2004 data are also similar to those obtained with 2003 data (Table 5.7). The increase or decrease in time to reach MPLP depends on the corresponding heavy metal concentration in the influent and the flow rates (Table 5.6). Since the heavy metal concentrations of the influent used in 2003 and 2004 were relatively low, the time to reach MPLP levels of these heavy metals in the soil are too long (Table 5.7). However, irrespective of low concentrations of heavy metal in the influent of 2004, compared to that of 2003, wastewater application continuously increased their levels in the soil (Table 5.6; Fig. 5.7). Hence, several physio-bio-chemical changes could take place in the soil over time with wastewater application, and thus the soil binding capacity may change. Therefore, the MPLP estimation, based on the results obtained from a short period study, may differ from long-term wastewater application.

Generally, the soil binding sites are more diverse in their ability to bind heavy metals. The weakly bonded heavy metals could leave their sites to accommodate the new entry of strongly bonding heavy metals. In addition, during the rainy season, the weakly bonded heavy metals may be re-mobilized easily. However, the levels of heavy metals in the flooded water may also contain both agricultural and polluted waters from industries. Therefore, the estimated time to reach MPL of these heavy metals might be low or high, and hence, a factor of safety must be applied to the estimated times to obtain a more reliable and practical estimate.

5.4 CONCLUSIONS

The results of heavy metals levels in the effluents and soil-filter used in the field lysimeters, simulating a floodplain-soil, to further treat the secondarily treated municipal wastewater, demonstrated that the heavy metal quantities in the effluents and SAR values of the soil-solutions under different application rates decreased, as compared to their initial levels. The water quality was improved with decreased quantities of As, Cd, Cr, Cu, Ni, Pb, and Zn in the effluent after filtration. The soil accumulated most of the heavy metals present in the wastewater. Heavy metal accumulation in the soil continued in the second year (2004), irrespective of low or similar levels of heavy metals in the influent. Although there were no significant differences in heavy metal accumulation in the soil under different flow rates, relatively low levels were observed with the intermediate flow rate of 0.19 m^3 m^{-2} d^{-1}. There were no significant vegetative effects on heavy metal accumulation. As heavy metal and organic matter inputs to soil are greater with increases in the wastewater application, associated time to reach MPLP levels for heavy metals decreased. Even though the estimated times taken to reach MPLP for the heavy metals in the soil are long, according to this study, the physio-bio-chemical properties of the soil may change over time with prolonged wastewater application. Hence, heavy metal burden in the soil may increase, and thereby decrease the time to reach MPLP levels. It would be expeditious to monitor the long-term changes in bioavailability of heavy metals within the soil-wastewater environment.

PREFACE TO CHAPTER VI

Land application of wastewater often deteriorates the quality of surface and ground water with the pollutants it bears, particularly nitrate which readily leaches through the soil. Therefore, better management options for wastewater land application must be explored in order to reduce the risks of nitrate pollution. Field studies on the fate and transport of nitrogen in the soil-water system are labor intensive, time consuming and expensive, and the results are site-and problem-specific. However, mathematical modeling can be used as an alternative tool to simulate the fate and transport of nitrogen through soil under different wastewater land application strategies, to explore the best or safest management option for such an application, and consequently to reduce nitrate pollution.

In this study, the nutrient version of the LEACHM model (LEACHN) was used to simulate nitrate leaching through soil under different wastewater application scenarios such as: different wastewater application rates, varying wastewater N-concentrations (low, medium, and high), and varying application patterns (continuous versus intermittent). This will allow a more accurate assessment of various wastewater land-application strategies.

Research paper based on the chapter:

Kunjikutty, S.P. and S.O. Prasher. 2005. Simulation of nitrogen transport in soil under municipal wastewater application using LEACHN (under preparation).

CHAPTER-VI

SIMULATION OF NITROGEN TRANSPORT IN SOIL UNDER MUNICIPAL WASTEWATER APPLICATION USING LEACHN

ABSTRACT

To reduce the risk of surface and groundwater pollution from nitrate, and in so doing improve the quality of receiving waters, better management options for land application of wastewater must be explored. Modeling can be done to simulate nitrogen transport through the soil under different wastewater application scenarios. The LEACHN model was calibrated with two years (2003 and 2004) of data from sand-filled, field lysimeters receiving wastewater at rates of 0.31, 0.19, and 0.06 $m^3 m^{-2} d^{-1}$. A well-calibrated LEACHN, successfully validated with five different data sets, was used to assess alternative wastewater land application scenarios: applications of low, medium, or high N-concentration wastewaters, at different rates (0.06, 0.19, 0.31, or 0.6 $m^3 m^{-2} d^{-1}$), under continuous or intermittent application.

In the simulations, the NO_3^--N levels decreased in the leachate with increases in wastewater application rates, due to enhanced denitrification in the upper anoxic zone of the soil generated under high flow rates. Under continuous application, NO_3^--N levels in the leachate increased with increasing wastewater N-levels. With low N-concentrated wastewater, under all tested flow rates, the NO_3^--N levels in the leachate were below the permissible limit. Therefore, even in tropical, sub-tropical or humid areas, wastewater with low-N concentrations may be continuously applied to soil at all tested flow rates, with minimal nitrate pollution problems. The simulation with intermittent application of low, medium, and high N-concentrated wastewater at different rates showed a 51~89% greater reduction in NO_3^--N levels in the leachate, than under continuous application, under all tested wastewater N-levels and flow rates. In addition, the levels of NO_3^--N in their leachate were below the permissible limit. Therefore, wastewater with high levels of nitrogenous compounds could be treated through an intermittent application to land.

6.1 INTRODUCTION

Land application of wastewater is a low cost, technologically and environmentally favorable technique to treat wastewater. However, the initial cost to build wetlands (the most common type of land treatment), the necessary energy inputs, and the availability of land with permeable soil for filtration proscribes their exploitation in many countries. Given the large number of rivers and streams in most south-Asian developing countries and the highly seasonal rainfall patterns occurring there, wide floodplains, predominantly made up of permeable alluvial materials, are available and only inundated during the short rainy season. These lands usually remain uncultivated, weedy or bare during the greater part of the year, and hence can effectively be used as a soil filter medium for wastewater treatment with no additional cost. However, if the application of wastewater to floodplain or land is not carefully managed, it can potentially cause surface and groundwater pollution with pollutants, mainly with nitrate (Barrett et al., 1999; Yang et al., 1999).

Even after primary and/or secondary treatments, wastewater contains large amounts of nutrients and other pollutants. Several studies have reported the discharge of untreated and/or partially treated municipal and industrial wastewaters into the water bodies as one of the main causes of nitrate pollution of waterways (Zhang and Jorgensen, 2005; Chowdary et al., 2004; Kanwar et al., 1985). Therefore, pollutants from the land receiving treated and/or untreated wastewater, could leach through the soil, and hence deteriorate the surface and ground water quality. Although, there are many pollutants in the wastewater, in many countries (e.g. Mexico), surface and groundwater contamination with nitrate is reported as one of the major concerns (Siebe and Fischer, 1996; Mahmood, 2005). For example, the nitrate (NO_3^-) and ammonium (NH_4^+) concentrations of the ground water in a wastewater-irrigated area in Haroonabad (Pakistan) were 68 and 19 mg L^{-1}, respectively, which are quite high compared to the World Health Organization (WHO) standards of 50 and 1.5 mg L^{-1}, respectively (Jeron et al., 2002).

It is well known that untreated or partially treated wastewater often contains more ammonium (NH_4^+) than any other forms of nitrogen in its organic matter. Due to its low replaceability, instead of getting adsorbed onto soil particles, it undergoes nitrification along with organic matter and is converted to NO_3^-, an easily leachable form of nitrogen in the soil, which can readily leach into groundwater. Thus, the abundant organic matter in the wastewater gets mineralized to NH_4^+ and NO_3^-, and thus increasing the soil-nitrogen content and leaching of NO_3^- to surface and ground waters. Therefore, there is a need to explore and develop better and safer management options for wastewater land application to minimize the risk of nitrate pollution of surface and ground water.

The nitrogenous organic matter in the wastewater undergoes different complex processes such as decomposition, nitrification, denitrification, micelle fixation to soil particles, NO_3^- leaching and volatilization in the soil-water system. These processes are very complex in nature, and hence, difficult to fully understand by conducting field experiments. Although wastewater land-application studies have been undertaken in the past, few of these studies have only focused on floodplain filtration of wastewater. Field experiments to examine these processes in a native soil would be quite labor-intensive, time-consuming, and expensive. Moreover, the results thus obtained would be highly site and problem specific. Therefore, computer modeling represents an excellent alternative tool to simulate the fate and transport of nitrogen through the soil, and even allow the exploration of a number of alternative wastewater application scenarios. These include: application at different flow rates, wastewater N-concentrations (e.g. low, medium, and high), and application patterns (e.g. continuous vs. intermittent).

Several mathematical models are available to simulate the fate and transport of nitrogen in soils (Tsuji et al., 1994; Shaffer et al., 1991(a)); Wagnet and Hutson, 1989). Indeed, according to Donald and Alker (2004), there are nearly 20 such models available. Most of these models are based on field study results, and can be applied to simulate the fate of N in the crop root-zone depth (Hansen et al., 1994). However, some of these models can predict NO_3^--N leaching beyond the root zone, by taking into account the soil, climate, management practices, vegetation and soil-water interaction characteristics (e.g. CREAMS: Knisel, 1980; GLEAMS: Leonard, 1987; NTRM: Shaffer and Larsen, 1987; LEACHN: Wagenet and Hutson, 1989; SOILN: Jansson et al., 1991, Bergstrom and Jarvis, 1991; CREAMS-NT: Deizman and Mostanhimi, 1991; NLEAP: Shaffer et al., 1991(b); CENTURY: Metherell et al., 1993; ManureN: Sri Ranjan et al., 1995; MANIMEA: Hengnirun, 1996; and DAINMOD-N, Brevé et al. 1997). Most of these soil-N models deal with sludge and sewage application to land or constructed wetlands, but do not examine the fate and transport of nitrogen in a floodplain filtration system, a promising new technique for municipal wastewater treatment, especially in areas with highly seasonal rainfall patterns and wide floodplains.

CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) is a model developed by the Agricultural Research Service of the U.S. Department of Agriculture (USDA-ARS; Knisel, 1980). It can be used to estimate field-scale nutrient, pesticide, and soil losses. Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) is a field-scale simulation model, developed as an extension to the CREAMS model. It assumes a field with homogeneous land use, soil and precipitation. It was developed to evaluate the impact of management practices on pesticide and nutrient leaching within, through, and below the root zone, but was not developed as an absolute predictor of pollutant loadings (Leonard et al., 1987).

Leaching Estimation and CHemistry Model (LEACHM) developed by Wagnet and Hutson (1987), is a deterministic model, which describes water and solute movement, transpiration, plant uptake, and chemical reactions in unsaturated soil zones. This model has four different modules: LEACHW for water only, LEACHN for nutrients, LEACHP for pesticides, and LEACHC for chemicals. The LEACHN model simulates NO_3^--N movement based on chemical, physical, and biological processes in the soil-water-plant system. It can be used to simulate nitrification, denitrification, ammonia volatilization, and plant uptake of fertilizers. The SOILN model was designed to simulate transport and transformations of nitrogen in the soils, and its uptake by plants. It uses some of the SOIL model output as its input (Ekerston et al., 1994). Many modules of this model, describing mineralization, nitrification, and denitrification processes in the soil are similar to those of LEACHN (Jansson et al., 1991), and both these models consider homogeneous, multi-layer soil profiles. However, the SOILN model requires more than 140 input parameters, and hence, it is very difficult to use this model to predict NO_3^--N leaching through the soil. The CREAMS-NT model is a modified version of the CREAMS model, developed to simulate nitrogen transformations and transport following land application of organic waste (Deizman and Mostaghimi, 1991). The Nitrate Leaching and Economic Analysis Package (NLEAP) is a field-scale model developed to determine the potential NO_3^- leaching associated with agricultural practices [Shaffer et al., 1991(b)]. The CENTURY model is used to simulate long-term dynamics of carbon, nitrogen, phosphorus, and sulfur for different soil-plant systems (Metherall et al., 1993). The ManureN model was developed to simulate crop production and irrigation management practices under various manure application strategies (Sri Ranjan et al., 1995). It includes a simulation of ammonia volatilization, mineralization, nitrate leaching, and nitrogen uptake by plants.

MAnurial NItrogen Management: Environmental Aspects (MANIMEA) is a one-dimensional, dynamic model which simulates nitrogen transformations such as volatilization, mineralization-immobilization, and denitrification, nitrogen transport through runoff and leaching, plant uptake, and adsorption, in a homogeneous, unsaturated soil (Hengnirun, 1996). The DRAINMOD-N is a quasi two-dimensional flow model, which simulates movement and fate of N in the shallow water table, and is developed mainly for artificially drained soils (Breve et al., 1997). Among all these models, NLEAP, CENTURY, and LEACHN were developed for use at the farm and regional level, rather than point or field-level applications (Wylie et al., 1994; Bleecker et al., 1990; Burke et al., 1989).

The water and chemical kinetics used in LEACHN make it more straightforward to use in field-level studies. It requires a smaller input parameter set, and can estimate the critical hydraulic properties that affect chemical transport in the soil, rather than using values derived from established relationships, thus increasing its predictive accuracy. Therefore, LEACHN appears to be a more robust and simple model. Moreover, among the above-described models, it has one of the best described N-simulation algorithms (Alan et al., 1999; Donald and Alker, 2004), and has been tested in many regions of the world (Jemison et al., 1994; Ramos and Carbonell, 1991). Consequently, the LEACHN model was selected in this study to simulate the fate and transport of nitrogen compounds in lands receiving wastewater, and to explore various wastewater land-application management scenarios, in order to select best management strategy for reducing N.

After establishing LEACHN's suitability for nitrogen fate and transport in a floodplain filtration system, it was used to explore better management strategies to more safely apply wastewater to land, so as to minimize nitrate pollution to surface and ground waters. It also sought to simulate NO_3^--N concentrations in the leachate for different wastewater land-application management scenarios: different application rates and influent concentrations, and continuous versus intermittent application patterns.

6.2 MATERIALS AND METHODS

LEACHN is a deterministic model, which simulates chemical, physical, and biological processes that influence the fate and transport of nitrogen compounds in transient/steady/interrupted flow conditions in soil. It can be applied to both laboratory and field situations (John, 2003). The model runs in daily time steps, and requires input data such as simulation time, water flow conditions, physical and chemical properties of soil, crop and cultivation details, nitrogen transformation rate constants, fertilizer applications, and rain or irrigation details.

Water flow in the model can be described in one of three ways: (i) Richards' equation, (ii) Addiscott's tipping bucket, or (iii) by steady state conditions. The lower boundary of the soil profile can be fixed to a known (i) water table depth, (ii) free drainage, (iii) zero flux or (iv) as lysimeter. The soil profile is divided into segments, and hence, the model requires segment-wise particle size distribution, initial soil water content, water retention parameters, bulk density, initial C and N concentrations, saturated hydraulic conductivity, and dispersivity. Other soil properties, such as particle density and organic matter content, are also required. All the parameters, except water retention parameters and dispersivity, were measured in the field and in laboratory experiments (Table 6.1). A utility-model, "RETFIT," which comes with the LEACHN model, was used to predict best-fit water retention parameters for Campbell's (1974) water retention function (Table 6.1). A dispersivity of 20 mm was chosen, based on recommendations from previous studies (Paramasivam et al., 2002; Barbara, 2000).

The model also requires chemical properties of nitrogen and carbon forms, depth-wise nitrification and denitrification rate constants, depths to water table, and weekly climatic details, such as evapotranspiration, mean temperature and amplitude. Chemical properties of nitrogen and carbon forms and mineralization rate constants (nitrification and denitrification) were taken from other published studies (Table 6.2; Paramasivam et al., 2002; Van Alphien, and Stoorvogel, 2000; Roy et al., 2000; Barbara, 2000; Unlu and Yurteri, 1999; Pennel et al., 1990; Lamb, 1996; Graham and Wheaton, 1999; Lamb et al., 1999; Pramasivam et al., 2000, Alan et al., 1999).

Table 6.1 Model parameters for the entire soil profile depth

Model parameter	Value
Soil and water flow properties	
Steady-state flow water content (volume fraction m^3m^{-3})	0.3
Clay (%)	2
Silt (%)	2
Organic carbon (%)	0.03
Starting soil moisture, θ	0.3
Particle density (Mg m^{-3})	2.65
Organic matter (%)	0.05
Soil bulk density (Mg m^{-3})	1.78
Air entry value (kPa)	-10
Exponent in Campbell's water retention equation (BCAM)	5.44
Hydraulic conductivity (m d^{-1})	15
Pore interaction parameter (P) in Campbell's conductivity equation	2.01
Dispersivity (mm)	20
Chemical properties	
K_d-Urea-N (L kg^{-1})	0
K_d-NH_4^+-N (L kg^{-1})	3.7
K_d-NO_3^--N (L kg^{-1})	0
Diffusion	
Molecular diffusion coefficient	120
Nitrogen transformations	
Synthesis efficiency factor	0.5
Humification fraction	0.2
C/N ratio: biomass and humus	10
Ammonia volatilization from the surface ($days^{-1}$)	0
Denitrification half-saturation constant (mg L^{-1})	10
Limiting NO_3^-/NH_4^+ ratio in solution for nitrification	8

Table 6.2 Nitrogen pools and mineralization rate constants for different soil depths

Soil layer (m)	Model parameter	Value
Mineralization rate constants		
	$NH_4^+ \rightarrow NO_3^-$ (d^{-1})	$NO_3^- \rightarrow N$ (d^{-1})
0.0-0.1	0.6	0.1
0.1-0.2	0.4	0.1
0.2-0.4	0.3	0.1
0.4-0.6	0.4	0.1
0.6-0.9	0.3	0.1
Nitrogen pools		
	$NH_4^+ \rightarrow NO_3^-$ (mg N kg^{-1} dwb)	$NO_3^- \rightarrow N$ (mg N kg^{-1} dwb)
0.0-0.05	0.30	0.350
0.05-0.3	0.187	0.261
0.3-0.5	0.183	0.146
0.5-0.8	0.283	0.214
0.8-0.9	0.29	0.19

dwb: dry weight basis

6.2.1 Data collection

The experiment was carried out in field lysimeters at the Macdonald Campus of McGill University (Ste. Anne-de-Bellevue, QC) during the summer months of 2003 and 2004 (July-September). Each lysimeter was constructed of a PVC pipe (0.45 m I.D. × 1.0 m height) and equipped at the bottom with a 50 mm drain pipe. Rhizospheric ceramic probes were installed at 0.1, 0.2, 0.4, and 0.6 m depths from the soil surface. The lysimeters were filled with sand (95:2:2 sand:silt:clay; O.M. 0.5%) and sheltered with a rain cover to prevent the entry of rain water. The lysimeters were packed with soil to a bulk density of 1.7 Mg m^{-3}. The porosity, saturated hydraulic conductivity and initial levels of N, P and K contents of the soil, prior to the experiment, were 0.33 m^3 m^{-3}, 15.0 m d^{-1}, 52.0 mg kg^{-1}, 14.4 mg kg^{-1}, and 92.0 mg kg^{-1}, respectively. Secondarily treated municipal wastewater, obtained daily from the Vaudreuil (in 2003) and Pincourt (in 2004) wastewater treatment plants, was used as the influent. Wastewater was applied to the lysimeters at flow rates of 0.31, 0.19, and 0.06 m^3 m^{-2} d^{-1}, and replicated three times.

Each day, overhead tanks were filled with the appropriate volumes of wastewater. Drippers, connected to the end of the pipe and fixed to the overhead tanks, regulated the water flow to the lysimeters. The number of drippers controlled the flow to each lysimeter ($0.06\,m^3\,m^{-2}\,d^{-1}$ dripper^{-1}). As the flow conditions were unsaturated under all three flow rates, a vacuum pump was used to collect water samples through the probes (0.1, 0.2, 0.4, and 0.6 m). During the wastewater application, water samples were taken weekly from the probes (0.1, 0.2, 0.4, and 0.6 m) and the effluent (0.9 m); the influent samples were collected daily.

Water samples were analyzed for NO_3^--N according to standard analytical methods with a flow injection type Lachat Instrument (QuickChem Method; APHA, 1998). The analysis was done immediately after sample collection, whenever possible. Otherwise, the samples were refrigerated at 4°C until they were analyzed.

6.2.2 Model development and performance analysis

The 0.9 m soil column was divided into 90 segments, each with an equal segment thickness of 10 mm. Particle density, organic matter content, carbon and nitrogen concentrations of the soil, segment-wise particle size distribution, water retention parameters, bulk density, saturated hydraulic conductivity, dispersivity, and initial soil water content were provided in the model input file. Since the experiment was done in field lysimeters under steady state water flow conditions, the lower boundary was set to the depth of the lysimeter and water flow conditions were deemed steady state. Chemical properties of nitrogen and carbon forms and mineralization rate constants, taken from other similar studies, were used to calibrate the model by varying their values within a reasonable range (Table 6.2). Climatic data, such as weekly evapotranspiration, depths to water table, as well as annual mean temperature and amplitude, were also provided. Daily wastewater application volumes and their NO_3^--N and NH_4^+-N concentrations were provided as irrigation data.

Two years of experimental data, obtained from three different wastewater application rates (0.31, 0.19 and $0.06\,m^3\,m^{-2}\,d^{-1}$), were used in modeling. The data set for the $0.31\,m^3\,m^{-2}\,d^{-1}$ flow rate (2004) was used for model calibration, while the other five data sets (flow rates of 0.06 and $0.19\,m^3\,m^{-2}\,d^{-1}$ in 2004 and 0.06, 0.19, and $0.31\,m^3\,m^{-2}\,d^{-1}$ in 2003) were used for model validation. The statistical indices, i.e., correlation coefficient (r), root mean square error (RMSE), relative root mean square error (RRMSE), modeling efficiency, regression parameters and plots of measured versus predicted results (proposed by Addiscott and Whitmore, 1987; Loague and Green, 1991), were used to evaluate model performance. An example of the main input data file used in the LEACHN model is given in Appendix 1.

6.2.3 Simulation of different wastewater application scenarios

Once validated, the LEACHN model was used to simulate different management scenarios of land application of wastewater, with particular emphasis on the leaching of nitrogenous compounds. Due to differences in the level of treatment, density of population and industries, N concentrations in wastewater will vary in different parts of the world. Hence, the model was simulated under application of wastewater with low, medium, and high N levels.

From the viewpoint of wastewater management, one hopes to treat a maximum volume of wastewater with the available land area, and so, in all scenarios, the model was simulated under different flow rates. The hydraulic conductivity of the sand filter used in this study was high enough to accommodate wastewater application rates up to 9.6 $m^3 m^{-2} d^{-1}$ without flooding. For all scenarios, flow rates of 0.06, 0.19, 0.31, and 0.6 $m^3 m^{-2} d^{-1}$ were used in the NO_3^--N simulation study. As the model was calibrated with the data from a field lysimeter study, carried out under steady state water flow conditions, similar flow conditions were considered for simulations. Due to the few months of snowfall in humid and sub-tropical countries, and rainfall in tropical countries, all the scenario simulations were done for a period of 10-months a year.

In more developed countries, the level of treatment is high, so a secondary treatment is usually applied to wastewater, thus resulting in lower levels of N in wastewaters. Thus, the first scenario was to simulate nitrate leaching under continuous application of low-N concentration wastewater at different flow rates, with weather conditions similar to humid or sub-tropical countries (e.g. Canada). In the second scenario, with tropical weather conditions, nitrate leaching through soil was simulated under continuous application of low, medium, and high-N concentration wastewaters, at different flow rates. As the simulations were done with medium-N and high-N concentration wastewaters, nitrate concentrations of the leachate might be expected to exceed the permissible levels, at least under the high flow rates. Hence, in the third scenario, low, medium, and high concentration wastewaters were also applied intermittently to land, at different rates. The intermittent pattern of wastewater application was arbitrarily set as 14 days of continuous application, followed by 14 days with no application, and so on. The results of the continuous and intermittent application of low-N, medium-N, and high-N concentration wastewater were used to assess the nitrate reduction in the leachate under intermittent applications.

6.3 RESULTS AND DISCUSSION

6.3.1 Model calibration and validation

In the model calibration, measured depth-wise NO_3^--N concentrations of leachate from the lysimeters, receiving wastewater at 0.31 m^3 m^{-2} d^{-1} flow rate (2004), over time, were compared with those predicted by the model (Fig. 6.1). A linear regression equation was fitted to the data, and the slope and intercept values have calibrated. Ideally, the slope and intercept should be one and zero, respectively, indicating a perfect match between predicted and measured values. However, this is a very strict requirement and rarely met in practice. In this study, the slope of the line was 0.85 and intercept value was 0.88, which although significantly different from their ideal values ($P \leq 0.05$, Table 6.3), were numerically fairly close to their ideal values (Fig. 6.1; Table 6.3). The close similarity between the measured and predicted NO_3^--N content at different soil profile depths over time resulted in a high correlation coefficient (0.97), high modeling efficiency (0.93), low RRMSE (7%), and low RMSE (0.47 mg L^{-1}), demonstrating a very good calibration of the model (Table 6.3; Fig. 6.1).

The calibrated model was then validated with five different data sets (data from the flow rates of 0.19 and 0.06 m^3 m^{-2} d^{-1} in 2004, and with 0.31, 0.19, and 0.06 m^3 m^{-2} d^{-1} flow rates in 2003; Fig. 6.2). The depth-wise nitrogen transformation rate constants and nitrogen pools, determined using model calibration, resulted in very good conformity between the measured and simulated NO_3^--N concentrations at different soil depths for all five validation sets (Fig. 6.2). High correlation coefficients (>0.9 in 2004 and 0.87 in 2003), modeling efficiencies (>0.91 in 2004 and >0.75 in 2003), and close conformity between the measured and predicted NO_3^--N at different soil profile depths pointed to a good validation of the model (Table 6.3; Fig. 6.2). The results also indicated that the validation with the 2004 data

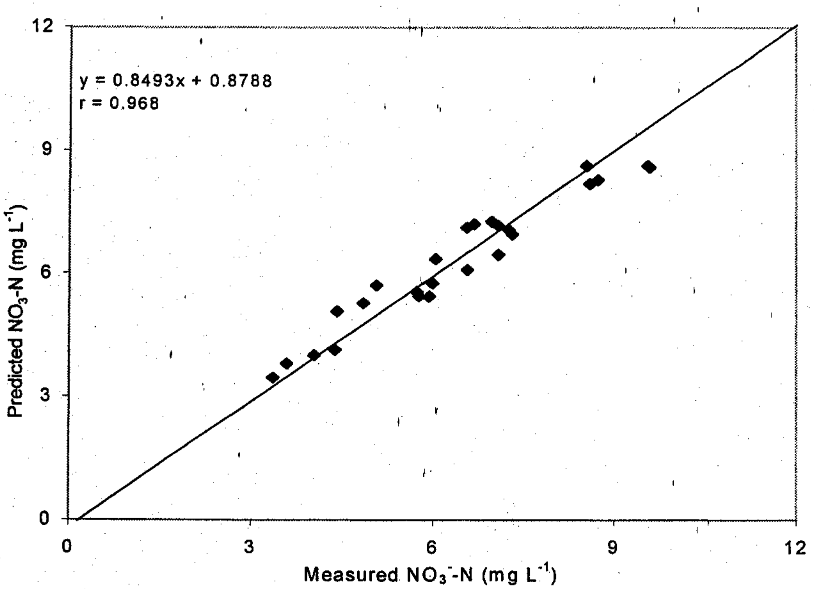


Figure 6.1: Observed and predicted NO_3^--N for calibration of LEACHN

Table 6.3. Statistical indexes for calibration and validation of LEACHN

Data Sets Year - Flow rate (m^3 m^{-2} d^{-1})	r	Slope	Intercept	RRMSE (%)	EF	RMSE (mg L^{-1})
Calibration						
2004 - 0.31	0.97	0.85*	0.88*	7.0	0.93	0.47
Validation						
2004 - 0.19	0.94	0.94	0.55	9.0	0.88	0.56
2004 - 0.06	0.96	0.87*	0.93*	8.0	0.91	0.49
2003 - 0.31	0.90	0.93	0.60	13.0	0.79	1.23
2003 - 0.19	0.87	0.68*	3.11*	20.0	0.75	2.09
2003 - 0.06	0.90	0.82*	1.60*	13.0	0.80	1.43

r: Correlation coefficient; RRMSE: Relative Root Mean Square Error; EF: Efficiency of the model;

RMSE: Relative Mean Square Error; *: Slope and intercept significantly different from 1 and 0, respectively, at 0.05 probability level

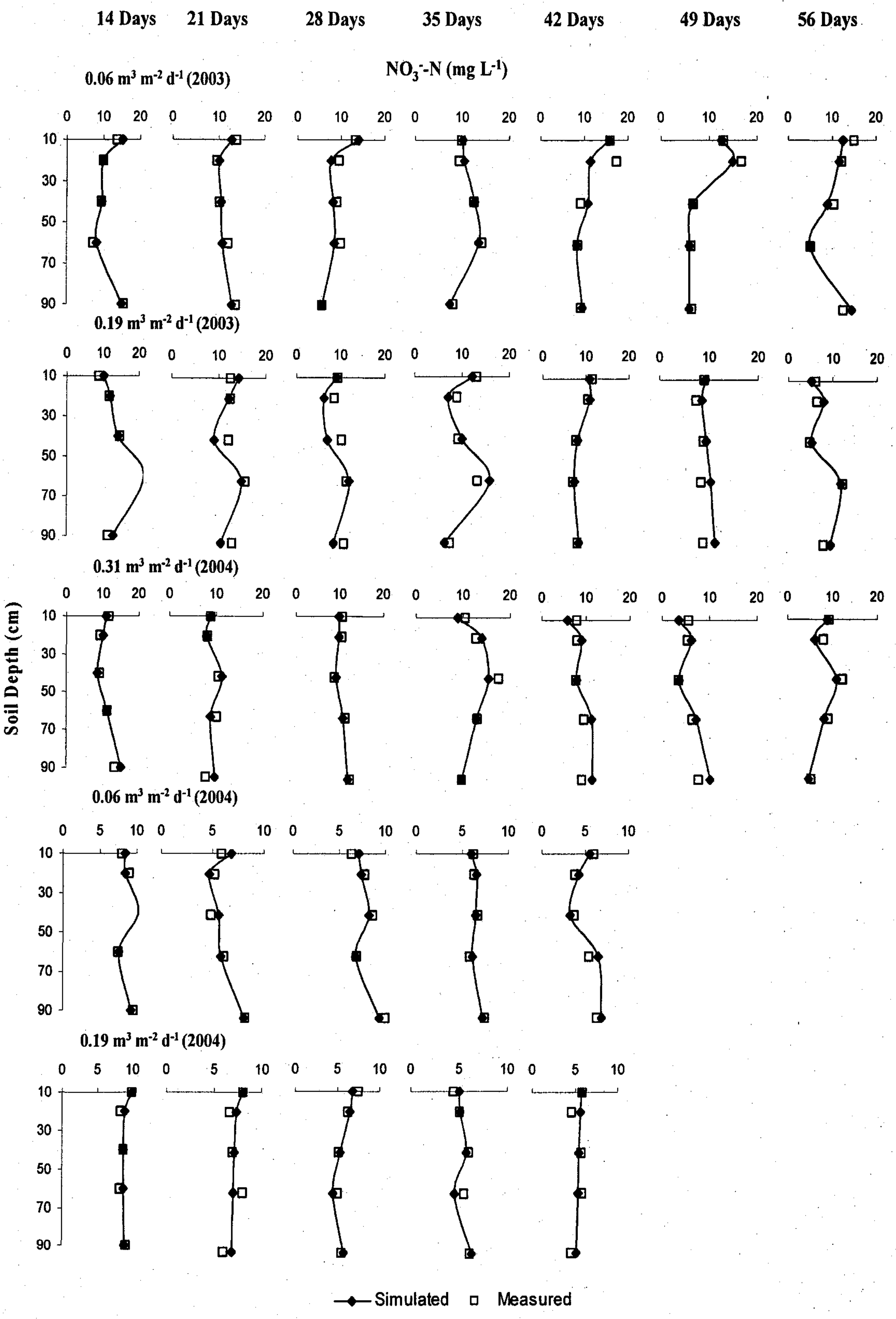


Figure 6.2: Validation results of LEACHN with all five data sets: depth-wise NO_3^--N concentrations over time

sets were relatively superior to those with the 2003 data (Table 6.3; Fig. 6.2). Since the calibration of the model was done with one of the data sets from 2004, the validations with the other data sets of this year were expected to perform slightly better, as compared to that with the 2003 data sets. Nevertheless, the validations with all the five data sets were good (Fig. 6.2; Table 6.3). Therefore, we concluded that LEACHN was able to simulate the fate and transport of nitrogenous compounds in a simulated floodplain filtration lysimeter study in a satisfactory way.

6.3.2 Simulation of different scenarios

The model was run to simulate different scenarios in order to identify appropriate management options for safe disposal of wastewater on land. In the first scenario, the daily NO_3^--N and NH_4^+-N concentrations in the influent applied were 4 and 2.5 mg L^{-1}, respectively (mean concentrations of wastewater used in 2004), and the levels used in the second and third scenarios under continuous and intermittent application of low-N, medium-N, and high-N concentration wastewater were 10 and 0.5, 25 and 2.5, and 42 and 12 mg L^{-1}, respectively and were denoted respectively as LC, MC, and HC. These values represent the range of NH_4^+-N and NO_3^--N concentrations found in the wastewater of many developed and developing countries (Asano and Tchobanoglous, 1987). The simulation results under these scenarios are discussed in the following sections.

6.3.2.1 Continuous application of low concentration wastewater to land at different flow rates under sub-tropical or humid weather conditions

The details of daily wastewater applications for a 10-month period in a year, with low range wastewater-N levels and sub-tropical weather conditions at four different flow rates (0.06, 0.19. 0.31, and 0.6 m^3 m^{-2} m^{-1}), were provided to the model to simulate monthly, depth-wise NO_3^--N in the leachate. Since, the predicted NO_3^--N concentration values at different soil depths were similar after the first few months of continues application under steady state flow condition, its level in the soil in the last month of the simulation period is representative of the effect of different wastewater application rates on NO_3^--N in the leachate. Hence, nitrate levels in the leachate under different wastewater application rates in the last month of the simulation period are shown in figure 6.3.

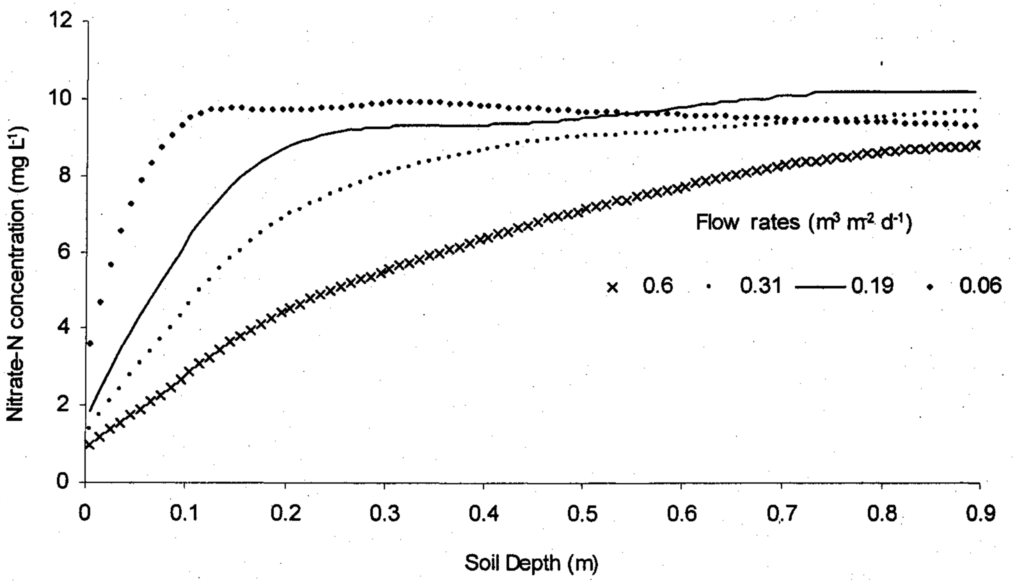


Figure 6.3: Simulated leachate NO_3^--N at different soil depths under continuous application of low-N concentration wastewater at different rates in the last month of the simulation period

Under all tested flow rates, the NO_3^--N concentration rapidly increased at the 0-0.15 m depth due to nitrification of organic and inorganic nitrogen in the influent (Fig. 6.3). The high nitrification rate constant and nitrogen pools (0.6 and >0.3, respectively; Table 6.2) at this depth compared to deeper depths, resulted in high nitrification and further denitrification of this high nitrified organic matter. Comparatively, little nitrification occurred with low nitrification rate constants and the smaller nitrogen pools at the deeper depths (Table 6.2), thus resulting in the slow increase of NO_3^--N at the 0.15-0.7 m depths under all flow rates. The denitrification rate constant (0.1; Table 6.2) was constant throughout the soil depth, hence, the increase or decrease of nitrate levels were based on the depth-wise nitrification rate constants and nitrogen pools. In deeper layers (>0.7 m), the more anoxic conditions and lower levels of carbon sources in the soil-filtered wastewater hindered subsequent denitrification, and thus resulted in almost constant NO_3^--N levels at these depths under all tested flow rates (8~10 mg L^{-1}, Fig. 6.3).

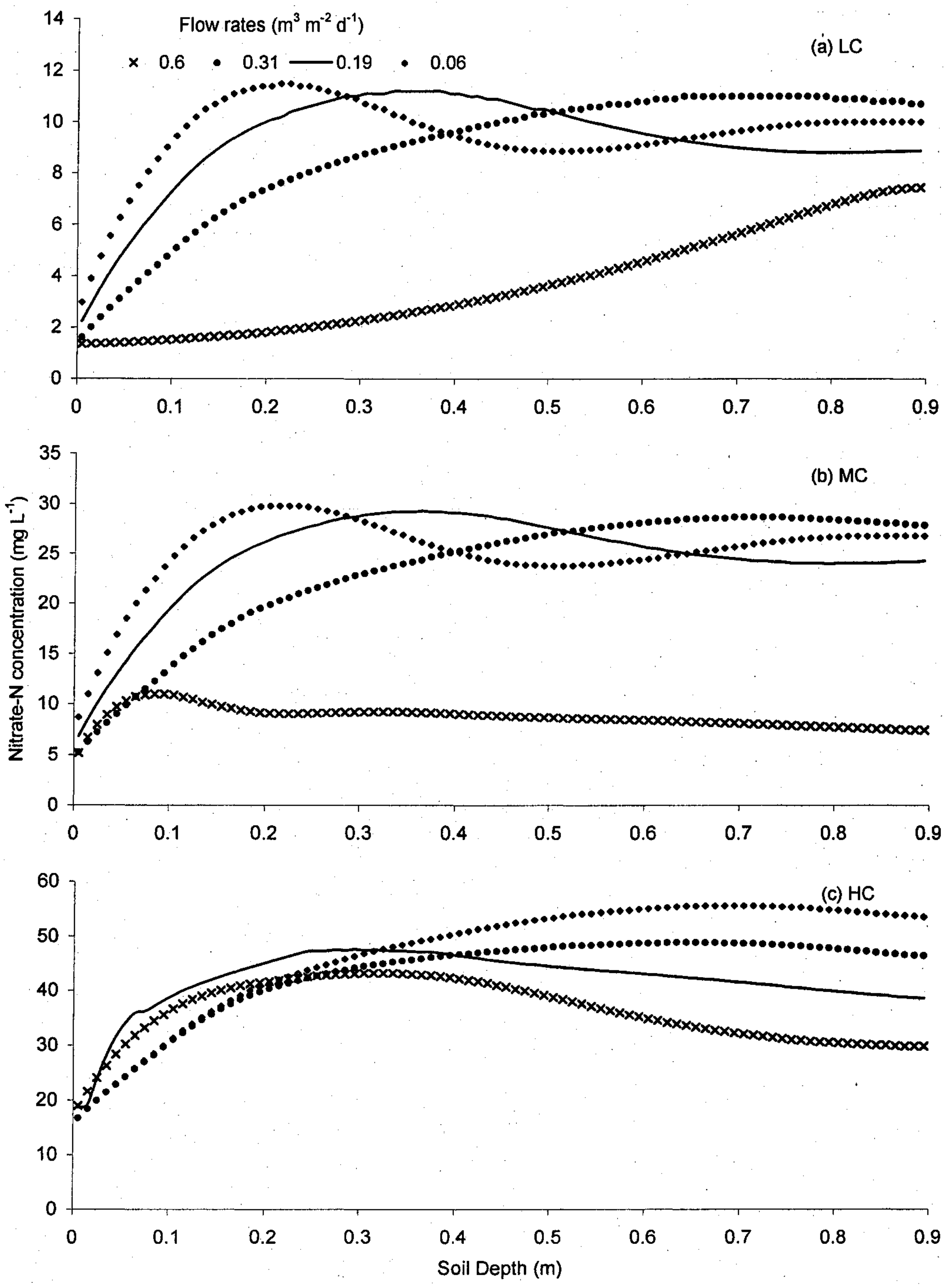
With an increase in flow rate, a greater decrease of NO_3^--N levels was observed in the 0~0.2 m soil layer (Fig. 6.3). This was due to the high rate of nitrification (with high nitrification rate constant and nitrogen pools), and simultaneously enhanced denitrification in the anoxic topsoil zone with high application rates (Table 6.2). However, even at higher flow rates, further nitrification and low denitrification in deeper layers increased NO_3^--N levels. Therefore, although higher flow rates can be used for this soil, NO_3^--N levels in the deeper layers will increase with an increase in application rates. It can be seen from the results that NO_3^--N concentrations in the leachate under all tested flow rates, were below the permissible limit (Fig. 6.3), and so, the low-N concentration wastewater (mostly after secondary treatment) can be applied to land without much nitrate leaching problems.

6.3.2.2 Continuous application of low-N, medium-N, and high-N concentration wastewater to land at different flow rates under tropical weather conditions

Similar to the simulation of nitrate leaching in scenario one, details of wastewater application for a 10-month simulation period in a year, under different rates were used as input to the model. However, the weather conditions were replaced with tropical conditions and the wastewater was tested with low-N, medium-N, and high-N levels. The NO_3^--N and NH_4^+-N concentrations of the wastewater in LC, MC, and HC, respectively, were 10 and 0.5, 25 and 3.5, and 42 and 12 mg L^{-1} [Fig. 6.4 (a), (b), and (c)].

With all ranges of wastewater N-concentrations, under higher flow rates, the NO_3^--N levels in the leachate were less than those observed under low flow rates. This was due to more denitrification at the anoxic top-soil profile associated with higher flow rates [Fig. 6.4 (a), (b), and (c)]. Under all flow rates, the average leachate NO_3^--N levels were less than the permissible limits with low-N concentration wastewater application [Fig. 6.4 (a)]. The mean NO_3^--N levels, observed in the leachate, were 9.5, 9.3, 8.9, and 3.7 mg L^{-1}, under the 0.06, 0.19, 0.31, and 0.6 $m^3 m^{-2} d^{-1}$ flow rates, respectively (maximum levels were respectively, 11.5, 11.2, 11.0, and 6.7 mg L^{-1}; Table 6.4).

Medium-N concentration wastewater applied at the highest flow rate of 0.6 m^3 m^{-2} d^{-1} also resulted in NO_3^--N levels in the leachate less than the permissible limits [mean: 8.7 mg L^{-1}; Fig. 6.4 (b); Table 6.4]. This might also be due to enhanced denitrification occurring at the upper anoxic soil profile, which was associated with the higher flow rate. Under other flow rates (0.06, 0.19, and 0.31 m^3 m^{-2} d^{-1}), the mean NO_3^--N levels in the leachate were 25.3, 24.7, and23.4 mg L^{-1}, respectively [Table 6.4; Fig. 6.4 (b)]. With high-N concentration wastewater application, all the flow rates showed leachate NO_3^--N levels above the permissible limit [Fig. 6.4 (c)]. The mean concentrations were 47.1, 42.0, 43.0, and



(a) LC-Low contracted, (b) MC-Medium concentrated, and (c) HC- High concentrated wastewater application

Figure 6.4: Simulated leachate NO_3^--N at different soil depths under continuous application of low-N, medium-N, and high-N concentration wastewater at different rates in the last month of simulation period

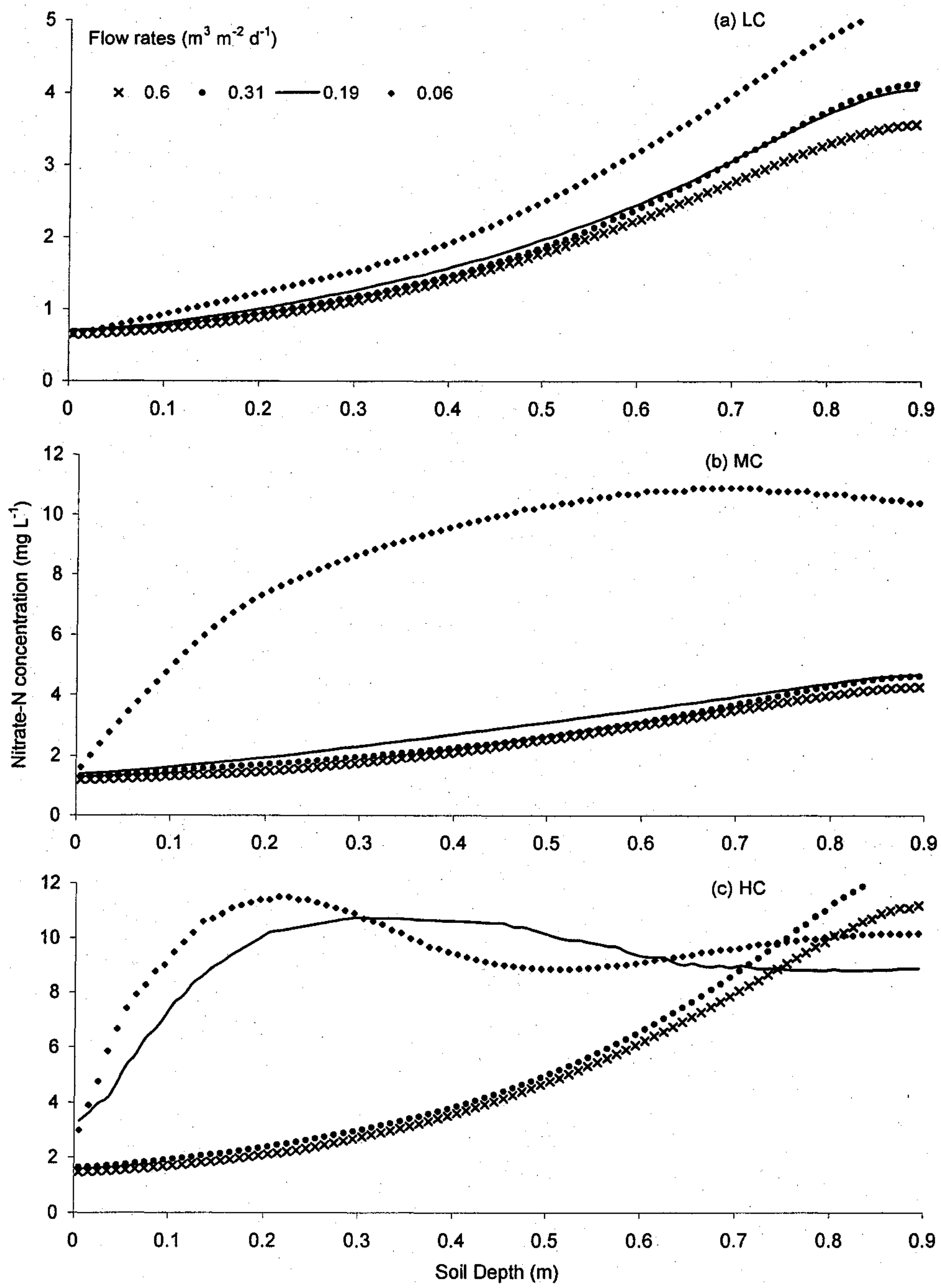
Table 6.4 Comparison of the reduction of leachate NO_3^--N levels under continues and intermittent application of low-N, medium-N, and high N-concentration wastewater

	NO_3^--N levels in the leachate (mg L^{-1})			
Flow rates (m^3 m^{-2} d^{-1})	Continuous application	Intermittent application	Difference	Reduction (%)
Low Conc. (LC)				
0.06	9.52	2.55	6.96	73
0.19	9.25	2.02	7.22	78
0.31	8.91	1.98	6.93	78
0.6	3.72	1.81	1.91	51
Medium Conc. (MC)				
0.06	25.28	8.84	16.44	65
0.19	24.67	2.95	21.72	88
0.31	23.43	2.68	20.75	89
0.6	8.73	2.48	6.25	72
High Conc. (HC)				
0.06	47.08	9.58	37.50	80
0.19	42.00	9.05	32.96	78
0.31	43.04	5.51	37.53	87
0.6	36.22	5.01	31.21	86

36.2 mg L^{-1}, under the 0.06, 0.19, 0.31, and 0.6 m^3 m^{-2} d^{-1} flow rates, respectively [Fig. 6.4 (c); Table 6.4). It can be concluded from the simulation results that, even in tropical countries, the low-N concentration wastewater can be safely applied to land without much nitrate leaching problems; however, the application of medium and high-N concentration wastewater could pose nitrate pollution problems.

6.3.2.3 Intermittent application of low-N, medium-N, and high-N concentration wastewater to land at different flow rates under tropical weather conditions

The previous scenario indicated that high-N concentration wastewater land applications could seriously deteriorate the quality of surface and ground waters. However, by managing the water application strategy and loading, it might be possible to reduce nitrate leaching through the soil. Thus, the model further simulated low-N, medium-N, and high-N concentration wastewater applied in an intermittent pattern (Fig. 6.5). The model simulations were done under all flow rates, as the land availability for wastewater treatment is a crucial factor in most developing countries. In this scenario, the wastewater was applied continuously for



(a) LC-Low contracted, (b) MC-Medium concentrated, and (c) HC- High concentrated wastewater application

Figure 6.5: Simulated leachate NO_3^--N at different soil depths under intermittent application of low-N, medium-N or high-N concentration wastewaters at different rates in the last month of simulation period

14 days, then interrupted for 14 days, then continued for a further 14 days, and so on. This wastewater application procedure was continued for the entire simulation period. Practically, this application pattern can be practiced in most developing countries, where wide floodplains are available for a good part of the year, and intermittent switching of wastewater discharge from one area to another is possible.

Figures 6.4 and 6.5 indicate that with low-N, medium-N or high-N concentration wastewater applications, there were noticeable reductions in NO_3^--N levels in the leachate under all four flow rates. The mean concentrations of NO_3^--N in the leachate under low-N, medium-N or high-N concentration wastewaters were 2.6, 2.0, 2.0, and 1.8 mg L^{-1}, 8.8, 2.9, 2.7, and 2.5 mg L^{-1}, and 9.6, 9.1, 5.5, and 5.0 mg L^{-1}, respectively under the 0.06, 0.19, 0.31, and 0.6 m^3 m^{-2} d^{-1} flow rates (Table 6.4). The comparatively low NO_3^--N levels observed in the leachate with medium-N and high-N concentration wastewater applied at higher flow rates, were due to the high denitrification in the upper soil profile associated with these flow rates, and the same trend was also observed under continuous wastewater application (Table 6.4; Figs. 6.4 and 6.5). Thus, under different wastewater N-concentrations of LC, MC, and HC, NO_3^--N levels in the leachate were significantly reduced ($P \leq 0.05$, t-test), on average, by 70%, 78%, and 83%, respectively. Greater reductions were observed under intermittent application, as compared to those under wastewater application (Figs. 6.4 and 6.5; Table 6.4). Under different wastewater N-concentrations, there were 73%, 82%, 85%, and 70% more nitrate reductions observed under intermittent application at tested flow rates of 0.06, 0.19, 0.31, and 0.6 $m^3 m^{-2}$ d^{-1}, respectively, as compared to those under continuous application (Figs. 6.4 and 6.5; Table 6.4). Thus, NO_3^--N levels in the leachate were significantly reduced when highly concentrated influent wastewater was applied in an intermittent, rather than continuous manner to the land.

6.4 CONCLUSIONS

Inappropriate management practices in land application of wastewater deteriorate surface and ground water quality, mainly by causing nitrate pollution. The LEACHN model was calibrated and validated with five different data sets from a lysimeter experiment, and then used to simulate nitrate leaching through soil under different wastewater application scenarios to explore and develop better and safer wastewater land application strategies.

The simulation of NO_3^--N under continuous application of low N-content wastewater at different application rates showed a decrease in NO_3^--N levels with an increase in flow rates. This occurred because of the high nitrification rate at the top-soil depth, and the further denitrification being enhanced in the anoxic zones created under the high flow rates. The simulation with continuous application of low-N, medium-N, and high-N concentration wastewater, under tropical climatic conditions showed an increase of NO_3^--N levels in the leachate with an increase in the wastewater N-concentrations. Leachate NO_3^--N levels remained below the permissible limit for the low-N concentration wastewater application. Therefore, even in tropical or sub-tropical areas, low-N concentration wastewater can be applied to soil at all tested flow rates, with minimal environmental problems.

However, under most of the flow rates with medium and all tested flow rates with high-N concentration continuous wastewater applications, leachate NO_3^--N levels exceeded the permissible limit. With intermittent application strategy, under all tested wastewater N-concentrations and flow rates, there were 51~89% greater reductions in NO_3^--N levels in the leachate, than those that occurred under continuous wastewater application. Also, under intermittent application, the NO_3^--N levels in the leachate remained below the permissible limit. Therefore, an intermittent land application of wastewater can be practiced in many developing counties, where highly N-concentrated wastewaters are most common, to reduce nitrate leaching problems under wastewater land application.

CHAPTER-VII
SUMMARY AND CONCLUSIONS

7.1 SUMMARY

The main objective of this research study was to evaluate the potential efficiency of a floodplain-soil filter system to improve water quality by removing various contaminants from the wastewater. This study comprised of two parts: a lysimeter study with two different soils, sandy soil (3.5% O.M) and sand (0.5% O.M), and model simulation studies. Lysimeters were used to evaluate the performance of floodplain filtration of secondary treated municipal wastewater applied to vegetated lysimeters at three flow rates (0.31, 0.19 and 0.06 m^3 m^2 d^{-1}), and at a flow rate of 0.19 m^3 m^{-2} d^{-1} to bare lysimeters.

To estimate the efficiency of the proposed floodplain filtration as a biological filter technique in removing contaminants from municipal wastewater, the nutrient version of Leaching Estimation And CHemistry Model (LEACHN) was used to simulate nitrate leaching through the soil. The well calibrated LEACHN model was then used to simulate nitrate leaching through soil under different scenarios: wastewater application rates, low-N, high-N, and medium-N concentration wastewater, and application patterns (continuous and intermittent).

7.2 CONCLUSIONS

7.2.1 Nitrogen and COD removal in land application of wastewater

In 2002, the study with sandy soil was focused on NH_4^+-N, NO_3^--N, and COD removal from the wastewater. This was repeated in the following years (2003 and 2004) with sand-filled lysimeters. In all three years, the effect of vegetation on contaminant removal was evaluated. The initial and final soil nitrogen content and nitrous oxide gas emissions from the soil surface were monitored in the latter years, so a nitrogen mass balance was also done. From this study the following general conclusions were drawn:

1. Across all flow rates, the floodplain-soil filtration respectively, removed 62 to 84%, 96 to 99%, and 6 to 67% of TKN, NH_4^+-N, and COD from wastewater in all the three years (2002-2004).

2. The nitrogen mass balance accounted for 85~98% and 67~96% of input nitrogen during 2003 and 2004, respectively, and the remaining portions were attributed to vegetative effects and volatilization of non-N_2O nitrogenous gases.
3. Compared to bare soil, under the same flow rate of 0.19 m^3 m^2 d^{-1} and in all three years, the vegetated surface was more effective in lowering NH_4^+ N, NO_3^-N, and COD levels in the leachate. Even the under-established vegetation in this study reduced nitrogen leaching through soil and showed 6% (2003) and 60% (2004) vegetative effects on nitrogen transformations and reductions. Hence, a well-established vegetative floodplain filtration system could reduce NO_3^--N levels in the effluent to a greater extent, and thus would considerably reduce groundwater pollution from land application of wastewater.
4. Most NH_4^+-N, NO_3^-N and COD removal occurred in the top 0.1 m of soil. This was perhaps due to the establishment of a better rhizosphere at this depth.
5. The study showed a slight increase of NO_3^--N and TKN levels in the soil and N_2O emissions from the soil surface with an increase in application rates. Hence, wastewater should be applied to land at an appropriate rate, and effluent water quality and N_2O emissions from soil surface should be monitored regularly.

7.2.2 Heavy metal removal by the floodplain soil

In order to assess the feasibility of using floodplain soil as a filtering medium, the experiments done in 2003 and 2004 with sand filled lysimeters also focused on heavy metal removal from wastewater and their retention in soil. Also, times to reach maximum permissible limits of pollutant levels of heavy metals in soil under various wastewater application rates were estimated. The following general conclusions were drawn from this part of the study.

1. Soil filtration improved water quality with decreased heavy metal loads in the effluent. For average of all flow rates, the filtration respectively, decreased the amounts of As, Cd, Cu, Ni, Pb, and Zn in the effluent by 58%, 9%, 3%, 37%, 63%, and 52% (2003), while As, Cd, Cr, Cu, Ni, Pb, and Zn were reduced by 20%, 63%,

5%, 23%, 18%, 57%, and 79%, respectively in 2004, as compared to their corresponding influent levels.

2. Heavy metal accumulation in soil changed SAR and CEC of the soil with wastewater application. The wastewater application reduced the SAR value of the soil solution, as compared to their initial level in the soil, and the lowest and highest values were observed under intermediate and highest flow rates (0.19 and 0.31 m^3 m^2 d^{-1}), respectively. The soil pH remained in the same range of 6~6.5 in both the years with wastewater application, whereas soil CEC increased from its initial level of 0.65 cmole kg^{-1} to 0.56-1.06 cmole kg^{-1} in 2003, to 0.68-1.63 cmole kg^{-1} in 2004.
3. Irrespective of the influent concentrations, heavy metals accumulated in the floodplain sand. Even though, the influent concentration in heavy metals was lower in 2004, as compared to that in 2003, heavy metals accumulation in the soil ranged from 6-179%, compared to their levels at the end of the 2003 experiment.
4. As organic burdens to soil increase with increases in application rates, the associated times to reach the maximum permissible limit of pollutant levels for heavy metals decreased. Even though these estimated times were found to be quite long in this study, prolonged wastewater application may change the physio-bio-chemical properties of the soil, and thereby increase heavy metal accumulation and consequently decrease the time to reach MPLP levels in the soil. Therefore, it would be expeditious to monitor the long-term changes in bioavailability of heavy metals within the soil-wastewater environment.

7.2.3 Modeling of nitrogen transport through soil

Field studies on the fate and transport of nitrogen in soil-water system are labor intensive, time consuming and expensive, and the results are generally site-and problem-specific; hence, modeling could be used as an alternative. It can also be used to simulate a number of different scenarios to explore the best or safest management options for wastewater application to land, and to reduce nitrate pollution. In this study, the LEACHN model was used to simulate nitrogen transport through soil, under scenarios such as different wastewater application rates, low, medium, and high N-content wastewaters, and continuous and intermittent applications. From this study, the following conclusions were drawn:

1. The LEACHN model successfully simulated the observation made on NO_3^--N leaching through a sand filter in this study. The simulation of NO_3^--N under continuous application of wastewater at different rates showed a decrease in NO_3^--N levels with an increase in flow rates, due to enhanced denitrification caused by anoxic zones associated with high flow rates.

2. As expected, simulations with continuous application of low, medium, and high N-concentrated wastewater, at different rates, showed an increase of NO_3^--N levels in the leachate with the increase in wastewater N-concentrations.

3. The low N-concentrated wastewater application, at all tested flow rates, resulted in the leachate NO_3^--N being lower than the maximum permissible limit. Therefore, in tropical, sub-tropical or humid conditions, wastewater with low N-concentrations used in this study can be continuously applied to the soil at all tested flow rates with minimal nitrate pollution.

4. Simulations with intermittent application of low, medium, and high N-concentrated wastewater, at different rates, resulted in leachate NO_3^--N levels below the permissible limit, and showed a 51~89% more reduction in NO_3^--N levels in the leachate, as compared to their levels under continuous wastewater application, under all tested wastewater N-concentrations and flow rates. Therefore, wastewater with high nitrogenous compounds, as may occur in many developing countries, can be treated by land under intermittent application patterns.

CHAPTER-VIII

CONTRIBUTIONS TO KNOWLEDGE AND RECOMMENDATIONS FOR FUTURE RESEARCH

8.1 CONTRIBUTIONS TO KNOWLEDGE

Based on the results obtained in this study, the following contributions to existing knowledge were made:

1. To the best of author's knowledge, this is the first study of its kind that investigates the use of a floodplain filtration system, with worst-case soil scenarios, i.e., sandy soils, for municipal wastewater treatment under different wastewater application rates and top-soil conditions.
2. LEACHN model can be use to investigate different management options in wastewater applications on floodplains such as different flow rates, different concentrations of NO_3^--N and NH_4^+-N in the influent, and continuous versus intermittent applications.
3. This is the first study where heavy metal removal and their retention in soil with wastewater floodplain treatment was studied, and the time to reach maximum permissible limit of pollutant levels estimated for metals, to assess the long-term feasibility of a floodplain filtration system.

8.2 RECOMMENDATIONS FOR FUTURE RESEARCH

The following areas of further research are suggested:

1. Since the natural conditions are different from the lysimeter experimental conditions, a field level study is needed to evaluate the effectiveness of a floodplain filtration system for wastewater treatment.
2. Vegetation is observed to be effective in removing NH_4^+-N, NO_3^-N, and COD from the wastewaters. However, the vegetation used in this study was garden sod, and was placed in the lysimeters prior to the experiments in each year. Hence, an active rhizosphere might not have fully established in the system; therefore, experiments should be done with properly established natural floodplain vegetation species.
3. The study should be done with different types of soils available in natural floodplains.

4. The study was carried out under steady state flow conditions; however, in a natural system, transient flow condition would also exist. Therefore, studies should also be conducted under transient flow conditions.

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Appendix A1

Input file for LEACHN Model

```
CALI5014 <DOS "Filename," 8 characters with no extension. Used in batch Runs (started as
LEACHF<filename).
-----------------------------------------------------------------------------------------------------
LEACHN: NITROGEN AND PHOSPHORUS DATA FILE.
A value must  be present for each "item," although  it may not be used in the simulation. The
file is read free format with blank delimiters. Preserve division      and  heading records.  The
number of      depth segments may be changed.
**********************************************************************
1        <Date  format (1: month/day/year; 2:00day/month/year). Dates must be 6"digits," 2
each     for "day,"  "mo," yr.
72803 <Starting  dat e.  No date in the input  data should precede this date.
90703 <Ending d ate or day number.  The starting    date is day 1 (A value <010101        is
treated as a      day number).
0.1      <Largest time  interval within a day   (0.1dayor less).
 1       <Number of    repetitions of   "rainfall," cropand chemical   application data.
900      <Profile depth "(mm)," preferably     a multiple of  the segment thickness.
10       <Segment thickness mm).  (The number of segments should be between about 8   and
30)
4        <Lower boundary condition: 1:fixed  depth water table; 2:free "drainage,"  3:zero
         flux 4:lysimeter.
900      <If the lower   boundary is     1 or 4:00 initial water table    depth   (mm).
-----------------------------------------------------------------------------------------------------
The steady-state flow option uses constant water fluxes during the application periods
Specified in the rainfall data "table," and a uniform  water   content specified here. Steady-
state flow implies a lab "column," and crop  and evaporation data are ignored.
3        <Waterflow:   1:00    Richards;2:00 Addiscott' tipping  bucket;  3:00steady-state.  0.3
         <Steady-state  flow water content (volume fraction);999:00:00saturated column.
**********************************************************************
3 <Number of output files: 1:00 OUT only; 2:00 OUT + SUM; 3:00 OUT + SUM + BTC
-----------------------------------
For the *.OUT file :
4        <Units for  depth  data:  1:00  "mg/kg,"  2:00  mg/m2  per  "segment,"  3:00"g/m2,"
         4:00    kg/ha
1        <Node print     frequency (print data   for every node "(1),"   alternate nodes (2).
1        <Print  option: Select  one of  the following  two (enter 1     or       2)
7        <Option1:00Printatfixedtime  intervals (days between prints).999for          monthly
print. 1 <Option2:00   No. of  prints   (the times for which    are       specified       below)
2        <Tables printed: 1:00  mass balance;  2:00 + depth    data;  3:00 +   crop    data
1        <Reset cumulative values in   .OUT   after each print?  0:00 "No,"   1:00    Yes
-----------------------------------
For the * .SUM file : 15
999      <Summary print interval (d)  (for calendar months use 999)
```

```
0       <Surface to [depth 1?]mm (Three depth segments for the
0       <Depth 1to [depth 2?] mm summary file. Zero defaults to   nodes
0       <Depth 2 to [depth 3?] mm closest to thirds of the profile)
3       <4th segment: Root zone (1); profile (2); Depth 3 to lower boundary (3);   Surface  to
shallowest      of lower boundary or water table -4
        -------------------------------------
For the *.BTC (breakthrough)file:
1       <Incremental depth of drainage water per output (mm)
----------------------------------------------------------------------
List here the times at which the *.OUT file is desired for print option 2  The number of
recordsmust match the 'No. of prints' under option 2above.  Date  or  Time  of  day  (At  least
one must        be "specified," Day no. (to nearest tenth) even if print option is 1)
-------- ---------------
71603 0.2       (These dates can be past the last day)
****************************************************************************
        Soil Physical Properties
-------------------------------------------------------
--      Retentivity model 0 uses listed Campbell's retention "parameters,"  otherwise
--      the desired particle size-based regression model is used.
----------------------------------------------------------------------------------------
Soil     | Clay Silt Organic carbon| Retention|  Starting  |       Roots      |    Starting
layer no.|                          |model     |theta or potl|(for no growth)| temperature(C )
                                               |(one is used)|                |(not read in
          |  %    %       %  |                          kPa|  (relative)   | LEACHC)
---     ----   ----    ----     ------  -----    -----   ------   -----------   ---------
1         2    2      0.03        0             0.3      0        0              5
..................................................................................
...................................................................................
90        2    2      0.03        0    0.3            0          0              5
-----------------------------------------------------------------------------------------
1       < Use water contents "(1),"   potentials -2
Particle density: Clay  Silt     and      sand    Organic        matter
2.65    2.65    0.05
  ****************************************************
For a uniform  profile:Any non-zero value here will override those in the   table    below.
----------------------------------------------------------------------
1.78    2.65    <Soil bulk density and particle density (kg/dm3)    .
-10     <'Air-entry value' (AEV) (kPa).
5.44    <Exponent (BCAM) in Campbell's water retention equation.
15000 - 10      <Conductivity (mm/day) and corresponding matric  potential (kPa)(for
        potential-based version of eq. 2.5).
2.014   <Pore  interaction parameter(P) in Campbell's conductivity equation.
20      <Dispersivity  (mm).
0       <For Addiscott flow:  Matric potential (kPa)at field capacity
0       < : Division between mobile and immobile water (kPa)
****************************************************************************
```

```
Soil     |Soil retentivity| Bulk |MatchK(h)curveat:|Dispersivity|For  Addiscottflow option:
segment|  parameters |density| K Matric using   |              |Field Mobile/immobile
no.      |AEV   BCAM|          |    potl      P   |              |capacity threshold
         |       kPa    |kg/dm3|    mm/d   kPa  |      mm      |      kPa      kPa
-----    ------  -----   ------  ----    -----    -----    -----    ------  ---------
1        -10     5.44    1.78       1   -20       1       20                  0        0
..........................................................................................
..............................................................................................
90       -10     5.44    1.78       1    -20      1       20                  0        0
*************************************************************************
Runoff according to the SCS curve number approach. Curve number listed here    will    be
adjusted by slope. During periods of crop "growth," CN2  "  replaced  by  value  for  crop.
Procedure according to J.R. Williams(1991). Runoff and   Water   Erosion.   Chap   "18,"
Modeling Plant and Soil "Systems,"  Agronomy 31.)
---------------
75       <Curve number (CN2). In "LEACHM," water content use to adjust CN2 based on top
20 cm.
0        "<Slope," %. Used to adjust CN2 according to equation of Williams (1991).
 **      (Set slope to 0 to  bypass  the  runoff  routine.  Runoff  owing  to  profile  saturation
         will still be accumulated)
*********************************************************************************
         Crop Data
----------------------------------------------------------------------
Data for at least one crop must be "specified," even if no Crop desired.  For fallow "soil," set
flag     below  to "0,"  or  germination past the simulation end date.
1        <Plants present: 1 "yes," 0 no.
1        <No. of crops  (>0)
-1500  <Wiltingpoint (soil)   kPa.
-3000  <Min.root water potl(kpa).
1.1      <Maximum ratio of actual to potential T. 1.05 <Root resistance.
Growth Perennial N_uptake       Date or day of          Rel.   Crop    Pan  | Crop MinHarvested
1: No  1:  Yes    1:to maturit y    Maturity              root   cover  factor |uptake N fraction
2: Yes  2: No     2:to   harvest  Germ. Emerg. Root  Cover Harv. Depth fraction|NPfixed
-----------------------------------------------------------------------------------kg/ha---------------
    2   2  1  60104  60104  73104  73104  10300 4 0.2 0.7 1 100 27 0 0.1 A1
*************************************************************************
Initial "Nitrogen", Phosphorus and Carbon Pools (excluding soil humus)
-------------------------------------------------------------------------------------------------
     |              Nitrogen pools              |  Carbon pools  |  Phosphorus pools     |  (Humus C,""N,"&
                                                                                         P calculated from Org.C)
Soil| Urea-NH4 NO3 Residue Manure|Residue Manure|Laible Residue Manure|(Fertilizer  P absent
                                                                                                  at start)
Layer|  -------mg N/kg dry soil-------  | ---mg C/kg -----| ---mg P/kg  dry soil----|(Bound P pool in
                                                                                    equilibrium with liableP.
```

```
------------------------------------------------------------------------------------------------------------  1
      1    0    0.37   0.501  0    0    0    0    0    0    0
      ..................................................................................
      ..................................................................................
      5    0    0.37   0.501  0    0    0    0    0    0    0
      6    0    0.187  0.261  0    0    0    0    0    0    0
      ..................................................................................
      ..................................................................................
      30   0    0.187  0.261  0    0    0    0    0    0    0
      31   0    0.183  0.146  0    0    0    0    0    0    0
      ..................................................................................
      ..................................................................................
      50   0    0.183  0.146  0    0    0    0    0    0    0
      51   0    0.283  0.214  0    0    0    0    0    0    0
      ..................................................................................
      ..................................................................................
      80   0    0.283  0.214  0    0    0    0    0    0    0
      81   0    0.29   0.19   0    0    0    0    0    0    0
      ..................................................................................
      ..................................................................................
      90   0    0.29   0.19   0    0    0    0    0    0    0
      ---------------------------------------------------------------------------
Concentration (mg/l) below   "profile," used with lower boundary 1
0       0       0 "(NH4," NO3 and P)
0       <       Depth  (mm) of water in mixing cell. Enter 0 for no mixing cell.
Chemical Properties
        ------------------
              Kd
        Name        L/kg
        ----------  --------
        '     Urea-N'       0
        '     NH4-N'        3.7
        '     NO3-N'        0
'Residue-N'   (Plant  'residues' and 'manure'pools representing added organic sources    '
Humus-N'      of "N," P and  C. They differ in that the plant residue pool is supplied

' Manure-N'   by the non-harvested portion of annual "crops," 'Residue-C' and the "non-
' Humus-C'    harvested," non-perrenial portion of' Manure-C' perennial crops)
' CO2-C'
' Fert-P' 10000 0.693 <Solubility;      Dissolution rate (d**-1)
' Labile-P' 1  100    0.6 <1: Freundlich or 2:00 Langmuir; [Freundlich Kd;
                          Exponent OR Langmuir Qm; k]
'Residue-P'
' Humus-P'
'Manure-P'
' Bound-P' 300 0.4     0.05    0.5     <Freundlich sorption: Kd; Exponent; Phase transfer:
```

```
                              Dissolution "rate," precipitation "rate," (days^-1)
****************************************************
Diffusion
-------------------------------------------------
120    <Molecular diffusion coefficient
****************************************************
Nitrogen Transformations
-------------------------------------------------
 0.5   <Synthesis efficiency factor.
 0.2   <Humification fraction.
 10    <C/N  ratio:biomass and humus.
 50    <C/P  ratio:biomass and humus.
---------Temperature and water content adjustments------
 1     <Temperature subroutine? "yes(1)," no(0).  If "no,"base temperature used.
 20    <Base "temperature," degrees C
 2     <Q10: rate constant adjustment factor per 10C temperature change.
 0.08  <High end of optimum water content "range," air-filled porosity.
 -300  <Lower end ofoptimum water "content," kPa
-1500 <Minimum matric potential for "transformation," kPa
 0.6 <Relative transformation rate at saturation (except "denitrification)," days^(-1)
****************************************************
Rate Constants [days^(-1)]
-------------------------------------------------

          Urea       NH4->NO3  NO3->N  Mineralization
    Layer hydrolysis                   Residue  Manure  Humus
    ----- -----  ------  -----  -----  -----    -----
    1     0.00E+00     0.6    0.1    0.01     0       1.00E-07
    ..............................................................
    ..............................................................
    10    0.00E+00     0.6    0.1    0.01     0       1.00E-07
    11    0.00E+00     0.4    0.1    0.01     0       1.00E-07
    ..............................................................
    ..............................................................
    20    0.00E+00     0.4    0.1    0.01     0       1.00E-07
    21    0.00E+00     0.3    0.1    0.01     0       1.00E-07
    ..............................................................
    ..............................................................
    40    0.00E+00     0.3    0.1    0.01     0       1.00E-07
    41    0.00E+00     0.4    0.1    0.01     0       1.00E-07
    ..............................................................
    ..............................................................
    60    0.00E+00     0.4    0.1    0.01     0       1.00E-07
    61    0.00E+00     0.3    0.1    0.01     0       1.00E-07
    ..............................................................
    ..............................................................
    90    0.00E+00     0.3    0.1    0.01     0       1.00E-07
```

```
        --------------------------------------------------
        Additional rates and constants used for calculating N transformations:
        0       <Ammonia volatilization from the "surface,"days^(-1)
        10      <Denitrification half-saturation constant (mg/l).
         8      <Limiting NO3/NH4 ratio in solution for nitrification
**************************************************************************"Ni
trogen," Pjosphorus and Carbon applications (kg/ha)
----------------------
0       <       No. of nutrient applications
-----------------------------------------------------------------------------------------
Date or| Incorp n |       Nitrogen              | Carbon    |    Phosphorus
Day no.| segments|Urea NH4 NO3 Residue Manure|Residue Manure| Fertilizer Residue Manure
------- -------------   ---     ---     ------  ------  -------  ------  ------  ------  ------
**************************************************************************
Cultivations
------------
1       < Number of cultivations. At least one must be specified. Can be past last day.
--------------------------------------------------
Date or   Depth of cultivation
 day no.     mm
 -------     -----
 40104       200
**************************************************************************
Rain and water composition (Include irrigation "here," or specify in a separate file.)
42      < Number of water applications. Some or all can be past last day. (See manual on
           setting automated irrigation thresholds)
0       < For a separate irrigation "file," set to 1 and edit and rename NITRTEST.SCH.
-----------------------------------------------------------------
        Start| Time  | Amount|  Surface    |Dissolved in water (can be 0)
        Date/|               |flux Density |Urea-N|NH4-N|NO3-N|P
        day -  -day-  --mm--  --mm/d----   -------------mg/l--------------
         72803 1        314.5  314.5        0      0       0       0
         72903 1        314.5  314.5        0      0       0       0
         73003 1        314.5  314.5        0      0       0       0
         73103 1        314.5  314.5        0      0       0       0
         80103 1        314.5  314.5        0      0       0       0
         80203 1        314.5  314.5        0      2.684   3.373   0
         80303 1        314.5  314.5        0      2.490   3.920   0
         80403 1        314.5  314.5        0      2.658   4.166   0
         80503 1        314.5  314.5        0      2.389   5.136   0
         80603 1        314.5  314.5        0      2.840   5.728   0
         80703 1        314.5  314.5        0      2.753   6.669   0
         80803 1        314.5  314.5        0      2.560   6.591   0
         80903 1        314.5  314.5        0      2.772   6.323   0
         81003 1        314.5  314.5        0      1.773   3.112   0
         81103 1        314.5  314.5        0      4.011   1.074   0
```

81203	1	314.5	314.5	0	3.194	2.575	0
81303	1	314.5	314.5	0	3.696	3.091	0
81403	1	314.5	314.5	0	4.575	0.620	0
81503	1	314.5	314.5	0	3.851	3.463	0
81603	1	314.5	314.5	0	3.384	3.691	0
81703	1	314.5	314.5	0	6.204	0.701	0
81803	1	314.5	314.5	0	6.918	0.089	0
81903	1	314.5	314.5	0	4.749	2.822	0
82003	1	314.5	314.5	0	4.019	3.012	0
82103	1	314.5	314.5	0	4.679	2.615	0
82203	1	314.5	314.5	0	4.353	3.379	0
82303	1	314.5	314.5	0	4.508	3.050	0
82403	1	314.5	314.5	0	6.315	0.563	0
82503	1	314.5	314.5	0	5.032	1.497	0
82603	1	314.5	314.5	0	4.359	1.838	0
82703	1	314.5	314.5	0	4.376	1.919	0
82803	1	314.5	314.5	0	4.666	1.333	0
82903	1	314.5	314.5	0	4.844	2.371	0
83003	1	314.5	314.5	0	3.286	1.892	0
83103	1	314.5	314.5	0	3.617	0.802	0
90103	1	314.5	314.5	0	4.106	0.370	0
90203	1	314.5	314.5	0	5.138	0.099	0
90303	1	314.5	314.5	0	5.714	0.105	0
90403	1	314.5	314.5	0	5.313	0.041	0
90503	1	314.5	314.5	0	4.998	0.198	0
90603	1	314.5	314.5	0	4.771	0.679	0
90703	1	314.5	314.5	0	5.981	0.412	0

Potential ET (weekly 'Totals", "mm"), "Depth to water table (mm) Mean weekly Temperature and mean weekly Amplitude (degrees C)

Week	ET	Water table	Mean temp	Amplitude
62303	20.92	0	19.6	4.79
63003	19.56	0	20.11	5.49
70703	21.47	0	22.5	5.46

90103	8.24	0	17.11	4.83
90803	15.82	0	16.87	5.61
91503	13.74	0	18.43	6.01