A STUDY ON

PREVENTION OF GROUNDWATER CONTAMINATION

BY NITRATE IN ARABLE LAND

（農耕地における硝酸性窒素による地下水汚染の防止に関する研究）

Morihiro Maeda

2002

CONTENTS

Chapter1

Chapter2

Chapter3

Chapter6

ABSTRACT

Maeda, M. 2002. A study on prevention of groundwater contamination by nitrate in arable land. Doctoral Dissertation, Kyoto University, Japan.

The studies undertaken in the present thesis aimed at the prevention of groundwater contamination by nitrate (NO_3) from agricultural sources by gaining a better understanding of the mechanisms of NO_3 leaching in arable land. The use of wick samplers and monolith lysimeters was proposed as practical monitoring methods for NO_3 leaching in upland fields under natural conditions. Wick samplers, which enable to draw water from saturated and unsaturated soil without external application of suction, can be installed in actual upland fields. Monolith lysimeters, which are defined as a facility whereby undisturbed soil cores are placed into bottomed pipes with a drain below the ground, have a large potential to evaluate NO_3 leaching in structured soils where preferential flow may occur. Nitrate leaching from different fertilizers and in structured soil was monitored and the data obtained in the experiments were evaluated using simple mathematical approaches. Excessive N from chemical fertilizers caused substantial NO_3 leaching, while compost application was promising to achieve high yields and low N leaching during a few years but led to the same level of NO_3 leaching as that in the plots subjected to chemical fertilizer application over longer periods of time. Nitrate concentrations in soil water at 1-m depth in the plots with chemical fertilizer application could be described by an N and water balance equation. Preferential flow in soil had a substantial influence on NO_3 leaching. The preferential water movement was well described by a modified version of the 'tank-in-series model', which involves a distribution function of non-reactive tracer travel time. Thus, the experiments and mathematical approaches presented could provide full information on NO_3 leaching in upland fields for policy decisions or regulations to prevent groundwater contamination.

KEY WORDS

Andisols, Bromide, Chloride, Copper, Groundwater, Leaching, Methemoglobinemia, Monolith lysimeter, Natural abundance, Nitrate, Nitrogen and water balance equation, Preferential flow, Tanks-in-series model, Zinc, Wick sampler.

ACKNOWLEDGMENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Organizations:

EPA, Environmental Protection Agency; FAO, Food and Agriculture Organization; MAFF, Ministry of Agriculture, Forestry and Fishery; NARC, National Agricultural Research Center or National Agriculture Research Center; OECD, Organization for Economic Co-operation and Development; USDA, U.S. Department of Agriculture.

Chemicals:

NH_4, ammonium; Cl, chloride; Cu, copper; NO_3, nitrate; NO_2, nitrite; N, nitrogen; PVC, polyvinyl chloride; Zn, zinc.

Treatments:

SC, swine compost; CU, coated urea fertilizer; AN, ammonium fertilizer; NF, no fertilizer; N-C, exposed to natural precipitation and without chemicals; N-A, exposed to natural precipitation and treated with chemicals; D-A, exposed to 'double' natural precipitation and treated with chemicals; T-A, exposed to 'triple' natural precipitation and treated with chemicals.

Others:

AEC, anion CEC, exchange capacity; cation exchange capacity; ANCA-SL, automated nitrogen and carbon analysis–solid/liquid; PTO, power take-off system; SD, standard deviation; SE, standard error.

LIST OF SYMBOLS

Symbol	Definition
a	Fitting parameter for Eq. [3.1]
b	Fitting parameter for Eq. [3.1]
C	Concentration (mg L^{-1}) / Content (g kg^{-1})
C_{iNO3-N}	NO$_3$-N concentration resulting from denitrification (mg L^{-1})
C_{mix}	N content of a mixture of materials A and B (g kg^{-1})
C_{NO3-N}	NO$_3$-N concentration before the reaction of denitrification (mg L^{-1})
C_{SC}	N content of compost (g kg^{-1})
C_{soil}	N content of soil (g kg^{-1})
c	Fitting parameter for Eq. [3.4]
d	Fitting parameter for Eq. [3.4]
E	Distribution function of travel time
EW	Excess water (mm yr^{-1})
f_m	Ratio of water in mobile regions to maximum water content in soil (−)
f_{NO3-N}	Fraction of unreacted NO$_3$ to initial NO$_3$ in a volume
h	Total potential (cm)
k	Unsaturated hydraulic conductivity (cm s^{-1})
k (subscript)	kth tank in equally sized completely mixed flow tanks in series
K_{sat}	Saturated hydraulic conductivity (mm h^{-1})
K_d	Soil-solution distribution coefficient of a chemical (cm^3 g^{-1})
ℓ	Laplace transform function
M	Mass of tracer applied (mg m^{-3})
M_1	First moment of $E(\tau)$
M_2	Second moment of $E(\tau)$
$M_{fm,n}(\tau_{max}, E_{max})$	Peak coordinate of a function, $E(\tau)$
n	Number of equally sized completely mixed flow tanks in series (−)
PNC	Potential nitrate concentration (mg L^{-1})
PNP	Potential nitrate present in soil (kg ha^{-1} yr^{-1})
q	Water flow rate (cm s^{-1})
R	Infiltration rate (mm d^{-1})
R_f	Retardation factor of chemical transport in soil (−)
R_{sample}	^{15}N/^{14}N ratio of samples
$R_{standard}$	^{15}N/^{14}N ratio of atmospheric N$_2$
r	Radius distance (cm)

LIST OF SYMBOLS (CONTINUED)

Symbol	Definition
s	Laplace transform parameter
t	Time (d / s)
V	Maximum water content in a freely drained monolith (mm)
z	Vertical distance (cm) / Gravity potential (cm)
ε	^{15}N enrichment factor (‰)
Γ	Gamma function
$\delta^{15}N$	δ^{15}N values of a substrate after the reaction of denitrification (‰)
$\delta^{15}N_{SC}$	δ^{15}N value of compost (‰)
$\delta^{15}N_{soil}$	δ^{15}N value of soil (‰)
$\delta^{15}N_{mix}$	δ^{15}N value of a mixture of soil and compost (‰)
$\delta^{15}N_{ini}$	δ^{15}N values of a substrate before the reaction of denitrification (‰)
θ	Porosity of soil ($-$)
θ	Volumetric water content of soil for Eq. [3.1] (m^3 m^{-3})
θ_r	Residual soil water content for Eq. [3.1] (m^3 m^{-3})
θ_{sat}	Soil water content at saturation for Eq. [3.1] (m^3 m^{-3})
ρ	Bulk density of soil (g cm^{-3})
τ	Normalized time ($-$)
ψ	Matric potential (cm)

Chapter 1

INTRODUCTION

1.1 BACKGROUND

The provision of a safe and stable supply of food and water is essential for mankind. The increase in the world population was supported by the improvement of agricultural practices, including fertilizer application, irrigation, and plant breeding. In fact, total production of cereals in the world has increased by a factor of 2.3 while the world population has increased by a factor of 1.9 since 1961 (Fig. 1.1). Particularly, chemical fertilizers have played a major role in the increase of cereal production (Brown, 1999) and their world consumption has increased as much as 7.4 times since 1961 (Fig. 1.1). Also, the large population in the world requires more water for agriculture, industry, and living conditions (Brown, 1999). Groundwater became more important as an alternative source of water supply for surface water, because the water quality of surface waters had been adversely affected by intensive human activities.

Under these circumstances, excessive application of nitrogenous fertilizers was reported to cause groundwater contamination by nitrate (NO_3). Namely, we must strike a balance in the use of N fertilizer to fulfill the food demand while avoiding imperiling water demand. We must adopt proper measures to address this problem, because the amelioration of contaminated groundwater would be impossible or is very costly. The Japanese Government
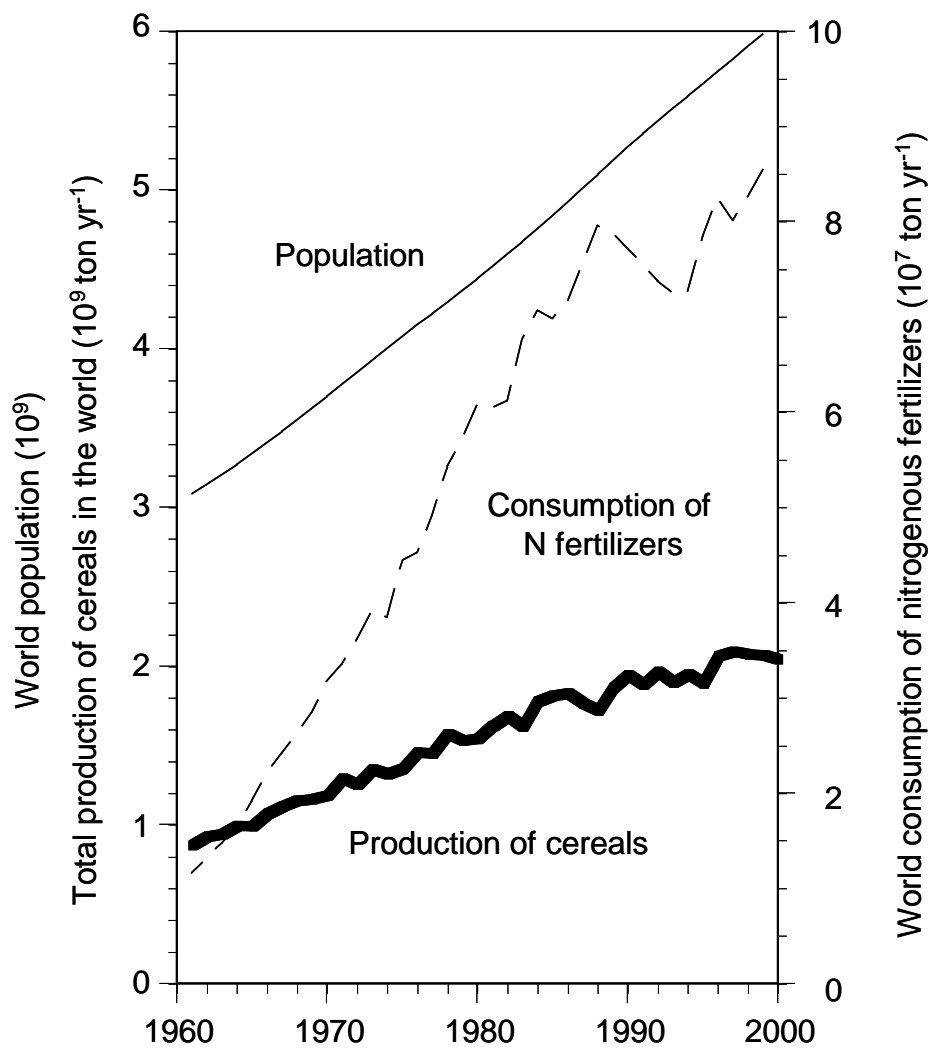
Fig. 1.1. **Trends of population (thin line, left axis for scale), total production of cereals (thick line, left axis for scale), and consumption of nitrogenous fertilizers (broken line, right axis for scale) in the world since 1961. Illustrated from data by FAO (2001).**

established an environmental quality standard for NO_3-N in groundwater (10 mg N L^{-1}) and enforced the Basic Law on Food, Agriculture, and Rural Areas to promote food self-sufficiency and sustainable agriculture in harmony with the surrounding environment in 1999.

Utilization efficiency of N fertilizers for outdoor cultivation of vegetables is mostly less than 40% (Nishio, 2000). A large proportion of the unused N may leach out of the root zone and eventually to reach groundwater. It is difficult for farmers or policy-makers to select the most effective measures in the field to improve the N utilization efficiency and to minimize the risk of N leaching, because the mechanisms of NO_3 leaching are not well

understood and thereby the effects of improved practices can not be evaluated.

The difficulty in the prediction of NO_3 leaching originates mainly from the following two facts: (i) most of the agricultural soils contain high levels of organic-N; (ii) water flow in soil is not straightforward. In most of the soils, more than 90% of soil-N is in organic forms (Vinten and Smith, 1993). Parts of organic-N of soils and manure applied to the soils are mineralized and, at the same time, parts of mineral-N in soil can be converted to organic forms. On the other hand, these reaction rates, which can not be ignored in considering the N mass balance owing to their large proportion, are very difficult to determine because they vary considerably depending on the environmental conditions. Furthermore, water filtration in the vadose zones is transient and uneven under natural conditions. Preferential water flow in soil would bring NO_3 to groundwater quickly beyond expectation. Many soil scientists have conducted studies on the complicated water flows in soil, but still their results are not easily adaptable to the prediction of NO_3 leaching.

1.2 OBJECTIVES AND ORGANIZATION

The study undertaken in the present thesis aims at the prevention of groundwater contamination by NO_3 in arable land by gaining a better understanding of the mechanisms of NO_3 leaching associated with agricultural practices, through experimental and theoretical modeling approaches (Fig. 1.2). The objectives of each chapter are to:

 (i)   Outline the NO_3 problems in groundwater (Chapter 2);

 (ii) Review and develop the monitoring methodology of NO_3 leaching (Chapter 3);

 (iii) Determine the effects of application of different fertilizers on NO_3 leaching (Chapter 4);

 (iv) Determine the effects of preferential flow on leaching of NO_3 and heavy metals (Chapter 5).

In Chapter 2, the relation between NO_3 contamination of groundwater and agricultural practices was reviewed. In the first section, human concern and standard limits related to the NO_3 concentration in water were presented. In the second section, the current status of groundwater contamination was described in some countries. Also, the reason why fertilizer is applied at higher N rates than the amount that crops would take up throughout the growing period was given based on the N uptake patterns of crops. In the following sections, N dynamics in soil and factors influencing NO_3 leaching were reviewed. In the last section,
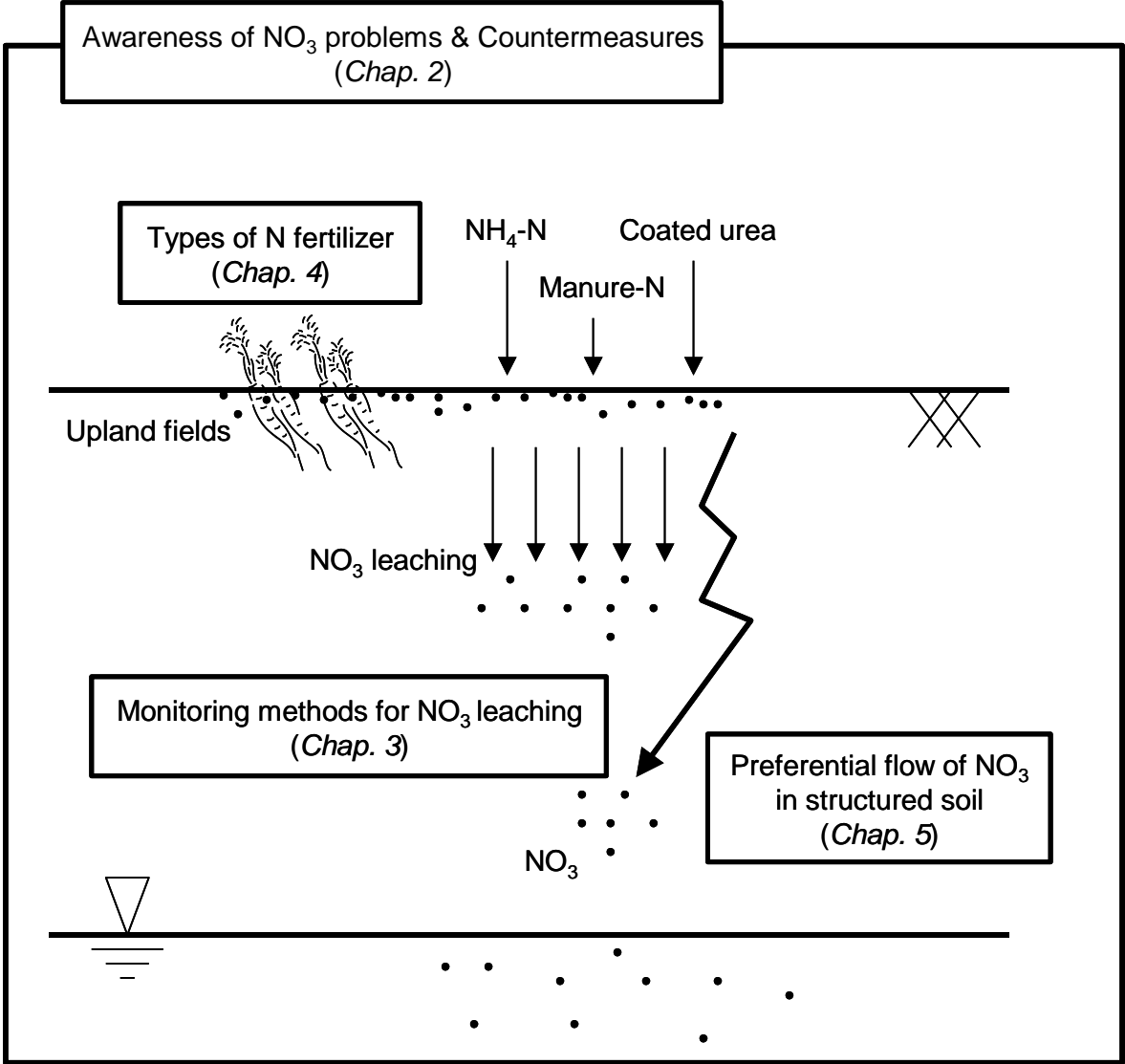
Fig. 1.2.　Organization of the thesis.

4

agricultural management practices to mitigate NO_3 contamination of groundwater were discussed.

In Chapter 3, monitoring methods for NO_3 leaching in upland fields were introduced and the practical use of wick samplers and monolith lysimeters were discussed in detail. The monitoring methods must be accurate, easy to use, and inexpensive, in order to evaluate many agricultural management measures under various environmental conditions. In the first section, several kinds of lysimeters, porous suction cup samplers, etc. were described together with their advantages and disadvantages. In the second section, the performance of wick samplers, which is a promising method for monitoring NO_3 leaching in fields, was investigated in terms of water collection efficiency. In the third section, a drilling system for collection of soil monoliths was developed. This unique model can be attached to the three-point hitch system, which is a standard for all tractors, on the rear of a tractor.

In Chapter 4, NO_3 leaching was examined in agricultural Andisol fields treated with ammonium N, coated urea, swine compost, or not subjected to fertilizer application for 7 yr. Nitrate concentration in the soil water at 1-m depth was monitored using porous ceramic cup samplers and subsequently evaluated using the N and water balance equation proposed by OECD, which calculates the risk of groundwater contamination (OECD, 1999). Also, total N and $\delta^{15}N$ in the topsoils and the vertical distribution of NO_3-N and $\delta^{15}N$ in soil water were studied after 6 yr of continuous fertilizer application.

In Chapter 5, the preferential flow of NO_3 and heavy metals in heavy clay soil was analyzed and a transfer function model was developed to evaluate the preferential flow occurring in soil. Ammonium (NH_4-N) and NO_3-N, zinc (Zn), and copper (Cu) were applied on the surface of monolith lysimeters containing heavy clay soil, in which preferential flow could have a substantial influence on chemical leaching (Bergström, 1995). The selected heavy metals are frequently occurring at relatively high levels in compost from livestock waste. Concurrently, bromide (Br) as a non-reactive tracer was applied on the lysimeters to

provide information on water movement through the profiles. A modified version of the tanks-in-series model for soil systems to describe a distribution function of non-reactive tracer travel time was used to characterize the flow behaviour of Br.

Lastly, in Chapter 6, the preceding chapters were summarized and general conclusions were drawn. In addition, based on the findings of this thesis project, the remaining but necessary themes related to NO_3 leaching in arable land were suggested for future research.

<div align="right">*Chapter 2*</div>

OVERVIEW OF NITRATE CONTAMINATION OF GROUNDWATER

2.1 HEALTH CONCERN RELATED TO NITRATE IN GROUNDWATER

Nitrate contamination of groundwater has received considerable attention due to potential human health impacts from groundwater use for drinking water. Nitrate causes a problem when it is converted to nitrite (NO_2), while nitrate (NO_3) itself is not toxic. The toxicity of NO_2 is associated with methemoglobinemia, which occurs when NO_2 oxidizes hemoglobin to methemoglobin, resulting in a decrease in the oxygen-carrying capacity of blood (Addiscott et al., 1991; Canter, 1996). Infants under 3 mo of age are the most susceptible because their stomach is not acid enough to inhibit the microbes that convert NO_3 to NO_2 (Canter, 1996).

The World Health Organization (WHO) recommended guidelines for drinking water quality (NO_3: ≤ 50 mg NO_3 L^{-1}; NO_2: ≤ 0.2 mg NO_2 L^{-1}) in 1992, and the U.S. limit for NO_3-N in drinking water is 10 mg N L^{-1} (Canter, 1996), to offer the greatest protection to infants. The European Community (EC) directive (80/778/EEC) implements the WHO recommendation. In Japan, the water quality standard of NO_3-N for drinking water has been 10 mg N L^{-1} since 1958 and that of NO_2-N (0.05 mg N L^{-1}) was added into the items relating to monitoring for drinking water in 1998. In addition, an environmental quality standard for NO_3-N in groundwater was set at 10 mg N L^{-1} to preserve water supply sources in 1999 (Hayami, 1993).

Another aspect for environmental concern is the potential eutrophication in closed

<div align="center">7</div>

water bodies like lakes and closed seas (Koshino, 1976; Tabuchi and Takamura, 1985), where increased N levels promote the growth of algae, resulting in a decrease in the amount of dissolved oxygen. Eutrophication should be avoided due to the simplification of the ecosystems in the water bodies and the implication for drinking water supply affected by the growth of toxic algae.

2.2 STATUS OF GROUNDWATER CONTAMINATION BY NITRATE AND FERTILIZER APPLICATION

Western countries have turned their attention to NO_3 in groundwater since the 1960s because their major source of drinking water is groundwater (Ooe et al., 1999; Ogawa, 2000), as shown in Table 2.1 (Kobayashi, 1994). According to the U.S. Environmental Protection Agency (EPA), 1.2% of community water system wells and 2.4% of rural domestic wells were projected to contain more than 10 mg L^{-1} NO_3-N; approximately 4.5 million people drank nitrate-contaminated water (U.S. EPA, 1992). Also, in the European countries, drinking water sources are contaminated by NO_3, exceeding the WHO guidelines of 11.3 mg L^{-1} (Kumazawa, 1999). In France, more than 1 million people drank water that contained more than 11.3 mg L^{-1} NO_3-N in 1981, with groundwater accounting for 91% (Fried, 1991). In the U.K., NO_3-N concentrations were found to exceed 11.3 mg L^{-1} in 192 wells for drinking water in 1990, and such polluted areas were designated as nitrate-sensitive areas (Ogawa, 2000). In eastern and central England, NO_3 concentrations were increasing in groundwater, which provides 30-50% of drinking water (Spalding and Exner, 1993). Eight percent of the public waterworks in Denmark and 5% of those in former West Germany supplied groundwater containing more than 11.3 mg L^{-1} NO_3-N (Fried, 1991). In the Netherlands, the average concentration of NO_3-N in 56 shallow wells was 20 mg L^{-1} with the highest value being 81

Table 2.1.   Contribution of groundwater to drinking water supply in selected countries.

	Year	Water supplied population (× 1000 persons)	Ratio of groundwater to drinking water supply (%)
Denmark	1986	3,084	100
France	1986	54,500	64
West Germany	1986	59,900	64
Netherlands	1986	14,590	59
Italy	1984	51,943	50
Finland	1986	39,710	49
U.S.A.	1986	219,000	30
U.K.	1986	56,000	28
Sweden	1986	7,242	25
Spain	1986	37,200	24
Japan	**1986**	**113,859**	**22**

After Kobayashi, Y. (ed.). 1994. Source protection of Drinking Water Supply. Gihoudou, Tokyo.

mg L^{-1} (Ogawa, 2000). In Japan, a national groundwater survey conducted by the Environment Agency revealed that 9% in 1982 and 6.3% in 1998 of groundwater contained more than 10 mg L^{-1} NO_3-N (Environment Agency, 1993; Environment Agency, 1999).

Agriculture was reported to be the leading source of NO_3 contamination in groundwater (Kawanishi et al., 1991; Hallberg and Keene, 1993; Kumazawa, 1999; U.S. Geological Survey, 1999). The Royal Society in the U.K. estimated that the total amount of N leached from agricultural land was about 326,000 t in 1987 while N inputs from sewage and industrial effluent to freshwater and lakes were 150,000-160,000 t (House of Lords, 1989). In the Big Spring Basin of northeastern Iowa, which is fully used for agriculture, the NO_3-N concentration increased from 3 mg L^{-1} in the 1960s to nearly 10 mg L^{-1} in the early 1980s, while the amount of fertilizer N applied in the areas increased 2.5 to 3 times as a function of increasing rates of N application as well as the increase in the vegetated area (Hallberg, 1986). In Japan, NO_3-N concentrations exceeding 10 mg L^{-1} were detected in 15% of agricultural wells, but only in 0.05% of the wells in paddy fields (Kumazawa, 1999). Nagai (1991) reported that the NO_3-N concentration in groundwater continuously increased from less than 5 mg L^{-1} in the early 1970s to 20 mg L^{-1} in the late 1980s under tea fields, where N fertilizer was intensively used, in Sizuoka. Hirata (1996) documented that the NO_3-N concentration in

groundwater reached a maximum level of 90 mg L^{-1} under vegetable fields receiving N fertilizer at 500 kg N ha^{-1}. Ogawa (2000) showed that, below upland fields, the NO_3-N concentration in groundwater increased along with the direction of the groundwater flow.

Nitrogen is one of the most important plant nutrients. Needless to say, N fertilizer played an important role in the Green Revolution in the 1960s. National average nitrogenous fertilizer application rates, which were calculated from the data provided by the Food and Agriculture Organization (FAO, 2001), are listed in Table 2.2. Necessary N doses are different among countries owing to the difference in cover corps and climate conditions. Nitrogen application rates had increased in all the countries, especially in the developed countries from 1961 to 1979 (Table 2.2). Since the late 1970s, the N application rates have decreased in some developed countries (indicated as III), including Japan, because of the awareness of the excess application. On the other hand, the N application rates are still increasing in developing countries (indicated as I). The national average N application rate in Japan is not high in this list and is decreasing. Nevertheless, groundwater contamination by NO_3 has been reported, as mentioned above.

Nitrogen application rates widely ranged from 90 kg ha^{-1} for rice to 958 kg ha^{-1} for celery in Japan (Table 2.3; Nishio, 2001). Excessive N in soil, which is shown as surplus N in Table 2.3, may cause large N gaseous and leaching losses from arable land, unless the patterns of N uptake by crops match N available in soil. Conversely, some excessive N is necessary as insurance when considering the N losses. Rainfall immediately after fertilization would bring a considerable amount of mineral-N in soil to deeper vadose zones, because crops at an early stage had not absorbed much N in soil by that time.

Nitrogen surplus increased with the N application rate (Table 2.3). Generally, crops need more N in soil at the stage of vegetative growth than at that of reproductive growth. Leaf vegetables such as celery and spinach are harvested at the stage of vegetative growth. Fruit vegetables such as tomato are continuously harvested at the stages of both vegetative and

Table 2.2.   National average N fertilizer applications to arable land in selected countries, in 1999, 1979, and 1961 (kg N ha^{-1}).

| | Type[a] | Year | | |
		1961	1979	1999
World average	I	9	43	63
Ireland	I	18	218	399
Netherlands	III	245	619	375
Egypt	I	77	217	354
South Korea	I	107	215	265
Malaysia	I	32	138	255
U.K.	II	69	192	220
China	I	5	109	196
Viet Nam	I	3	16	195
Sri Lanka	I	61	90	186
Germany	III	72	185	170
France	II	32	123	140
Bangladesh	I	2	29	124
Norway	III	58	136	121
Chile	I	4	15	119
Denmark	III	48	149	110
Indonesia	I	5	34	109
Japan	**III**	**112**	**159**	**106**
Greece	III	30	122	105
Italy	III	27	117	101
New Zealand	I	2	9	100
Philippines	I	7	44	87
Spain	I	20	58	86
Finland	II	22	82	81
India	I	2	21	79
Thailand	I	1	9	73
Sweden	III	31	86	69
U.S.A.	II	17	55	64
Mexico	I	6	36	52
Canada	I	2	18	35
Brazil	I	3	21	31
Australia	I	1	6	23
Kenya	I	1	5	15

[a] I, Increased throughout the period 1961-1999; II, Increased from 1961 to 1979, then did not change; III, Increased from 1961 to 1979, then decreased to 1999.

reproductive growth. Accordingly, leaf and fruit vegetables require a large amount of N in soil throughout the growing period, even at harvest (Type A), which induces more NO_3 leaching during the bare period after harvest. On the other hand, the crops of Types B and C do not need much N in soil at harvest because head-forming vegetables such as cabbage in Type B are harvested at the late stage of vegetative growth and other crops in Type C at the stage of

Table 2.3. **Nitrogen balance in fields for selected crops in Japan (modified after Nishio, 2001; Souma, 1988).**

N uptake pattern[a]	Crop	Mineral N application (kg N ha^{-1})	N uptake (kg N ha^{-1})	N surplus (kg N ha^{-1})
Type A	Celery	958	226	732
	Egg plant	643	160	483
	Tea	628	278	350
	Tomato	321	101	220
	Spinach	220	63	157
Type B	Chinese cabbage	315	130	185
	Cabbage	338	217	121
Type C	Onion	248	93	155
	Water melon	161	72	89
	Potato	156	74	82
	Radish	133	94	39
	Rice	90	96	-6

[a] Nitrogen uptake patterns are illustrated below:

Type A:
  Continuous uptake

Type B:
  Two-peak-chevron uptake

Type C:
  Chevron uptake
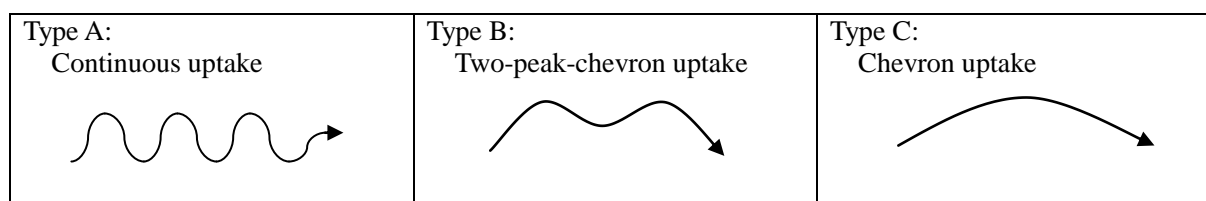
reproductive growth (Souma, 1988). This is the reason for the larger N application rates for crops in Type A.

Adequate application of livestock manure to arable land is recommended for recycling valuable nutrient resources. However, excessive use of livestock manure as well as chemical fertilizer on arable land may cause groundwater contamination (Thomsen et al., 1993; Adams et al., 1994; Chang and Entz, 1996). Although mineralized N from organic-N in manure must be considered as N input to arable land, evaluation of the mineralization rate of organic-N in manure is not easy (Addiscott, 1991).

2.3 THE NITROGEN CYCLING IN ARABLE LAND

The N cycling is shown in Fig. 2.1. The main N inputs to arable land are the application of fertilizer and manure, and precipitation. The average application rates of chemical fertilizer and manure are 113 and 60 kg N ha^{-1} in Japan, respectively (Mishima et al., 1999). The most common N fertilizer is urea (49% of total domestic demand in 1996; MAFF, 1998), followed by ammonium sulfate (20%), high-analysis compound fertilizer (13%), and ammonium phosphate (11%). Air-borne N inputs amount to about 10 kg N ha^{-1}yr^{-1} (Tabuchi and Takamura, 1985; Hirata, 1996).

Nitrogen can exist in various forms in soil. In most of the soils, more than 90% of soil-N occurs in organic forms (Vinten and Smith, 1993). The decomposition of organic
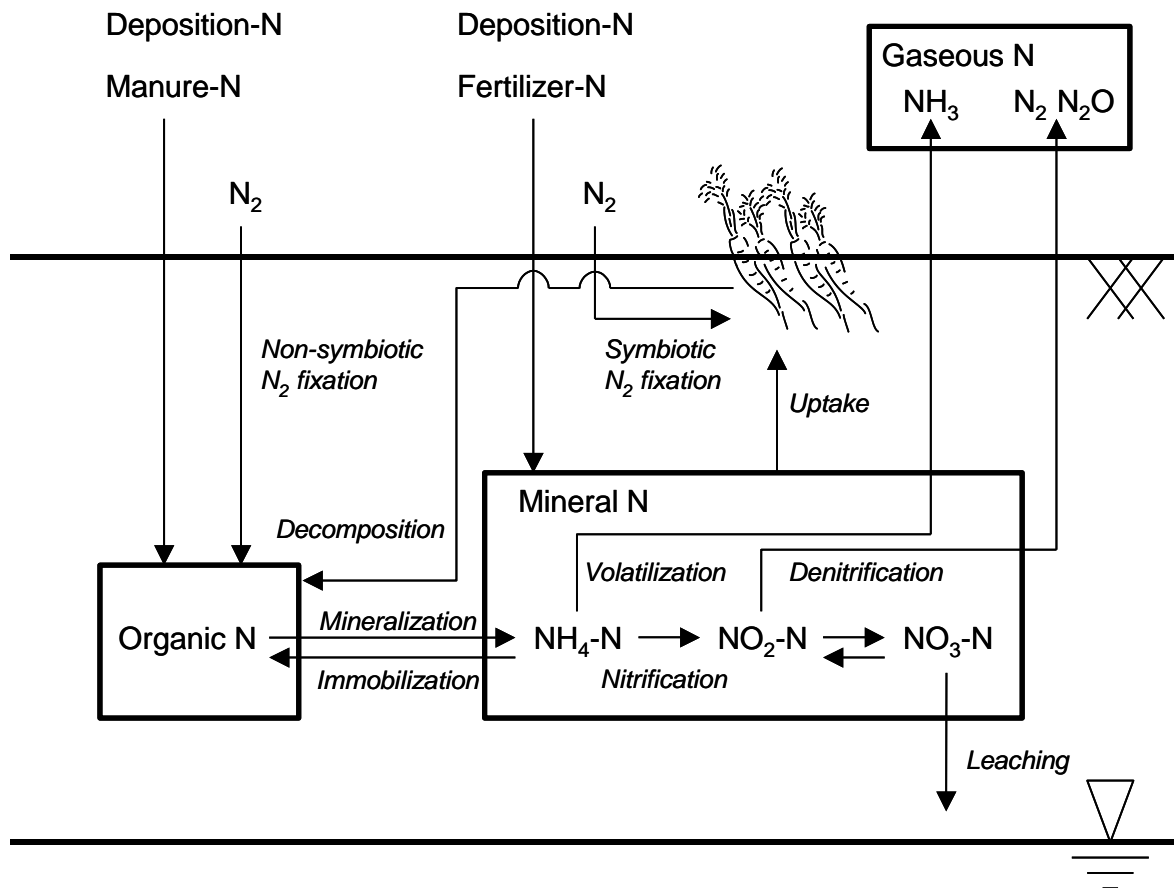
Fig. 2.1.   Nitrogen cycling in soil.

13

matter converts some organic-N to mineral-N (NH_4-N, NO_2-N, NO_3-N) through microbial processes (mineralization). At the same time, mineral-N can be converted to organic-N by microbial assimilation (immobilization). Ammonium N is oxidized to NO_2-N and then NO_3-N by microorganisms (nitrification). Crops take up mineral-N from fertilizer or N mineralized from organic matter. Nitrate N is freely leached below root zones, while NH_4-N is adsorbed onto the soil surface with negative charges. Gaseous N losses occur due to denitrification under anaerobic conditions and ammonium volatilization under alkaline conditions. Furthermore, a considerable extent of N_2 fixation occurs in specialized groups of microorganisms for grain and pasture legumes.

Nitrate leaching is the process whereby NO_3 in the soil solution is displaced from root zones by rainfall or irrigation water and eventually penetrates into groundwater. General knowledge of the N cycling must be considered to select fertilization practices in a field.

2.4 FACTORS INFLUENCING NITRATE LEACHING

A number of agricultural practices and hydrogeological factors influence NO_3 leaching. The magnitude of the adverse impacts of these factors must be evaluated to improve agricultural management, resulting in the maintenance of crop yield while reducing NO_3 leaching.

Fertilization management influences the amount of available-N in soil for crops. Substitution of slow-release fertilizers for readily available conventional fertilizers suppressed N leaching in short-term studies (Sakata et al., 1995; Matsumaru, 1997b; Maeda et al., in press). Split applications or banding of fertilizer reduced NO_3 leaching (Power et al., 2000). Nitrate leaching is also affected by manure types with different amounts of available-N (Beckwith et al., 1998). Residual N from previously applied manure is mineralized and may be available for leaching in continuously managed fields (Angle et al., 1993; Thomsen et al.,

1993; Bergstöm and Kirchmann, 1999; Maeda et al., in press).

Cropping systems, tillage, and other production practices can be considered as other influencing factors. Nitrate leaching was reduced by the introduction of catch crops such as perennial ryegrass and soybean (Aronsson and Torstensson, 1998; Power et al., 2000). The effects of tillage practices on NO_3 leaching were often site-specific (Power et al., 2000). Nitrate leaching was larger where crop irrigation was used (Burart and Kolpin,1992).

Local conditions such as climate and soil type also affect NO_3 leaching. Nitrate concentrations of leachate increased with larger precipitation in Wisconsin (Andraski et al., 2000) and Denmark (Eriksen et al., 1999), whereas they decreased in Minnesota (Randall et al., 1997). While watering treatment did not affect significantly NO_3-N leaching, soil types differing in texture and organic matter content affected it substantially (Bergström and Johansson, 1991). Matsumaru (1997b) showed, using repacked lysimeters, that 25-32% of fertilizer-N leached out in volcanic ash soil, while 58-66% of that in sandy soil at the same application rates of fertilizer as in the volcanic ash soil. Preferential water flow in soil brings NO_3 to groundwater quickly (Maeda and Bergström, 2000). Preferential flow refers to macropore flow, fingering, and funneled flow (Steenhuis et al. 1995). Macropores, which reflect soil structure, root decay, wormholes, etc., constitute preferred flow pathways for infiltration of water in soil. Fingering occurs due to wetting front instability such as changes in hydraulic conductivity with depth and compression of air ahead of the wetting front. Funneled flow takes place when sloping geological layers cause pore water to flow laterally, accumulating in a low region. Nitrate leaching increases as the organic matter content increases, due to increased mineralization rates (Bergström and Johansson, 1991). Anion exchange capacity (AEC) values of soil are often significant for NO_3 adsorption. Nitrate retention was mainly due to increased AEC at low pH values and was strongly correlated with the clay and oxide contents (Canter, 1996).

2.5 MEASURES FOR THE PREVENTION OF NITRATE CONTAMINATION

The attention of the present study focused on measures for the prevention of NO_3 contamination from the viewpoint of the 'polluter pays' principle. In addition, the remediation of contaminated groundwater is difficult and costly, since contaminants from a non-point source like arable land tend to diffuse. Preventive measures for minimizing agriculturally based NO_3 contamination of groundwater are listed in Table 2.4. Measures for the treatment of NO_3 in groundwater were reviewed by Canter (1996).

Several technical measures can be used for reducing NO_3 leaching in arable land. The basic concept is associated with matching available N in root zones to meet crop N demand all the time. Slow-release fertilizers, mulches, effective application methods of fertilizer, and use of catch crops can improve N recovery rates by crops, resulting in high yields and low N leaching. Based on a lysimeter study, Matsumaru (1997b) demonstrated that

Table 2.4. Management measures for mitigation of NO_3 impacts on groundwater.

Technical measures:
○ Improvement of N recovery rates by new types of fertilizer / cropping systems
  / optimum coordination of crop need and fertilizer application;
○ Recycling of organic wastes;
○ Provision of land use barriers to N losses from agricultural watersheds.

Policy measures:
○ The Basic Law on Food, Agriculture and Rural Areas (enacted in 1999):
  proper use of fertilizers; improvement of soil fertility by effective use of livestock manure;
○ Designation of Nitrate-sensitive Areas.

Educational measures:
○ Farmer extension;
○ Consumer awareness of the linkage between low-input products and the environment;
○ Community-supported agriculture.

Economic measures:
○ Taxation of N discharge / fertilizer;
○ Subsidies for sustainable agriculture;
○ Display for products grown under sustainable agriculture systems, enabling consumer choice.

slow-release fertilizer could markedly increase the yield of and N uptake by upland rice and taro in sandy soil, resulting in the suppression of N leaching, compared with conventional chemical fertilizer. The catch crops following intensive farming are also effective in the reduction of N leaching (Aronsson and Torstensson, 1998; Power et al., 2000). Mulching with a plastic film can lead to the increase of crop yields and reduction of N leaching by improving the water and biological conditions in soil. Split applications of fertilizer are also options for increasing N recovery by crops. Coordination of crop need and fertilizer application must be taken into account depending on the climate and soil conditions.

Inadequate treatments of organic wastes from livestock industries have resulted in N enrichment of water (Tabuchi, 2001). Application of livestock wastes to arable land is recommended for recycling valuable nutrient resources. In addition, some consumers have tended to prefer agricultural products grown with organic fertilizers in the last decade.

Wetlands and paddy fields can be barriers to N losses from agricultural land (Tabuchi, 2001). Nitrate concentrations in stream water that had penetrated from groundwater flowing below upland fields were reduced when the water flew through paddy fields (Abe et al., 1999), because the paddy fields have a large potential of N removal by uptake and denitrification (Maeda and Ozaki, 1994).

The other measures presented in Table 2.4 are potentially useful in controlling NO_3 contamination of groundwater associated with agricultural practices. These approaches can be used either singly or in various compatible combinations.

DEVELOPMENT OF MONITORING METHODS FOR NITRATE LEACHING

3.1 REVIEW OF MONITORING METHODS IN UPLAND FIELDS

3.1.1 Introduction

Many management measures have been proposed to reduce NO_3 leaching losses in upland fields as described in Section 2.5. Conventional lysimeter facilities have been found to be very useful for the assessment of NO_3 leaching. However, the size and cost of the facilities limit the number of experimental treatments or replicates. Substitutes for this conventional method have been developed and discussed for the last few decades (National Agriculture Research Center, 1999). In this section, the monitoring methodology of NO_3 leaching and its problems were reviewed.

Chemical analysis of NO_3 in water is only routine work; the difficulty in the measurements of NO_3 losses lies in collection methods of infiltrating water (Addiscott et al, 1991). Nitrate leaching is measured by the use of several methods: lysimeters, a combination of porous suction cup samplers and tensiometers, drainage systems, groundwater monitoring, etc. (Fig. 3.1) These methods must be accurate, easy to use, and inexpensive, in order to evaluate many management measures under various environmental conditions.
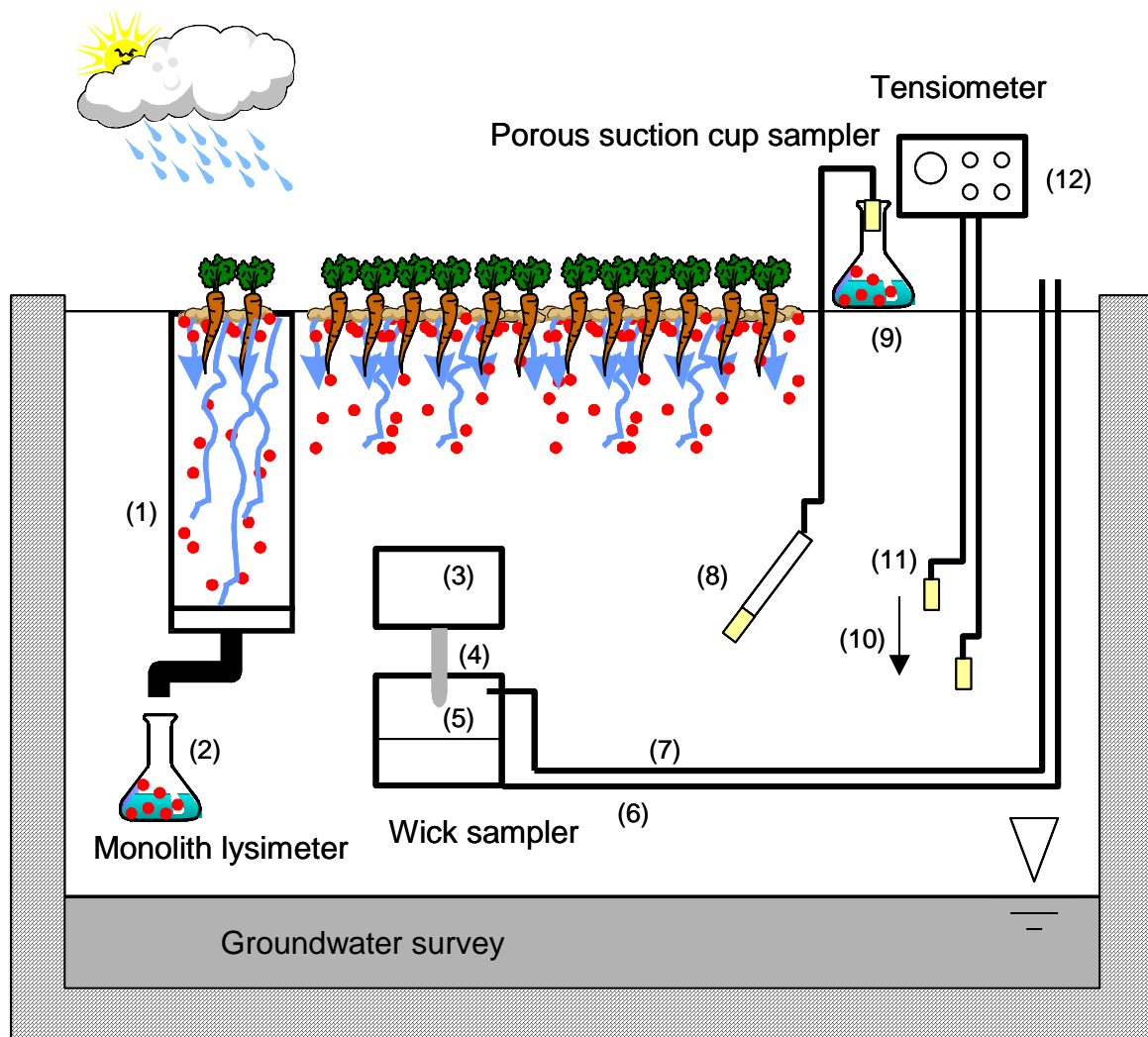
Fig. 3.1. **Monitoring methods for nitrate leaching in fields. (1) PVC pipe; (2) Leachate collection vessel; (3) Sampler bucket with wall; (4) Wicks; (5) Leachate collection vessel; (6) Sampling tube; (7) Vent tube; (8) Porous cup; (9) Leachate collection vessel; (10) Infiltrating-water flux; (11) Tensiometer; (12) Matric potential measurement system.**

3.1.2 Lysimeter facilities

Lysimeters, which are defined as blocks of soil enclosed in suitable containers and exposed to natural surroundings, have been used to determine water percolation over the past 300 yr (Bergström, 1990). The conventional lysimeters, which are made of concrete, contain repacked soil, and usually are a few meters in size, have been used for studies on N use

19

efficiency or water percolation since they can measure water balance accurately (Nonaka and Kamura, 1995; Matsumaru, 1997a, 1997b; Jinno and Honna, 1999). In constructing the lysimeter, the soil profile should be moved from the field to the lysimeter layer by layer, and the bulk density should remain as similar as possible to that of the original soil because repacking of soil affects the drainage volume and solute concentration from the lysimeter (Bergström, 1987; Bergström, 1990). Surface runoff is ignored when this method is employed. If tall plants are grown in the lysimeter, rain water may scatter at the level of the plant leaves and may not penetrate into the lysimeter. Soil in the lysimeter has less chances of becoming compacted than in actual fields.

3.1.3 In situ lysimeters

One way to overcome the above disadvantages of the lysimeter facilities would be to install in situ lysimeters in actual fields. The top of the in situ lysimeter should be placed below the tillage depth to allow management practices over the lysimeters.

Pan lysimeters are one kind of in situ lysimeters. A metal pan with a tube soldered to the raised edge of the pan is pushed into the side wall of a trench. Plastic tubing connects the pan-tube to a collection vessel (Wilson and Dorrance, 1995). The pan lysimeter collects gravitational water without disturbance of the soil structure above the pan. However, Kaneko and Yamamoto (1999) pointed out that the pan lysimeter should be improved so as to collect both matrix and gravitational flows when considering N and water balance.

Wick samplers, which use fiber wicks, are alternative systems. The wicks are self-priming and act as a hanging water column, which enable to draw water from saturated and unsaturated soil without external application of suction (Boll et al., 1992). Arimitsu (1982) used a sampler with a wall and showed that the soil column enclosed in the sampler

wall acted also as a hanging water column. However, the suction exerted by the wicks or wall is difficult to control, because it is a function of the flow rate (Boll et al., 1992). Furthermore, the water collection efficiency for wick samplers, defined as the volume of water collected by the sampler divided by the water flux from the root zone, changes with the rainfall intensity and wall height (Maeda et al., 1999). Accordingly, selection of the most suitable in situ lysimeters depends on the environment in the studied field and on the purpose of the study.

A larger in situ lysimeter can not be installed without soil disturbance above the lysimeter. Further studies should be carried out on the appropriate size of in situ lysimeters and the installation method.

3.1.4 Monolith lysimeters

Monolith lysimeters are filled with undisturbed soil (i.e., soil monolith) by driving metal or PVC (polyvinyl chloride) casings into soil. The advantages of the monolith lysimeters have been recognized for structured soils where preferential water flow often occurs. The soil enclosed in the casing is cut off from the underlying soil and a leachate collection system is attached to the base of the casing. Many different techniques for collecting soil monoliths were reviewed by Bergström (1990).

A new drilling method for the collection of soil monoliths up to a 100 cm depth was developed in Sweden (Persson and Bergström, 1991) and modified by our group in Japan so as to attach the drill system to any type of tractors (see Section 3.3). The drill consists of a steel cylinder with four mounted cutting teeth at the bottom, into which a PVC tube (286 mm i.d.) is inserted. The system is attached on the rear of a tractor. The hydraulic power of the tractor is used for pushing, lifting, and rotating the drill.

The monolith lysimeters seem to occupy an intermediate position in terms of cost

21

and convenience of use (Addiscott et al., 1991). Although large-sized monolith lysimeters often require high costs for installation and transportation, they have been extensively used because they offer more natural conditions. In contrast, medium- or small-sized monolith lysimeters (i.e., with a surface area of about 1 m^2 or less) are suitable for studies where a large number of treatments or replicates are needed (Bergström, 1990).

3.1.5 Porous suction cup samplers

Porous suction cup samplers have been widely used due to their easy installation and maintenance, and low cost (Addiscott et al., 1991). In contrast to the lysimeters described above, the porous suction cup sampler is used to obtain only solute concentrations in the soil water. The suction cup is installed in a hole prepared with a soil auger. Plastic tubing connects the suction cup to a collection vessel. For soil water sampling, suction is applied to the vessel by a vacuum pump.

For the determination of NO_3 leaching loss from soil, the water flux must be calculated using expensive tools such as tensiometers, which measure the matric potential of the soil. In addition, it remains to be determined whether the NO_3 concentration in the soil water extracted by the porous suction cup sampler is the same as that in water leaching from the soil. This method would be most useful for sampling the water likely to drain from non-structured soils with less preferential flow, and least relevant in structured clay soils (Addiscott et al., 1991).

3.1.6 Drainage systems

Tile drainage systems are often used to improve the drainage conditions in heavy clay soils. The drainage system is the best choice for the assessment of NO_3 discharge in fields where it is already established and an impermeable layer exists under the system, because it collects both preferential and matrix flows in the soil (Hayashi and Hatano, 1999). Surface runoff, interflow, and drainflow in the fields can be collected by the drainage system (Addiscott et al., 1991). However, depending on the groundwater conditions, the drainage system may give unreliable results of the total amount of water that moves from the root zone because a considerable amount of water percolates past the drainage system (Bergström, 1987).

3.1.7 Groundwater survey

Nitrate leaching losses in a field can be determined by the difference between inflow and outflow N-loadings in the groundwater below the field (Ogawa, 2000). Groundwater monitoring is important for evaluating the effects of certain agricultural practices above the groundwater. However, groundwater remediation will have already exacted a high cost or found to be impossible before groundwater contamination can be detected. Thus, this approach would not involve preemptive monitoring.

3.1.8 Soil sampling

Soil sampling using a soil auger or core sampler is a cheap and convenient option. It does not supply data on leaching rates of NO_3, but successive sampling provides information on the

changes in the amount of NO_3 in soil (Addiscott, 1991). This destructive sampling method does not allow to continue soil sampling in the same plot. Soil disturbance by soil sampling may affect the dynamics of N and water in the fields.

3.1.9 Conclusion

There is no perfect method of determining NO_3 leaching in fields at present. It much depends on the soils studied and the available resources. On fairly uniform unstructured soil, porous suction cup samplers are the best choice to determine the NO_3 concentration in the soil water while additional tools are necessary to determine NO_3 fluxes. Lysimeters offer more reliable results on N and water balance than the combination of the porous suction cup samplers and a method to determine the water flux. Larger monolith lysimeters enclosing undisturbed soil are preferable if the financial resources are sufficient, while small monolith lysimeters can be selected for studies that require a large number of treatments or replicates. In situ lysimeters are options if the financial resources are limited. Drainage collection systems can be used where impermeable clay subsoil exists under the system.

We must have answers to the following questions when selecting a NO_3-monitoring method (Maeda, 2000):

   (i)   What kind of soil is used for the study?

  (ii)   What depth do we define as leaching depth?

 (iii)   How much area is necessary for NO_3 monitoring, based on the scale of management practices?

 (iv)   What is the contribution of preferential flow to total infiltrating flow in the field?

  (v)   Does surface runoff occur in the fields?

After the NO_3-monitoring starts, the following aspects should be examined:

  (vi)   How large is the variance of replicates and thereby how many replicates are necessary?

 (vii)   How frequent time-intervals for sampling are suitable?

(viii)   How large is the impact of soil disturbance when sampling or the installation of the tools?

  (ix)   Is NO_3 concentration in sampled water the same as that in water leaching from the root zones?

3.2 WATER COLLECTION EFFICIENCY OF WICK SAMPLERS UNDER STEADY STATE FLOW CONDITIONS

3.2.1 Introduction

Wick samplers, which is one kind of in situ lysimeters as mentioned in Section 3.1.3, have been developed to measure the concentration and the flux of solute in the vadose zone (Holder et al., 1991; Boll et al., 1992). For wick samplers, hanging fiber wicks are used. The wick is self-priming and acts as a hanging water column, which enables to draw water from saturated and unsaturated soil without external application of suction (Boll et al., 1992). Wick samplers have several major advantages over other sampling techniques: (1) they provide information on the solute flux as well as the concentration, (2) they enable to collect samples continuously at the same spot, and (3) they do not need any power supply. Several researchers have studied the performance of wick samplers in terms of the water collection efficiency, which is generally defined as the volume of water collected by a sampler divided by the water flux from the root zone (Radulovich and Sollins, 1987). The water collection efficiency should be close to 100% to measure accurately the water and solute flux. Under near-saturated conditions in three kinds of soil (sand, silt loam, and clay soils) differing in their texture,

Holder et al. (1991) reported that the water collection efficiency of a wick sampler exceeded 100% at high water potentials and was less than 100% at low water potentials. Brandi-Dohrn et al. (1996) showed that the water collection efficiency was 66-88% in a silt loam soil under natural rainfall conditions, presumably due to the lack of accounting for the surface runoff. However, no satisfactory information on the factors affecting the water collection efficiency is available. Arimitsu (1982) used a sampler with a wall and showed that the soil column enclosed within the sampler wall acted also as a hanging water column, but the relation between the wall height and water collection efficiency was not described.

It is necessary for the improvement of wick samplers to better understand their performance in terms of water collection efficiency. In this study, the author used a wick sampler with a wall under constant rainfall intensity. The objective of this paper was to analyze the effects of the rainfall intensity and wall height of wick samplers on the water collection efficiency using experimental data and a numerical analysis. In addition, N leaching in an actual upland field was measured using the wick sampler and the validity of the wick sampler was discussed.

3.2.2 Materials and methods

3.2.2.1 Laboratory tests

The wick samplers were made of polyvinyl chloride (PVC) cylinders 29.8 cm in diameter with a drain hole 3.5 cm in diameter at the bottom (Fig. 3.2.1). Three capillary-wick tails (Daiki Rika, COMH-2-04, 0.8 cm in diameter, 10 cm long) hung down from the bottom. A capillary sheet (Sakata, AM-5000) was placed at the bottom to maintain a good contact with soil. Flow rates of the capillary-wick tail and the capillary sheet under saturated conditions, which were measured by hanging materials 20 cm long each on the beaker filled with water,
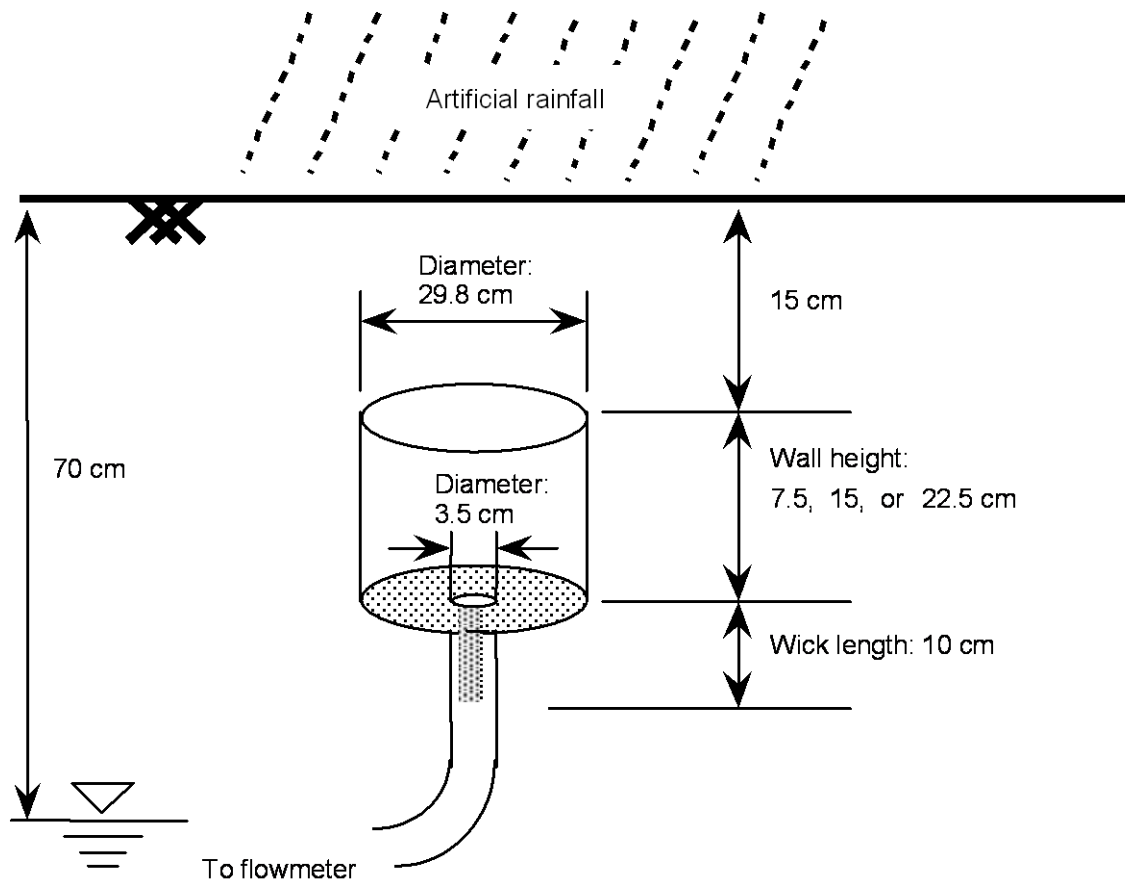
Fig. 3.2.1. **Laboratory setup to measure the water collection efficiency of wick samplers.**

were 0.14 mL s^{-1} for the tail and 0.29 mL s^{-1} for the capillary sheet 1 cm wide, respectively. The maximum flow rate through three capillary-wick tails was equivalent to a rainfall intensity of 21 mm h^{-1} on the PVC cylinder.

The effect of the wick sampler wall height on the water collection efficiency was studied under constant rainfall intensity using an artificial rainfall system (Sankei Rika, SK-7100-25). Three frame lysimeter facilities 100 cm $\times$100 cm in area and 80 cm in depth (Fig. 3.2.1) were uniformly packed with soil to reach a bulk density of 0.7 Mg m^{-3} in a greenhouse. The soil used was classified as an Andosil, Hydric Hapludand (Soil Survey Staff, 1990). Drain systems in the lysimeter facilities were set up to maintain a water table at 70 cm below the surface. The saturated hydraulic conductivity of the soil was measured by the

falling-head method. Soil water characteristic curve was obtained using the sand column method (0-10 cm) and the pressure plate method (10-100 cm). Three wick samplers with different wall heights, namely 7.5, 15, and 22.5 cm, were used. The wick samplers were set up in the soil so that the top of the wick samplers was located at a depth of 15 cm from the surface. The top of the wick sampler must be placed below the tillage depth for prolonged observations such as leaching studies from applied manure. The amount of water discharged from the wick samplers was measured using a tipping-bucket flowmeter (Hirose Rika, HR-YO-30).

Six rainfall intensities ranging from 1 to 5 mm h^{-1} (CV: < 4%) were applied for three or four days until the steady state flow was reached. Water collection efficiency of the wick sampler was calculated as the ratio of the discharge flow rate from the wick sampler to the rainfall intensity. A tensiometer (Sankei Rika, SK-5406) was also installed in the soil 15 cm apart from the wall of the 15 cm wick sampler to examine the matric potential at a depth of 15 cm.

3.2.2.2 Field tests

Wick samplers were set up, on 22 April 1997, to measure N leaching in a sweet corn field at the NARC (National Agriculture Research Center) Yawara Station in Ibaraki, Japan (36°01' N, 140°03' E). The field was 9 m×12 m and used to grow sweet corn in summer and Chinese cabbage in winter in three consecutive years preceding this test; 400 kg N ha^{-1} of chemical fertilizer was applied to the field each year. In the year of this test, 200 kg N ha^{-1} of chemical fertilizer was applied on 30 April 1997 and corn was planted from 5 May to 6 August.

Three wick samplers had walls 30, 40, and 50 cm high in triplicate. Each wick sampler had a collection chamber with a sampling tube and an air vent tube to prevent

28

pressure changes in the chamber. Wick samplers were installed as the bottom at a depth of 70 cm. To compare total N concentrations in sampled water, porous suction cup samplers (18 mm in outer diameter, 60 mm long, Nikkato Co., Japna) were installed in triplicate at the same depth as the bottom of the wick samplers.

Leachate in the collection chambers was collected immediately after rainfall events. Total N concentration of the leachate was determined using a T-N analyzer (TN-05, Mitsubishi Kasei Co., Japan). Rainfall was measured using a rain gauge (34-T, Ota-Keiki-Seisakusho Co., Japan). Total rainfall during the test period was 456 mm.

3.2.3 Results and discussion

3.2.3.1 Laboratory tests

The saturated hydraulic conductivity of the soil was 180 mm h^{-1} (0.005 cm s^{-1}). Soil water
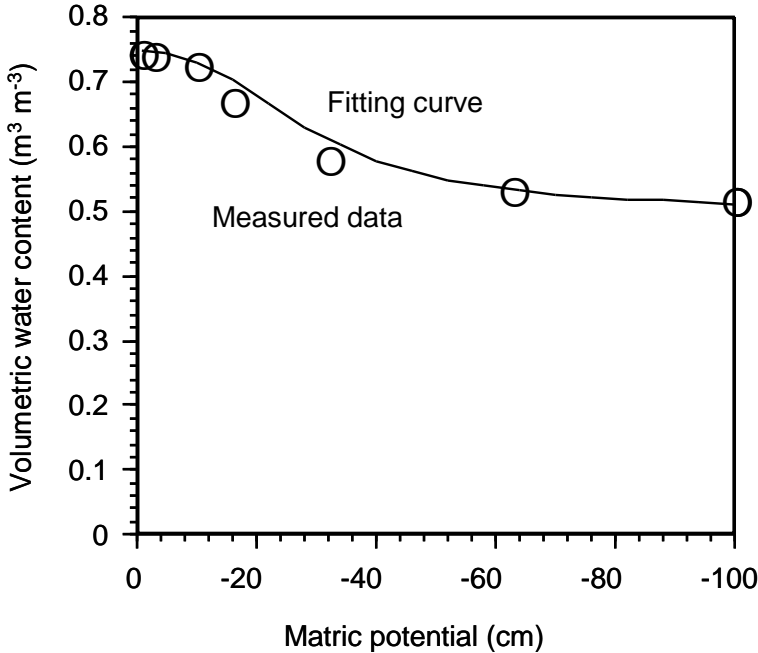
Fig. 3.2.2. **Relation between soil water content and matric potential ($\theta-\psi$).**

characteristic curve ($\theta-\psi$) was described by the following equation derived by Haverkamp et al. (1977) and the parameters were obtained by a least square fit (Fig. 3.2.2 and Table 3.2.1).

$$\frac{\theta(\psi) - \theta_r}{\theta_{sat} - \theta_r} = \frac{1}{1 + |a\,\psi|^b} \qquad [3.1]$$

where ψ is the matric potential (cm), θ_{sat} is the soil water content at saturation (m^3 m^{-3}), θ_r is the residual soil water content (m^3 m^{-3}), and a and b are parameters.

Figure 3.2.3 shows the relationship between the water collection efficiency and rainfall intensity for the wick samplers with three different wall heights. The figure shows that

Table 3.2.1. Numerical simulation parameters.

Parameter	Value	Parameter	Value
K_{sat} (mm h^{-1})	180	a	0.034
θ_{sat}	0.747	b	2.46
θ_r	0.50	c	0.21
		d	2.51

Parameters were obtained from measurements except for c and d.
Parameters c and d were obtained from Hasegawa et al. (1994).
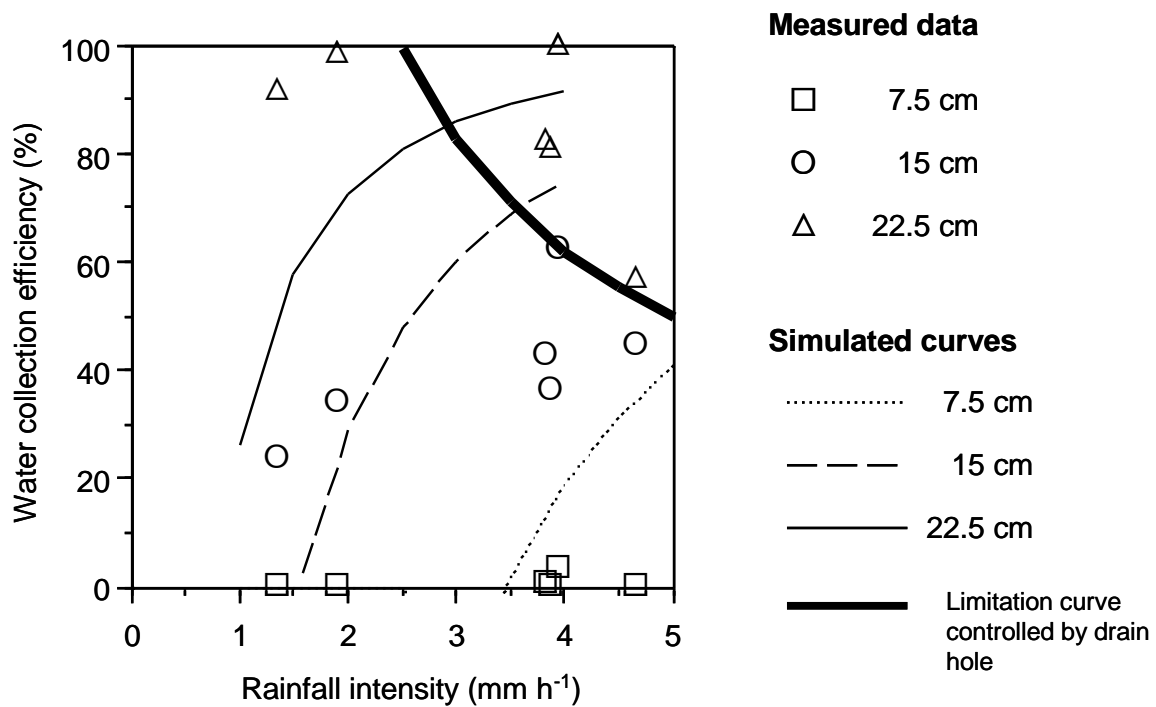
Fig. 3.2.3. **Water collection efficiency in relation to rainfall intensity for wick samplers with a wall height of 7.5, 15, and 22.5 cm.**

the water collection efficiency of the wick sampler with a 22.5 cm wall height was 60-100%

and that of the wick sampler with a 15 cm wall height was 20-60%, while that of the wick

sampler with a 7.5 cm wall height was extremely low. The water collection efficiency of the

wick sampler with a 15 cm wall height increased with rainfall intensity and leveled out at high

rainfall intensities, while the water collection efficiency of the wick sampler with a 22.5 cm

wall height decreased with increasing rainfall intensity. Holder et al. (1991) showed that the

water collection efficiency increased with increasing water potential in three kinds of soil.

Matric potential at the depth of 15 cm outside the wick sampler increased with the increase in

the rainfall intensity (Table 3.2.2). Taking it into account that a high rainfall intensity induces

a high water potential in soil, the increase in the water collection efficiency of the wick

sampler with a 15 cm wall height was in agreement with the observation of Holder et al.

(1991). On the other hand, the decrease in the water collection efficiency with rainfall

intensity of the wick sampler with a 22.5 cm wall height was considered to be due to the

restriction of the drain hole discharge when the rainfall intensity was high. The author shall

discuss this assumption later.

The author attempted to analyze the water collection efficiency using numerical

simulations in which Richards' equation (Richards, 1931) was solved by the finite element

method. Richards' equation, which consists of Darcy's law and the equation of continuity,

was formulated by the Gerlarkin finite element method (Neumann, 1973). Matric potentials

and flow rates of water in soil are simulated by a program coded in FORTRAN 77.

Darcy's law:

$$q = -k \cdot \nabla h = -k \cdot \nabla (\psi + z) \qquad\qquad [3.2]$$

Equation of continuity:

$$\frac{\partial \theta}{\partial t} = -\nabla q \qquad\qquad [3.3]$$

where q is the water flow rate (cm s^{-1}), k is the unsaturated hydraulic conductivity (cm s^{-1}), h

Table 3.2.2.   Changes of matric potential at a depth of 15 cm outside wick sampler.

Rainfall intensity (mm h^{-1})	Matric potential (cm)
1.31	−29
1.88	−
3.80	−24
3.85	−25
3.91	−22
4.62	−20

−, no data were collected because of the malfunction of the tensiometer.

is the total potential (cm), z is the vertical distance (cm) or gravity potential (cm), θ is the volumetric water content (m^3 m^{-3}), and t is time (s).

The following expression proposed by Haverkamp et al. (1977) was used for the unsaturated hydraulic conductivity − matric potential curve ($k-\psi$):

$$k(\psi) = K_{sat} \frac{1}{1 + |c\,\psi|^d} \qquad [3.4]$$

where K_{sat} is the saturated hydraulic conductivity (mm h^{-1}), and c and d are parameters.

Parameters c and d were obtained based on the measurements performed by Hasegawa et al. (1994) who used also Hydric Hapludands. The parameters were calculated by the least square fit based on the k value determined by Hasegawa et al. (1994) ($\psi > -100$ cm) and our data on K_{sat}. Equation [3.1] was used for the soil water characteristic curve ($\theta-\psi$).

Boundary and initial conditions are given as follows. Figure 3.2.4 shows the fictitious region in cylindrical coordinates, superimposed finite element network, and boundary conditions for the wick sampler with a 15 cm wall height. The same boundary conditions were used for the other wick samplers. The z coordinate in each node between 10 and 55 cm from the water table was modified for the other wick samplers: the nodes for the wick sampler with a 15 cm wall height have z coordinates of 0, 10, 20, 30, 40, 45, 50, 55, 60, 65, and 70 cm from the bottom to the top (Fig. 3.2.4), those for the wick sampler with a 7.5 cm wall height 0, 10, 22.5, 35, 47.5, 50, 52.5, 55, 60, 65, and 70 cm, and those for the 22.5 cm
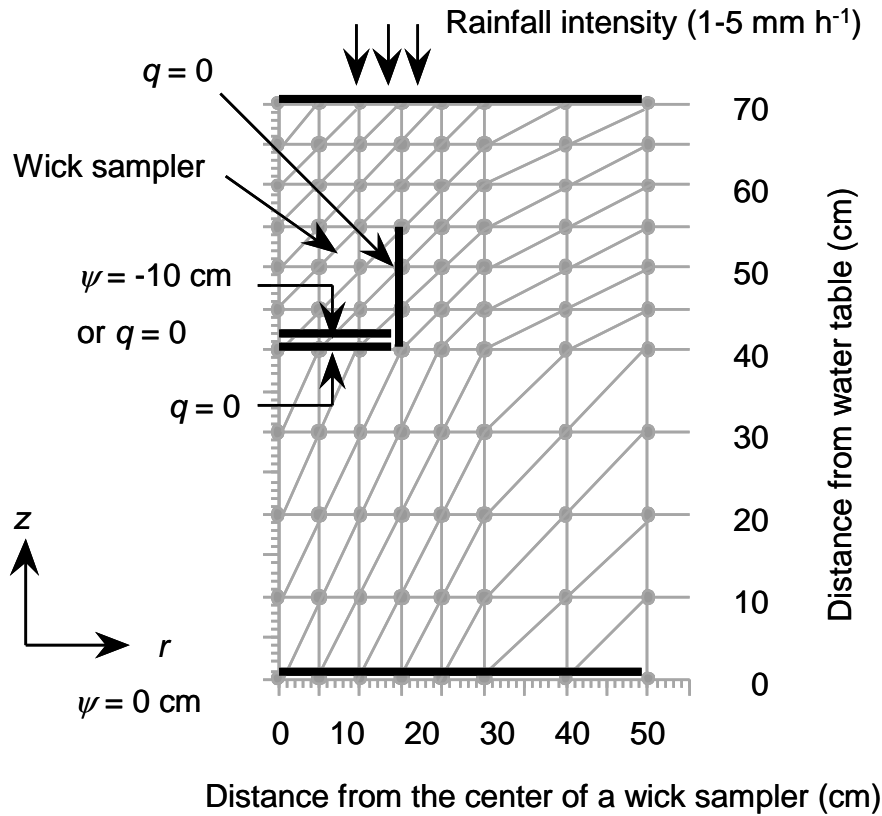
Fig. 3.2.4. **Fictitious region in cylindrical coordinates, superimposed finite element network, and boundary conditions. Condition: wick sampler with a wall height of 15 cm.**

wall wick sampler 0, 10, 17.5, 25, 32.5, 40, 47.5, 55, 60, 65, and 70 cm. r is the radius distance from the center of the wick sampler in Fig. 3.2.4.

Boundary conditions:

$\psi = -10$ cm or $q = 0$ (on the upper side of the wick sampler bottom)   [3.5]

Matric potentials at the wick sampler bottom were set up at a value of -10 cm, assuming that there is no pressure drop in the wicks and the soil-wick interface. And then, fluxes at the wick sampler bottom were set up at zero when the gradient of total potentials at wick sampler bottom became negative.

$\psi = 0$ (at the level of the water table)   [3.6]

$q = 0$ (on the wick sampler wall and the lower side of the wick sampler bottom)

     [3.7]

Initial conditions:

$\psi = 0$ (at the level of the water table)   [3.8]

$\psi = -10$ cm (except for the level of the water table)   [3.9]

Calculations were continued until the wick sampler discharge flow rate reached a steady state (about 2000 min) and then the water collection efficiency was calculated.

Numerical simulation results (lines in Fig. 3.2.3) show that the water collection efficiency increased with the wall height and rainfall intensity. In consideration that the discharge from the wick sampler drain hole is restricted, the limitation curve is expressed by the saturated hydraulic conductivity multiplied by the cross-sectional area ratio of the drain hole to the cylinder divided by the rainfall intensity. We also observed that the drain hole discharge rate was restricted when the rainfall intensity exceeded 3.5 mm h^{-1}. It is therefore necessary to design a wick sampler in which the cross-sectional area ratio of the drain hole (A cm^2) to the cylinder (S cm^2) exceeds the ratio of rainfall intensity (R mm h^{-1}) to saturated hydraulic conductivity (K_{sat} mm h^{-1}).

$A/S > R/K_{sat}$ [3.10]

The A/S ratio must exceed a value of 1/36 to avoid a restriction under a rainfall intensity of 5 mm h^{-1} because the saturated hydraulic conductivity was 180 mm h^{-1}. The A/S ratio in our experiment was 1/72. The area of the drain hole should have been twice as large as that of the used one.

The experimental values exceeded the simulated values under a low rainfall intensities. Although the wick sampler with a 7.5 cm wall height did not collect water in the experiment, simulation showed the presence of outflow when the rainfall intensity exceeded 3.5 mm h^{-1}. This discrepancy is probably due to the fact that the auther used the parameters on unsaturated hydraulic conductivity obtained from the literature. However, our argument is valid as the general trend in the experimental data was well simulated.

Since Eq. [3.2] shows that infiltrating water flows according to the gradient of the

34

total potential, it is necessary to examine the distribution of the total potential in soil for the determination of the water collection efficiency. Total potential was calculated by setting the gravity potential at a depth of 70 cm as zero and adding the matric potential and gravity potential. The distribution of the total potential inside the wick sampler must be consistent with that outside the wick sampler so that the water collection efficiency reaches 100%.

First of all, the water collection efficiency will be examined for wick samplers with a wall height of 7.5, 15, and 22.5 cm. The distribution of the matric and total potential inside and outside the three wick samplers was simulated at a low rainfall intensity (1.88 mm h^{-1}). Along with the increase of the wick sampler wall height, the gradient of the matric potential inside the wick sampler with depth became smaller (Fig. 3.2.5 a) and the distribution of the
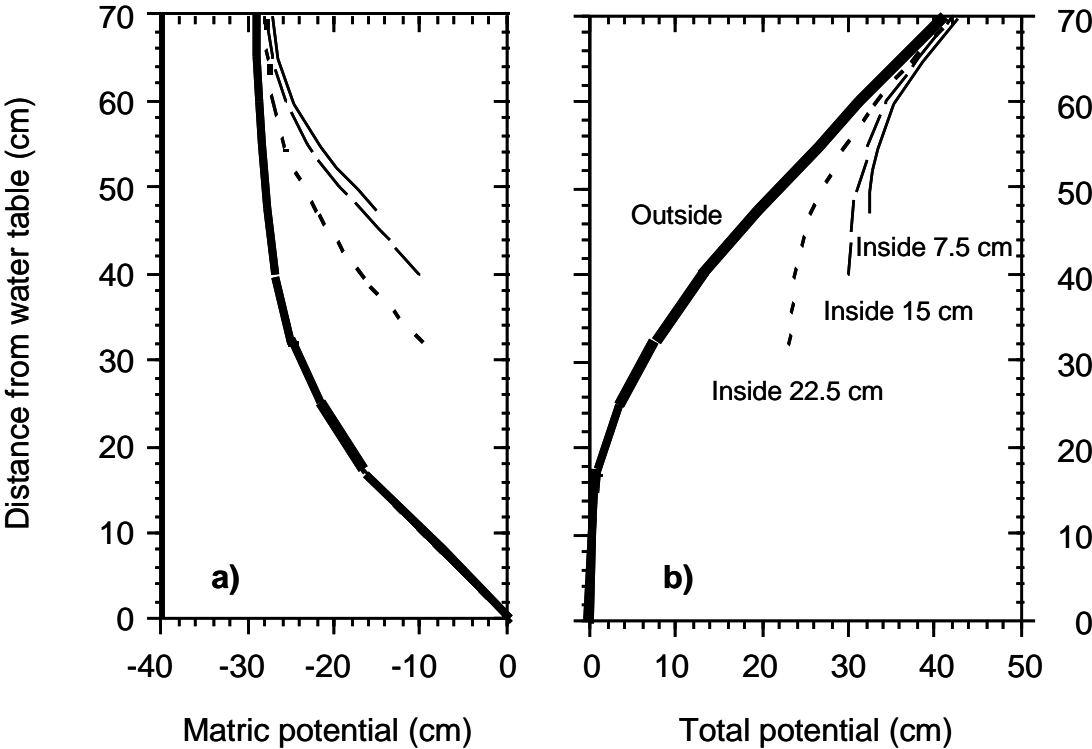
Fig. 3.2.5. **Simulated distribution of a) matric and b) total potential for wick samplers with a wall height of 7.5, 15, and 22.5 cm. Condition: Rainfall intensity, 1.88 mm h^{-1}. Gravity potential at the depth of 70 cm was defined as zero. Inside: center of the wick sampler. outside: 45 cm from the center of the wick sampler**

total potential was closer to that outside the wick sampler (Fig. 3.2.5 b). The difference in the matric potential inside and outside the wick sampler at the depth of 15 cm (i.e., at the top depth of wick samplers) resulted in a diversion of the flow from the wick samplers. The use of a higher wick wall resulted in the decrease of the difference in matric potential and consequently the diversion of the water flow was reduced. The water collection efficiency therefore increased with the increase of the wall height (see Fig. 3.2.3). There was no water flow in the wick sampler with a 7.5 cm wall height, because the matric potential at the bottom of the wick sampler with a 7.5 cm wall height was less than -10 cm exerted by wicks.

The water collection efficiency under different rainfall intensities will be examined. The distribution of the matric and total potential inside and outside the wick sampler with a 15 cm wall height was simulated under a low rainfall intensity (1.88 mm h^{-1}) and a high rainfall intensity (3.85 mm h^{-1}). Higher rainfall intensity led to a higher matric potential to a depth of 60 cm from the soil surface (Fig. 3.2.6 a). On the other hand, the values of the matric potential at the bottom of the wick sampler and at the level of the water table were fixed at -10 cm exerted by wicks and 0, respectively. As a result, under the higher rainfall intensity, the distribution of the matric and total potential (Fig. 3.2.6 b) inside the wick sampler was closer to that outside the wick sampler. It was not considered in this simulation that the discharge from the wick sampler drain hole may be restricted when the rainfall intensity was high. Taking this restriction into account, the matric potential inside the wick sampler is likely to increase due to the water flow interference at the bottom of the wick sampler.

3.2.3.2 Field tests

The author designed wick samplers in the same soil as in the laboratory tests. The water collection efficiency of wick samples with a wall height of 10, 20, 30, 40, and 50 cm was
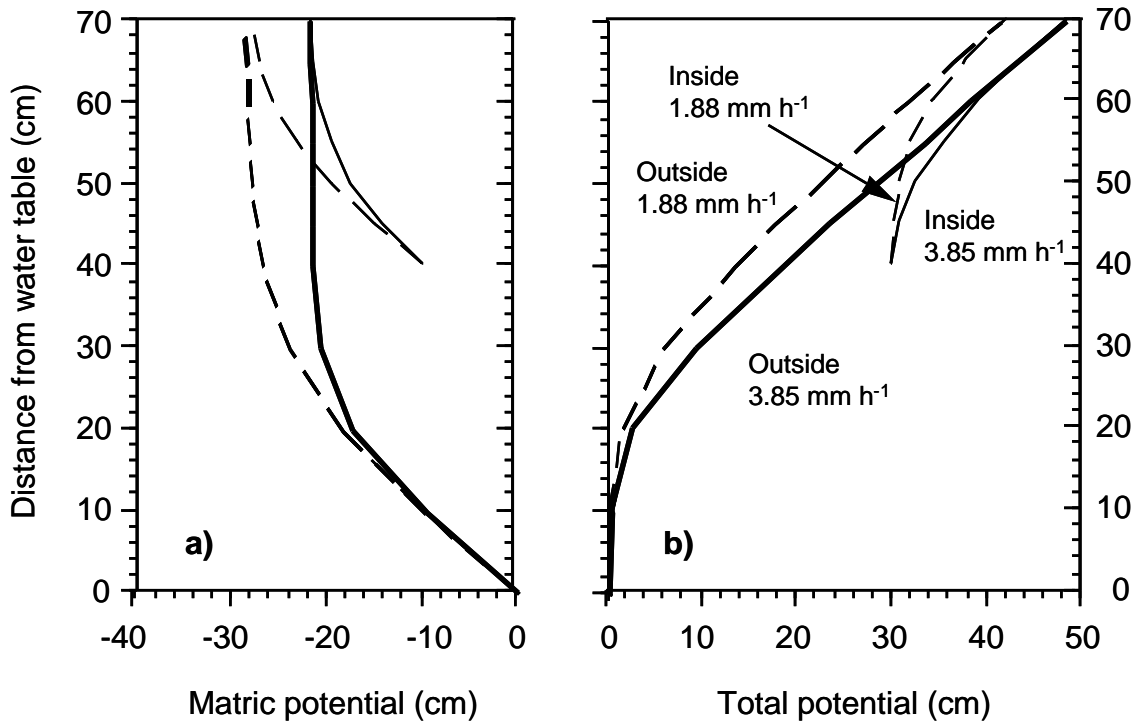
Fig. 3.2.6. **Simulated distribution of a) matric and b) total potential under the rainfall intensities of 1.88 and 3.85 mm h^{-1}. Condition: Wick sampler with a wall height of 15 cm. Gravity potential at the depth of 70 cm was defined as zero. Inside: center of the wick sampler. outside: 45 cm from the center of the wick sampler**

simulated under steady state flow conditions, assuming that the matric potential at 100-cm depth is −10 cm from observed data after heavy rainfalls in the field. The simulated results were shown in Fig. 3.2.7. It is clear that the wall height must exceed 30 cm to achieve high water collection efficiency in this condition. According to this result, wick samplers with a wall height of 30, 40, and 50 cm were used to test the performance under field conditions.

The average amount of leachate collected by wick samplers was illustrated in Fig. 3.2.8. Leacate was collected by the wick samplers only twice on 26 May and 22 June, when total amounts of rainfall for 48 h before the rain stoppage exceeded 70 mm. This is consistent with Hasegawa et al. (1994) who reported downwards water flux in the similar soil during the period from June to August was associated with rainfall that occurred twice and reached 65.0 mm and 85.5 mm for 24 h. The higher wall of the wick sampler, the more amount of the leachate was recorded, as indicated by the laboratory test.

37
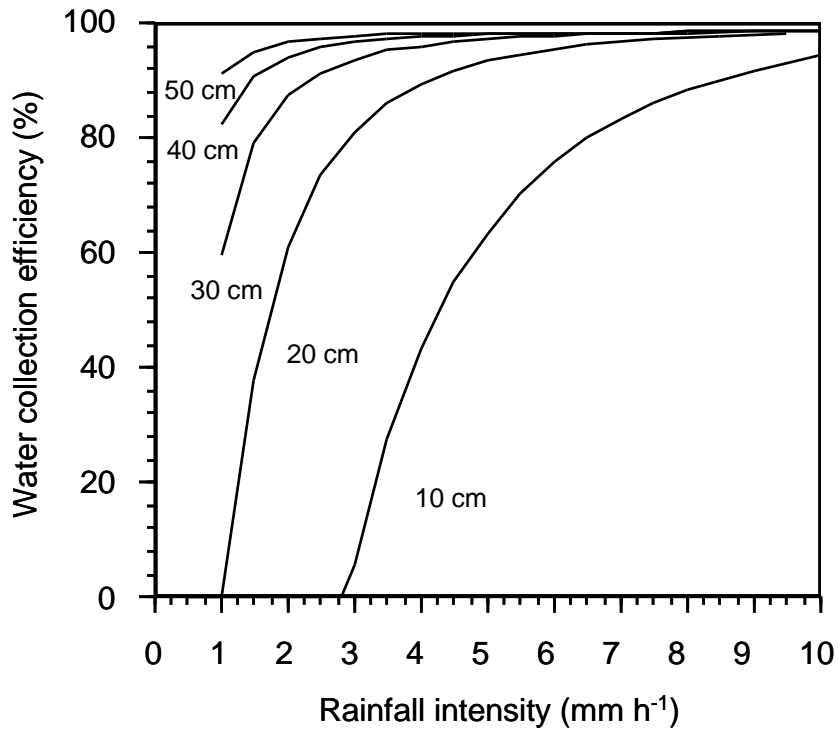
Fig. 3.2.7. Simulated water collection efficiency in relation to rainfall intensity for wick samplers with a wall height of 10, 20, 30, 40, and 50 cm. Gravity potential at the depth of 100 cm was defined as zero.
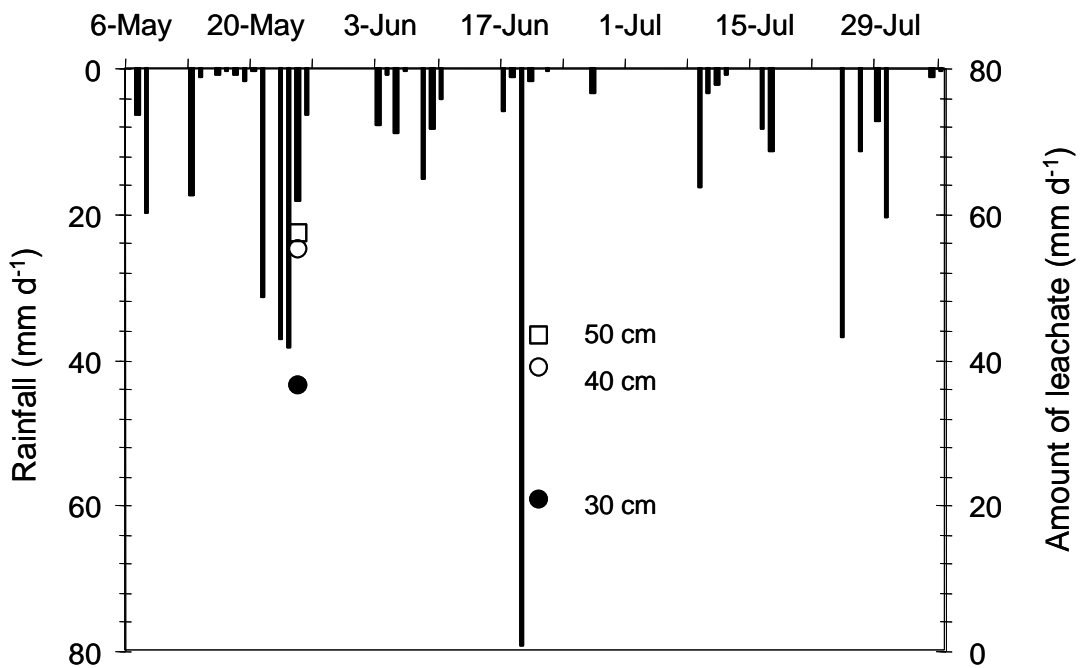
Fig. 3.2.8. Amount of leachate collected in wick samplers and rainfall distribution during corn planting. Test period: from 5 May to 6 August 1997.

The variance in the amount of leachates, which is plotted with the amount of rainfall for 48 h before rain stoppage in Fig. 3.2.9, decreased with the wall height of the wick sampler. This reason is not clear but the higher wall height may make the system stable.

There is no vital difference in mean, maximum, and minimum total N concentrations between the wick and porous suction cup samplers (Table 3.2.3). In contrast to this result, Steenhuis et al. (1995) documented that wick samplers could represent water through the vadose zone accurately in a loamy and clay loam soil, whereas porous suction cup samplers did not due to occurrence of water movement along the sampler tubes in the loamy and failure in catching preferential flow in the clay loam soil. Because the field in the present study has received the same management for 4 yr, the influence by the variety of infiltrating water flow may have been masked. The difference in maximum and minimum concentrations
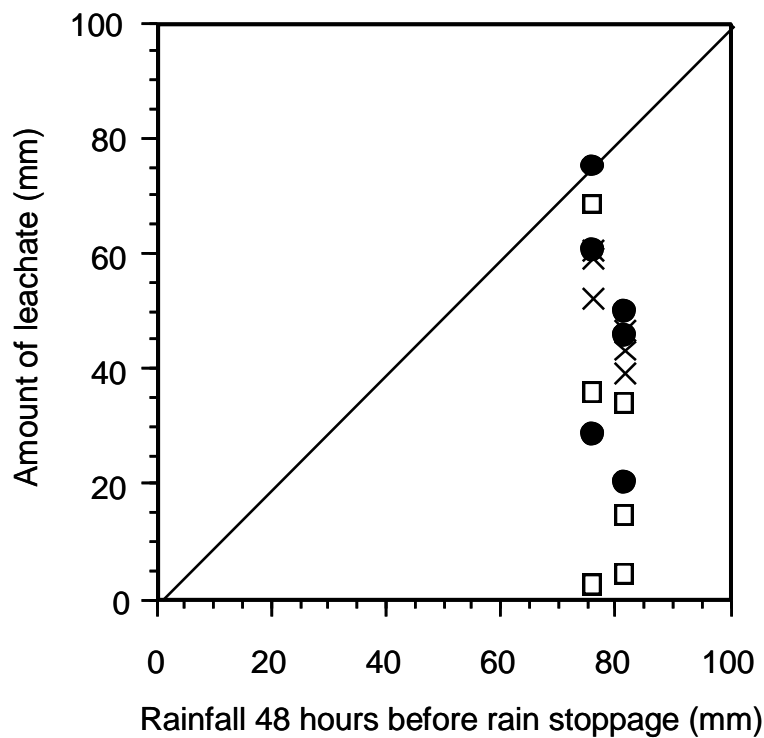
Fig. 3.2.9. Amount of leachate collected in wick samplers differing in wall height and rainfall 48 h after rain stoppage. Wall heights of wick sampler were 30 cm (□), 40 cm (●), and 50 cm (×).

Table 3.2.3. Mean, maximum, and minimum total N concentrations in water sampled by wick and porous suction cup samplers.

Type	Wall height (cm)	N	Mean	Maximum (mgN L^{-1})	Minimum
Wick sampler	30	3	59.7	83.6	45.8
	40	3	54.3	67.8	49.6
	50	3	61.0	72.6	54.4
Porous suction cup sampler		3	63.3	91.0	46.9

Sampled on 26 May 1997.

decreased with increasing the wall height of the wick sampler, indicating also that the higher wall height may make the system stable.

The total N concentrations, which were mostly NO_3-N, in leachates by all wick samplers were substantially higher than our water quality standard of 10 mg L^{-1} in groundwater or for drinking water (Table 3.2.3). To prevent the groundwater contamination, NO_3 concentration in this leachate is recommended to be less than 10 mg N L^{-1}, although the water with high NO_3 concentration may be diluted in groundwater and be mitigated by denitrification in groundwater. Total N leaching from the corn field was estimated to be 31 kg ha^{-1} for the wick sampler with 30-cm wall, 61 kg ha^{-1} for that with 40-cm wall, and 67 kg ha^{-1} for that with 50-cm wall. These values account for 16%, 31%, and 34% of the applied N for the sweet corn in the field, respectively. Sweat corn absorbed only 62 kg ha^{-1}, accounting for 31% of the applied N. On the N balance, considerable amount of N is unknown; part of this N may be retained by soil or lost by denitrification.

3.2.4 Conclusion

When both the rainfall intensity and wall height of the wick sampler increased, the distribution of the total potential inside the wick sampler became closer to that outside the wick sampler. As a result, the water collection efficiency, which is an indicator of the

performance of wick samplers, increased with the increase of the rainfall intensity and wall height. The author also suggested that the cross-sectional area ratio of the drain hole to the cylinder should be taken into account. Although these trials were performed under steady state flow conditions and using repacked soil, the results may contribute to the development and the use of wick samplers. Also in the field studies, the water collection efficiency of wick samplers increased with the increase of wall height. Total N concentrations in leachate collected by the wick samplers were the similar to those in soil water collected by the porous suction cup samples. Nitrogen leaching was estimated at 30-70 kg ha^{-1} in the sweet corn field, which received 200 kg N ha^{-1} as chemical fertilizer.

3.3 DEVELOPMENT OF A MONOLITH LYSIMETER FOR LEACHING STUDIES

3.3.1 Introduction

Monolith lysimeters were described in Section 3.1.4. Many methods for collecting soil monoliths employ hydraulic pressure to push the casings into the soil (Bergström, 1990; Shipitalo and Edwards, 1993; de Rooij and Wit, 1996), while the soil around the casing must be removed to reduce friction. In other cases, a large hammer was dropped onto the top edge of a casing to push it into the soil (Moyer et al. 1996). The method described here is an improvement of the method developed by Persson and Bergström (1991), which uses a drilling technique to remove the soil around a casing instead of pushing it down. The main advantage of this method is that the soil is less disturbed than by other methods because of the low friction between the soil and the casing-wall. However, this drill unit could not be attached to any types of tractors because the unit was mounted on the front-end loader of a tractor, which selected a certain type of tractors and was costly. Therefore, the author modified the Persson and Bergström model to attach the whole drill unit to the three-point

hitch system, which is a standard for all tractors, on the rear of a tractor.

One problem related to lysimeter studies is the potential 'sidewall flow', which refers to the process that water or solute runs along the lysimeter wall, if there is a significant gap between the soil and the lysimeter-wall. This problem affects solute movement in the same way as preferential flow. Accordingly, the sidewall flow in a monolith lysimeter collected by the developed drill system was evaluated using two anions as tracers of water.

3.3.2 Development and performance of a drill system

This drilling method enables to collect soil monoliths up to a 100 cm depth. This drill system consists of 3 parts: (i) a system-lifting part; (ii) a drill-rotating part; and (iii) a drill-pressing/lifting part (Fig. 3.3.1). The hydraulic power of a tractor is used for pressing, lifting, and rotating the drill; the Power Take-Off system (PTO) is used for lifting the whole system when the system is transported or the drill-cylinder is installed. Since the whole system is mounted on a Massey Ferguson 3060 machine (main hydraulic pump: 50 L min^{-1}; 180 kgf cm^{-2}, second pump: 29 L min^{-1}; 175 kgf cm^{-2}) in our experiments, the moment for the rotation was 479 kgf m (4.6 kN m) at 30 r.p.m. and the forces for pushing and lifting the drill-unit were 3.4 t (34 kN) and 2.4 t (23 kN), respectively (see APPENDIX). The system is 1234 mm wide, 1000 mm deep, and 2371 mm high when the cylinder-rod is housed at the lowest position (Fig. 3.3.1). This height is appropriate for transporting the drill system on Japanese roads by truck (maximum legal height: 3.8 m including the height of a truck).

The drill unit consists of a steel cylinder with four mounted cutting teeth at the bottom, into which a polyvinyl chloride (PVC) casing (VP300; 1180 mm long; 286 mm i.d.) is inserted (Fig. 3.3.1). The cutting teeth and the PVC casing have the same inner diameter.
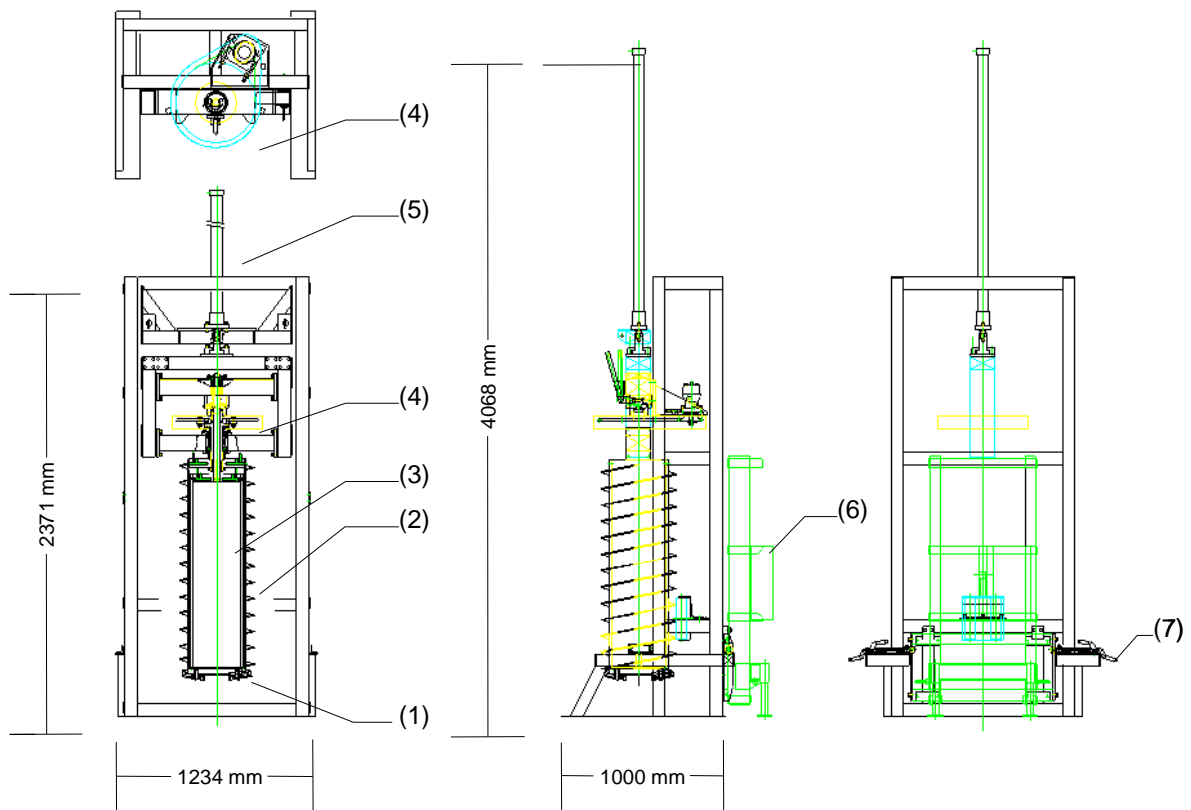
Fig. 3.3.1. Schematic diagram of the drilling unit for collection of soil monoliths. (1) Cutting teeth; (2) Drill cylinder; (3) PVC casing (VP300); (4) Gear box; (5) Extension rod; (6) System lift connected to PTO (Power Take-Off); (7) Lock for lift-up prevention.

3.3.3 Collection process and placement of soil monoliths

Manipulation procedures of the drill system are presented in Fig. 3.3.2 and Fig. 3.3.3. During the transport of the whole drill system to a sampling field, the cylinder-rod is housed at the lowest position as shown in Step1 (Fig. 3.3.2). In the field, the cylinder-housing is lifted by extension of the cylinder and then the housing unit is connected to the upper beam of the frame (Fig. 3.3.3a). In Step 2, the gearbox is lifted by compressing the cylinder-rod, to make room for fixing the PVC casing. After fixing the PVC casing (Fig. 3.3.3b), the whole system

is further lifted by operating a system-lifting part to install the drill cylinder outside the PVC casing (Step 3; Fig. 3.3.3c and d). The whole system is settled on the ground by connecting the frame with the tractor to prevent the system from being raised by the counterforce to pressing the drill (Step 4; Fig. 3.3.3e). After balancing the whole system upright, the drill rotates around the PVC casing with being pressed (Fig. 3.3.3f). The soil shaved off by the tooth of the drill is transferred to the soil surface through the plane of the drill. The soil monolith inside the drill does not rotate while the drill goes down (Step 5). Removal of the soil on the plane may facilitate the soil transport (Fig. 3.3.3f). When the bottom of the PVC casing reaches a 1060 mm depth, the drill rotates together with the PVC casing to shear the soil inside the casing from the underlying soil (Step 6). Lastly, the soil monolith enclosed in the drill unit is lifted out of the hole and is separated from the drill cylinder on the ground in the inverse steps.

The time required for attaching the whole system to the tractor is approximately 60 min. Sampling times for a soil monolith up to a 100-cm depth of Andisoils (Kuroboku soil), Ultisols (Red soil), and Entisols (Sandy soil) are approximately 20 min, 1.5 h, and 2 min, respectively. For the Entisols, the bottom of the soil monolith collected should be covered at the base of the hole before lifting the drill, to prevent the soil from falling out of the PVC casing.

The soil at 60 mm from the bottom is replaced by a sheet of nylon mesh (200 mesh; NXXX 25, NBC Industry), 3 kg (ca. 30 mm high) of clean gravel (particle size: 5-10mm), and a stainless punched (about 1000 holes with a diameter of 5.5 mm) dish 30 mm high, to prevent soil particles from leaching out of the monolith. The resulting monolith is placed into a bottomed PVC pipe (VU350) with a drain below the ground (Fig. 3.3.4). The drained water from the soil monolith is led through the PVC pipe (VP30) to the collection vessel in a basement. Gallon glass (3.8 L, equivalent to 59 mm) or polyethylene bottles (20 L, equivalent to 311 mm) are used as the collection vessels. This whole system is called a monolith
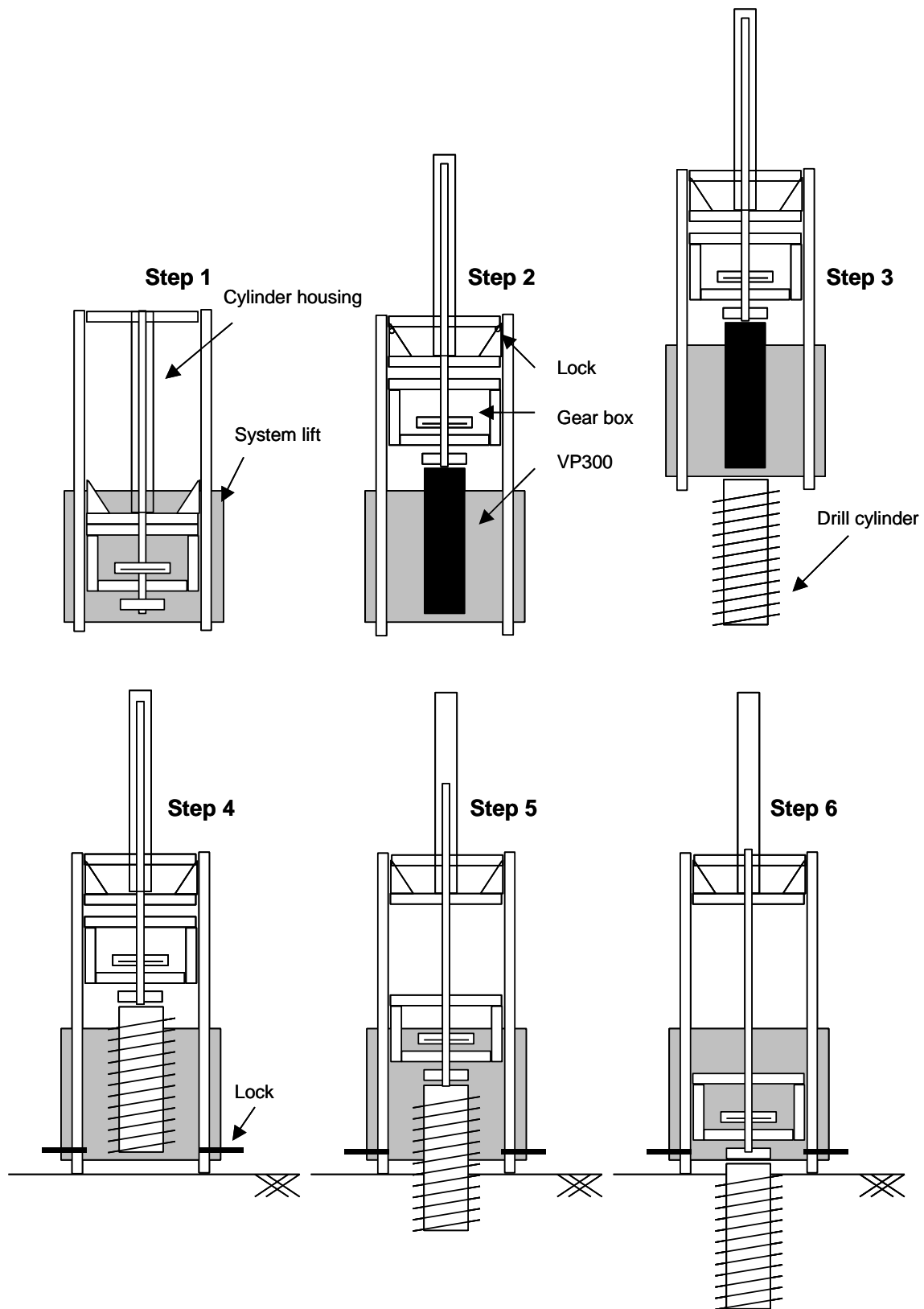
Fig. 3.3.2. Basic movements of the drilling system for the collection of soil monoliths. Step 1: Transporting position; Step 2: Setting of the PVC casing; Step 3: Setting of the drill cylinder; Step 4: Starting position; Step 5: Collecting the monolith; Step 6: Shearing the monolith from the underlying soil.

a) Lock the cylinder-housing at the upper beam of the frame

b) Fix the PVC casing

c) Install the drill cylinder outside the PVC casing

d) Lock the drill cylinder

e) Place and balance the system on the ground

f) Press the drill down with rotation; Removal of the soil on the plane

Fig. 3.3.3.   Manipulations of the drilling system for the collection of soil monoliths.
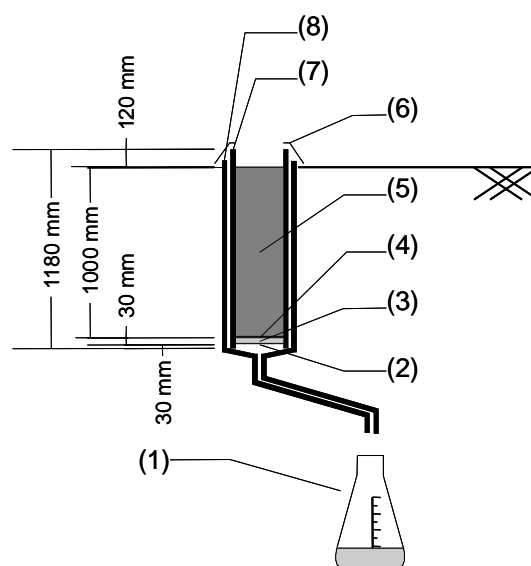
Fig. 3.3.4. **Structure of a monolith lysimeter station for leaching studies.** **(1) Leachate collection vessel; (2) Bottom-supporting dish (SUS); (3) Gravel (5-10 mm); (4) Nylon mesh (200 mesh); (5) Undisturbed soil; (6) Collar to maintain rainproof conditions; (7) PVC tube (VP300); (8) PVC tube (VU350).**

lysimeter. The soil surrounding the monolith lysimeters is managed in the same way as in the lysimeters to secure similar conditions to those for crops in the fields, including adequate solar radiation.

3.3.4 Effect of sidewall flow in a monolith lysimeter

3.3.4.1 Materials and methods

A soil monolith, 100 cm long, was collected at the Yawara Experimental Station of NARC on 20 December 2000, and was installed into a monolith lysimeter station at NARC (Kannondai) on 4 January 2001. The soil is classified as an Andisoil according to the USDA soil classification system (Soil Survey Staff, 1999). Two solutes were applied to different parts of the soil surface of the soil monolith. No plant was grown on the lysimeter during the test

period. Ten mmol of KBr and KCl were dissolved in each 50 mL of distilled water. The KBr and KCl solutions were sprayed on the equally large annular and central disc zones of the lysimeter surface, respectively. Thereafter, 1 L of distilled water, which is equivalent to 15.6 mm for the lysimeter, was irrigated using a watering pot (taking >30 min) twice in a day (9:30 a.m. and 3:30 p.m.) on 5-7 January, 9-20 January, 22-24 January, and on 5-7 April (21 d). No water was irrigated on 26-27 January, 17-18 February, 1 March, 4-6 March, and 26 March (9 d). One liter of water was irrigated at 9:30 a.m. on the other days from 4 January to 4 April (64 d). The lysimeter also received rainfall.

3.3.4.2 Results and discussion

The total amount of water input by irrigation (1591 mm) and precipitation (275 mm) was 1866 mm while that of water leached out of the lysimeter was 1552 mm (Fig. 3.3.5). The difference between the input and the output corresponded to the full amount of evaporation and increase in the water content of the soil monolith throughout the test period. Since the water holding capacity of a similar soil was estimated to be ca. 620 mm (Hasegawa, 2000), the water input was sufficient to replace the soil water in the monolith twice.

Bromide (Br) concentration in the leachate increased after ca. 400 mm of water input whereas the chloride (Cl) concentration decreased towards 400 mm and thereafter increased (Fig. 3.3.6). The recovery rates of Br and Cl were 87.3% and 421%, respectively. The peaks of the breakthrough curves of Br and Cl appeared at 600 mm and 800 mm, respectively. Preferential transport of Br was not observed in this test, although Br was applied near the edge of the lysimeter. Again, the accumulated leachate showing the Br peak indicates that the water holding capacity of this monolith was ca. 600 mm, which was well consistent with an estimate made by Hasegawa (2000). These results led to the conclusion
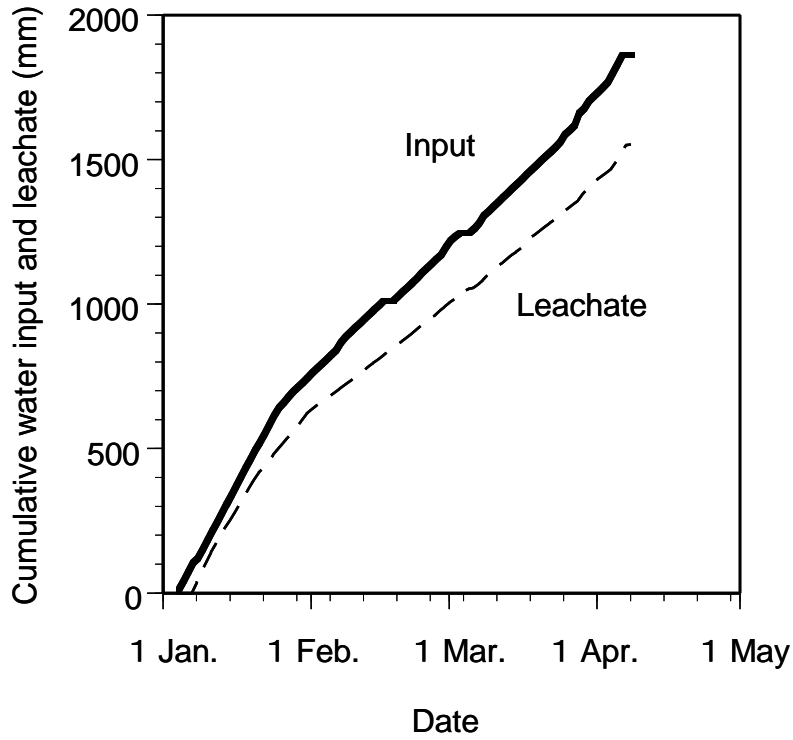
Fig. 3.3.5. Accumulated amounts of water input and leachate from a lysimeter.
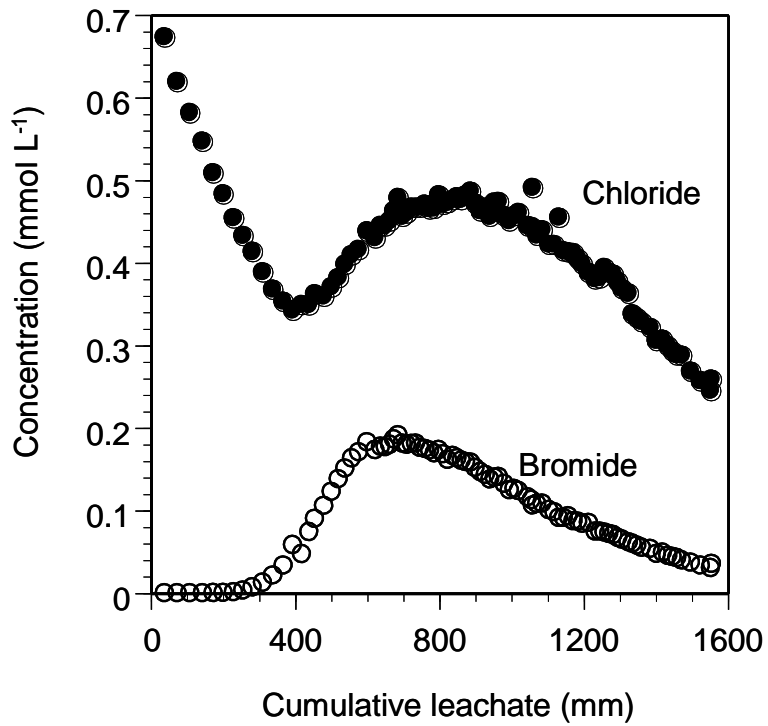
Fig. 3.3.6. Bromide and chloride concentrations vs. cumulative leachate from a lysimeter.

49

that the 'sidewall flow' should be small in this monolith. In contrast to Br, the recovery rate of Cl was remarkably high because agricultural soil usually contains a large amount of Cl derived from chemical fertilizers KCl or NH_4Cl. The Cl that was derived from fertilizer and occurred in the soil was presumably eluted from the monolith, together with Cl applied in this test. Thus, the initial distribution of Cl in the soil may have caused the difference in the peak appearances of Cl and Br.

To sum up, sidewall flow in terms of soil sampling was not obserbed for Andisols. This problem is more serious for some clay soils or soils with a very high organic matter content and may occur after the soil shrinks under natural dry-wet cycles (Bergström, 1990). Bergström et al. (1994), who analyzed this problem for the same kind of monolith lysimeters, concluded that the effects of sidewall flow on solute movement were negligible for clay and sandy soils. This problem, however, must be further assessed for other Japanese soils.

APPENDIX:

Calculation of the forces and moment of the drill powered by MF3060:

The main pump was used for rotating the drill.

Flow rate of oil in the main pump (S_m): $\quad$ 50 L min^{-1} = 0.83×10^{-3} m^3 s^{-1}

Oil pressure in the main pump (P_m): $\quad$ 180 kgf cm^{-2} = 1.76×10^7 N m^{-2}

Work for the main pump (W_m): $\quad$ $W_m = S_m \times P_m$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad = 0.83 \times 10^{-3} \times 1.76 \times 10^7 = 14.6$ kW

$\therefore$ When the drill was rotated at 30 r.p.m. (= π rad s^{-1}, R),

The moment of the drill: $\quad\quad\quad\quad$ $W_m/R = 4.6$ kN m

The second pump was used for pressing and lifting the drill.

Oil pressure in the second pump (P_s): 175 kgf cm^{-2} = 1.72×10^7 N m^{-2}

Diameter of the cylinder-rod (D_1): 2.8 mm = 28×10^{-3} m

Inner diameter of the cylinder-housing (D_2): 5.0 mm = 50×10^{-3} m

$\therefore$ Force for pressing: $P_s \times D_1{}^2 \pi/4 = 1.72 \times 10^7 \times (50 \times 10^{-3})^2 \pi/4 = 34$ kN

Force for lifting: $P_s \times (D_1{}^2 - D_2{}^2) \pi/4 = 23$ kN

NITRATE LEACHING IN AN ANDISOL TREATED WITH DIFFERENT TYPES OF FERTILIZERS

4.1 INTRODUCTION

Nitrate leaching from arable land, which causes contamination of groundwater, has become a matter of worldwide concern. In Japan, NO_3-N concentrations exceeding 10 mg L^{-1} were found in 6.3% of groundwater samples investigated in 1998 (Environment Agency, Japan, 1999). Excessive use of readily available conventional chemical fertilizers and livestock manure on agricultural land is the main source of groundwater contamination (Thomsen et al., 1993; Adams et al., 1994; Chang and Entz, 1996). To reduce N loss from agricultural land, it is essential to substitute slow-release fertilizers for readily available fertilizers and to establish proper application rates of manure. However, little information is available on the impact of such fertilizers on NO_3 leaching in Japanese Andisols.

Application of livestock manure to arable land is recommended for recycling valuable nutrient resources. Some consumers prefer agricultural products grown with organic fertilizers. Nitrate leaching is affected by the type of manure, because of the different amounts of available N (Beckwith et al., 1998). Compost, which has an advantage in handling as water content and offensive odors are reduced and pathogens are eliminated, is a major product of livestock manure in Japan. Because most livestock farmers do not have sufficient farm land for recycling manure, excessive manure must be transferred to other farmers (Harada and

Yamaguchi, 1998). Accordingly, livestock compost has been applied not only to pastures but also to vegetable fields, where fertilization is usually more intensive. Although compost is considered as a slow-release fertilizer, excessive application may cause unintended NO_3 leaching (Gerke et al., 1999). Residual N from previously applied manure is mineralized and may be available for leaching in continuously managed fields (Angle et al., 1993; Thomsen et al., 1993; Bergstöm and Kirchmann, 1999). Although many studies have clarified the relationship of NO_3 leaching to manure application in grasslands, few studies have been done in intensive vegetable cropping systems.

In Japan, slow-release fertilizers have been used to save labor in farming systems where frequent application of chemical fertilizer is needed and to increase N recovery by crops (Saigusa et al., 1993). Substitution of slow-release fertilizers for readily available conventional fertilizers has shown a decrease in N leaching in short-term studies (Sakata et al., 1995; Matsumaru, 1997). Although NO_3-N concentrations in subsurface flow under pastures increased more rapidly with readily available fertilizer than with slow-release fertilizers, NO_3-N concentrations for both systems continued to increase even after 10 yr (Owens et al., 1992).

Nitrate leaching may be influenced by local conditions such as climate and soil type, as well as fertilization practice. Nitrate concentrations of leachate increased with increased precipitation in Wisconsin (Andraski et al., 2000) and Denmark (Eriksen et al., 1999), whereas they decreased in Minnesota (Randall et al., 1997). Bergström and Johansson (1991) noted that NO_3-N concentration was not significantly affected by watering treatments, but substantially by soil type (texture and organic matter content). The climate in most of Japan belongs to the Asian monsoon category, in which average annual rainfall reaches 1800 mm (Kuwabara, 1989), and heavy rainfall events often occur with typhoons in summer. More than half of the upland fields in Japan are covered with Andisols (Soil Conservation Survey Conference, 1991), which are volcanic ash soils. Andisols have special properties such as high

anion exchange capacity, low bulk density, and high organic matter content (Shoji et al., 1993; Kimble et al., 2000), which have a profound effect on NO_3 leaching.

The present study examined the effects of repeated application (over 7 yr) of different fertilizers (swine compost, coated urea, ammonium N, and no fertilizer) to an Andisol on NO_3 leaching under the Japanese climate. Nitrate concentration in soil water at 1-m depth was evaluated with an N and water balance equation, which calculates the risk of groundwater contamination by nitrogen (OECD, 1999). Total N and $\delta^{15}N$ in the topsoils and the vertical distribution of NO_3-N and $\delta^{15}N$ in soil water were studied after 6 yr of continuous fertilizer application.

4.2 MATERIALS AND METHODS

4.2.1 Experimental site

Field experiments were set up in April 1994 and continued for 7 yr. The experimental field was located at the Yawara Experimental Station of the National Agricultural Research Center, Ibaraki, Japan ($36^o01'$ N, $140^o03'$ E). Prior to this experiment, komatsuna (*Brassica campestris* L. var. *perviridis*) had been grown in the whole field at low fertilizer application rates of 48 kg ha^{-1} N, 21 kg ha^{-1} P, and 40 kg ha^{-1} K. The soil is classified as an Andisol (Hydric Hapludand) according to the USDA soil classification system (Soil Survey Staff, 1999). The soil texture was loam in the Ap horizon (0-22 cm), and clay loam in the AB (22-34 cm), Bw (34-60 cm), $2A_1$ (60-78 cm), and $2A_2$ (78-100 cm) horizons. Soil texture in layers deeper than 1 m were as follows: 1-2.8 m: clay loam, 2.8-3.75 m: clay, 3.75-3.9 m: sandy clay, and 3.9-4.4 m: sandy clay loam. The soil structures were weak subangular blocky to a depth of 60 cm and subangular blocky from 60 to 100 cm. Hydraulic conductivity was quite high to a depth of 1 m (Table 4.1). Although no runoff was observed throughout the experimental

period, water was sometimes ponding on the soil surface after heavy rainfalls. The groundwater usually fluctuated around 3 to 4 m below the soil surface and was sometimes shallower after heavy rainfall. Selected soil properties are listed in Table 4.1.

Table 4.1.   Selected properties of the investigated soil.

Soil profile (cm)	pH(1:2.5)	CEC^b ($cmol_c kg^{-1}$)	AEC^c ($cmol_c kg^{-1}$)	$T-N^d$ ($g kg^{-1}$)	$T-C^d$ ($g kg^{-1}$)	C/N ratio	$\delta^{15}N^e$ (‰)
Chemical properties of the topsoil (n=3)[a]							
0–15	4.6 ± 0.0^f	36.7 ± 0.6	3.4 ± 0.3	4.0 ± 0.1	44.9 ± 1.6	11.3 ± 0.1	$+5.9 \pm 0.1$

Soil profile (cm)	Hydraulic conductivity[h] ($mm\ h^{-1}$)	Water content at tension[i] ($m^3 m^{-3}$)			
Physical properties of the soil (n=2)[g]					
		0 kPa	1 kPa	10 kPa	100 kPa
15–20	5.6	0.72	0.68	0.43	0.35
35–40	4.1	0.72	0.71	0.54	0.43
55–60	3.5	0.75	0.73	0.54	0.45
75–80	5.3	0.75	0.72	0.53	0.47
95–100	2.9×10^{-1}	0.56	0.55	0.46	0.36
195–200	6.9×10^{-4}	—	—	—	—
295–300	1.7×10^{-4}	—	—	—	—
395–400	7.0×10^{-3}	—	—	—	—

[a] The topsoil sample was obtained before the start of the experiment (in April 1994) and air-dried for 2 weeks.
[b] Cation exchange capacity (CEC) for the soil was measured at pH 7 by the Schollenberger method (Kamewada, 1997).
[c] Anion exchange capacity (AEC) for the soil was measured at the soil pH (Rowell, 1994)
[d] Total N and C content in soil was analyzed with a NC analyzer (NC-95A, Sumitomo Bunseki Center, Japan)
[e] $\delta^{15}N$ was measured with an ANCA-SL mass spectrometer (Europa Scientific, UK; Yoneyama and Yoshida, 2000).
[f] Mean ± SE.
[g] The soil cores were sampled in August 1996.
[h] Saturated hydraulic conductivity was measured by the falling-head method (Katou, 1997).
[i] Water content at different tensions was obtained by using the sand column method for 0 and 1 kPa and the pressure plate method for 10 and 100 kPa.

4.2.2 Experimental design

The four N fertilizer treatments (SC: swine compost, CU: coated urea, AN: ammonium N, and NF: no fertilizer) with 2 replicates for each were initiated in the spring of 1994 (Table 4.2). Eight plots (8 m by 7 m each) were installed in a 0.12 ha field. Each plot was at least 5 m apart and surrounded by wooden boards, which were 15 cm above and 30 cm below the soil surface, to prevent soil in different plots from mixing. The outer area for the experimental plots was treated by the same procedure as AN plots, which is conventional management for farmers in this region (Ibaraki Agricultural Center, 1998), to minimize the difference in the amount of solar radiation for crops on the edge of plots. Fertilizers were applied twice a year just before crop cultivation at rates of 800 kg N ha^{-1}yr^{-1} for the SC plots and 400 kg N ha^{-1} yr^{-1} for the AN and CU plots during the experiment except for the first year, when N was applied at rates of 1000 kg ha^{-1} yr^{-1} for the SC plots and 500 kg ha^{-1} yr^{-1} for the AN and CU plots

Table 4.2. Crop rotation and N application rate and δ^{15}N value of the different N-sources.

Year	Growing period	Crop	Compost (SC)	Coated urea (CU)	Ammonium N (AN)
			Application rate of N (kg ha^{-1})		
1994	May – Aug.	sweet corn	600	300	300
	Sep. – Nov.	Chinese cabbage	400	200	200
1995–1996	May – Aug.	sweet corn	400	200	200
	Sep. – Nov.	Chinese cabbage	400	200	200
1997	May – Aug.	sweet corn	400	200	200
	Sep. – Jan.	cabbage	400	200	200
1998–2000	May – Aug.	sweet corn	400	200	200
	Sep. – Dec.	Chinese cabbage	400	200	200
Total			5800	2900	2900
			δ^{15}N *value of fertilizers* (‰)		
			+14.3 ± 0.0[a]	+0.2 ± 0.1	+0.7 ± 0.1

[a] Mean ± SE, *n*=2.

(Table 4.2). The application rate of SC was based on the assumption that application of a double amount of N as SC has the equivalent fertilizer effect on crop growth to that as inorganic fertilizer under Japanese field conditions (Harada, 1997). The fields were plowed to about 15-cm depth after the fertilization. For AN, N fertilizer containing 70% of N as $(NH_4)_2SO_4$ and 30% as $(NH_4)_2HPO_4$ was used. This fertilizer contained phosphorus (P) and potassium (K), as well as N at a ratio of 10: 4.3: 8.3 for N: P: K. For CU, polyolefin-coated urea, LP100[®] (which requires 100 d for 80% N release in water at 25°C, Chisso-Asahi Co., Japan), was used for sweet corn and LP40[®] (which requires 40 d for 80% N release) for Chinese cabbage or cabbage, and P and K were compensated for by PK compound fertilizer at the same rates as for AN plots. SC was produced without any admixtures. The N content of SC was 44 g kg^{-1} on a dry matter basis and only 3.6% of N was in inorganic form (ammonium N). The C/N ratio of SC was 6.6. The water content of fresh SC was 22% (average for 7 yr). The application rates changed from 1.0 to 1.4 t ha^{-1} based on the compost character. The concentrations of P and K of SC were 27 and 24 g kg^{-1}, respectively, resulting in higher application rates of P and K in this plot than in the AN and CU plots.

Sweet corn (*Zea mays* L.) was grown from May to August, Chinese cabbage (*Brassica rapa* L. var. *amplexicaulis*) from September to December, and cabbage (*Brassica oleracea* L. var. *capitata*) from September to January. Sweet corn was planted at 30-cm intervals between plants and 70-cm between ridges, whereas Chinese cabbage and cabbage were at 40-cm between plants and 70-cm between ridges. Seeding of sweet corn and transplanting of Chinese cabbage and cabbage were conducted about 4 d after fertilizer application. All parts of sweet corn, Chinese cabbage, and cabbage were removed from plots except for the roots of Chinese cabbage and cabbage.

The field was once irrigated 40 mm on 7 September 1994 using irrigation tubes, because the soil was too dry for transplanting Chinese cabbage. Otherwise the field was rainfed.

4.2.3 Sampling and measurements

Daily precipitation was recorded in the field with a rain gauge (34-T, Ota-Keiki-Seisakusyo, Japan). Air temperature was measured at a meteorological station located about 1 km from the experimental field.

To monitor the groundwater in the field, the author used 3 observation wells made of 4-m long PVC tubes, having a screen reaching 1.5 m from the bottom end. Two wells were set up in the AN and NF plots before the experiment started, and an additional well was set up in the other AN plot in the summer of 1997. Ground water was sampled and water table was measured by using a water level dip meter (WL50M, Imai Co., Japan) on the same days as soil water sampling. Hourly monitoring was made using two tensiometers with a data logger (SK-5500-EL-3SD, Sankei-Rika Co., Japan), which measure not only negative but also positive water head (−1000 to +1000 cm), installed in March 1998 with 2 replicates at a depth of 4 m in the outer area for the plots.

At harvest, the fresh weight of crop samples was measured. Ten plants in each plot were cut into 1×1 cm pieces and dried at 70 ^{o}C for one week. Dried plant samples were then ground into powder and digested by a modified Kjeldahl method using conc. H_2SO_4 and 30% H_2O_2 (Mizuno and Minami, 1980). Total N of digested plant samples was determined using a continuous flow analytical system (Traccs 800, Bran+Luebbe, Germany).

Topsoil up to a 15-cm depth was sampled at 2 places in each plot, after Chinese cabbage was harvested in December 1999. These soil samples in each plot were mixed and air-dried for 2 weeks. Total N and C content in the soil was determined with an NC analyzer (NC-95A, Sumitomo Buseki Center, Japan) and natural abundance of ^{15}N (δ^{15}N) was analyzed with an ANCA-SL mass spectrometer (Europa Scientific, UK; Yoneyama and Yoshida, 2000). The δ^{15}N value (‰) was expressed according to the following equation:

$$\delta^{15}N = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000 \qquad [4.1]$$

where R_{sample} and $R_{standard}$ are the ratios of $^{15}N/^{14}N$ of the sample and the atmospheric N_2, respectively.

Five porous ceramic cup samplers (18 mm in outer diameter; 60 mm long, Nikkato Co., Japan) were installed at a depth of 1 m in one plot of each fertilizer treatment. Wick samplers were established in the other plot of each treatment as described elsewhere (Maeda and Ozaki, 1998). The whole systems, including porous cups, acrylic supporting-pipes (18 mm in outer diameter; 800 mm long), and polyethylene sampling tubes (1-mm inner diameter), were placed below 30-cm depth to allow management practices above the systems in the experimental plots. After a trench was dug to 30-cm depth, the porous cup samplers, supported by an acrylic pipe, were installed at an angle of 30° on the bottom of the trench. Polyethylene sampling tubes were connected to samplers, buried at a depth of 30 cm, and brought to the soil surface outside the experimental plots. After placement of the porous cup samplers in their positions, trenches were backfilled with the original soil. Three of the 5 porous cup samplers were installed in the spring of 1994 and the other 2 were added in the winter of 1994. The porous cup samplers were at least 2 m apart. Additional porous cup samplers were added in 1998 at depths of 200, 250, 300, 350, 400, and 430 cm with 3 replicates at each depth. These porous cup samplers at deeper than 200 cm were vertically installed and at least 1 m apart after a trenches was dug to 50-cm depth. For soil water sampling, a suction of 80 kPa was applied by an electronic vacuum pump (Daiki-Rika Co., Japan). The sampling flasks were covered with an aluminum sheet and placed in the field for 24 hours. Soil water sampling was conducted at least once a month, depending on precipitation. By the summer of the second year of the experiment, soil water was often sampled to make clear the change in NO_3-N concentration. From March 1997 to March 1998, soil water sampling was discontinued, although field management by the same fertilizer

treatments was conducted for crops.

Water samples were stored at $5^{\circ}C$ until chemical analysis. Nitrate N and Cl concentrations of filtered samples (0.20 μm membranes; 25A, GL Science Co., Japan) were analyzed with an ion chromatgraph (DX320J, Dionex, Japan). $\delta^{15}N$ of water samples, which were concentrated on a hot plate and then freeze-dried, was analyzed with the ANCA-SL mass spectrometer.

An experimental year refers to the 12-month period from 1 April of a year to 31 March of the following year.

4.2.4 Nitrogen and water balance equation

The following N and water balance equation on the soil surface (OECD, 1999) was used for predicting NO_3-N concentration in soil water at 1-m depth:

$$PNC = \frac{PNP}{EW} \times 100 \qquad [4.2]$$

where PNC (mg L^{-1}) is the potential nitrate concentration, PNP (kg ha^{-1} yr^{-1}) the potential nitrate present in soil, and EW (mm yr^{-1}) excess water (the difference between water input and evapotranspiration). PNP is obtained by subtracting the amount of N uptake, which refers to N in all parts of the crops removed from the plots, from that of N application in a year. In this calculation, N content changes in soil during the management are not considered.

4.2.5 Rayleigh equation

The following Rayleigh equation can be applicable to the relation between NO_3 concentration

and $\delta^{15}N$ values in soil water during denitrification processes (Mariottti et al., 1981):

$$\delta^{15}N = \delta^{15}N_{ini} + \varepsilon \ln f_{NO3-N} \qquad [4.3]$$

where $\delta^{15}N$ and $\delta^{15}N_{ini}$ are $\delta^{15}N$ values of the substrate after and before the reaction of denitrification (‰), respectively. ε is an enrichment factor (‰), and f_{NO3-N} the fraction of unreacted residual substrate, which is obtained by dividing NO_3-N concentration (C_{NO3-N}) resulting from denitrification, by initial NO_3-N concentration (C_{iNO3-N}). Böttcher et al. (1990) investigated the contribution of denitrification in groundwater using this equation of Eq. [4.3]. Equation [4.3] can be rearranged to predict NO_3-N concentration after denitrification as:

$$C_{NO3-N} = C_{iNO3-N} \exp(\frac{\delta^{15}N - \delta^{15}N_{ini}}{\varepsilon}) \qquad [4.4]$$

4.2.6 Statistical analysis

Statistical treatments of data were performed to determine the effects of fertilizer application on N uptake by crops, N in topsoil, and NO_3 concentration in soil water, using Tukey's multiple-comparison test at the 0.05 significance level (SAS Institute Japan, 1993). Student's t test was used at the 0.05 significance level to evaluate the differences in N content and $\delta^{15}N$ values between the topsoils sampled before the start of the experiment and after 6-yr continuous fertilizer application.

4.3 RESULTS AND DISCUSSION

4.3.1 Climate, groundwater, and N uptake by crops

The combined water input by precipitation (7890 mm) and irrigation (40 mm) during 1 April

1994 to 31 March 2001 totaled 7930 mm, with an annual average (1 April-31 March) of 1133 mm (Fig. 4.1 and Table 4.3), varying from 880 mm in 1994/1995 to 1455 mm in 1998/1999. This level is almost the same as the annual average precipitation (1154 mm) of 30 yr (1971-2000) for this region (Japan Meteorological Agency, 2001). Average temperature during the experimental period was 14.6^{o}C (Table 4.3). The average potential evapotranspiration estimated by the Thornthwaite method (Thornthwaite, 1948) was 795 mm yr^{-1}. The actual evapotranspiration (70% of the potential evapotranspiration, Kobayashi, 1989) and the resulting excess water (*EW*) were 557 and 576 mm yr^{-1}, respectively.

The groundwater fluctuated between 120 and 400 cm during the experimental period (Fig. 4.1). The groundwater rose to less than 2-m depth a few times in summers after heavy rainfall, but did not within 1-m depth where the soil water was sampled.
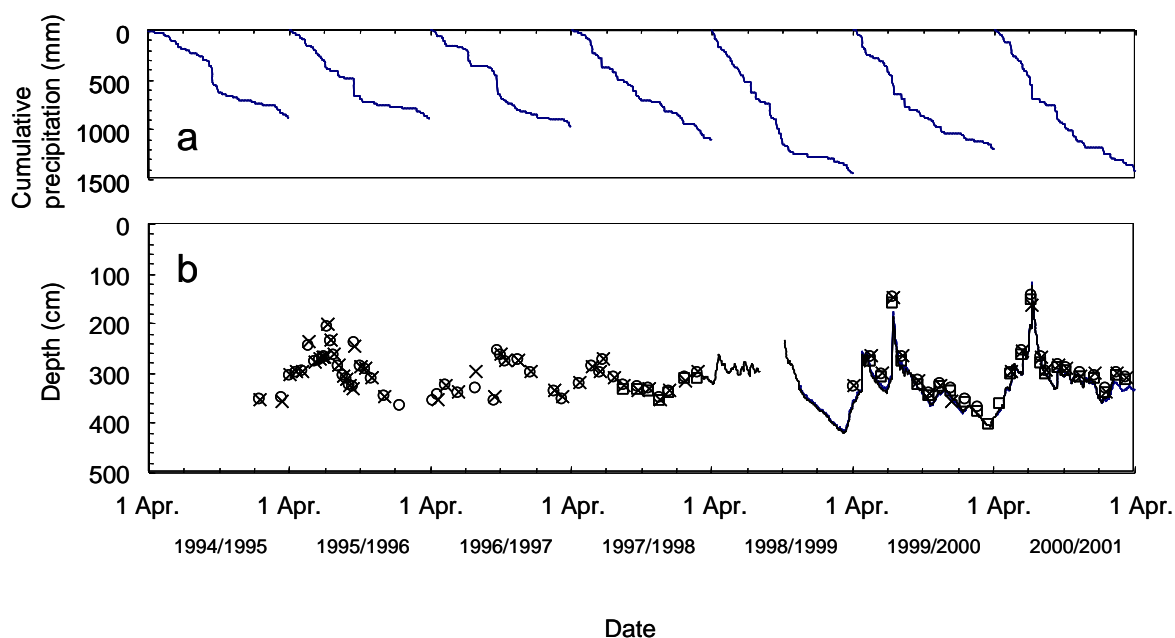
Fig. 4.1. (a) Annual cumulative precipitation and (b) groundwater changes in two plots receiving ammonium fertilizer (□; ○) and one plot without fertilizer (×) , from 1994 to 2001. Solid lines refer to hourly data in ammonium fertilizer plots using tensiometers.

Table 4.3. **Precipitation, potential evapotranspiration, and air temperature in the field.**

	1994 /1995	1995 /1996	1996 /1997	1997 /1998	1998 /1999	1999 /2000	2000 /2001	Average
Precipitation (mm)	880	894	978	1105	1455	1194	1424	1133
Potential evapotranspiration[a] (mm)	847	798	726	774	791	827	801	795
Annual average air temperature (^{o}C)	15.4	14.5	13.4	14.4	14.7	15.2	14.6	14.6

[a] Calculated using the method of Thornthwaite (1948)

Annual N uptake by crops under different fertilizer treatments is listed in Table 4.4. The 7-yr average N uptake was highest in the SC plot (257 ± 5 kg N ha^{-1} yr^{-1}; 31 % of the applied N), which was significantly ($P < 0.05$) higher than the other plots, followed by the CU

Table 4.4. **Nitrogen uptake by crops (kg N ha^{-1} yr^{-1}, $n=2$) [a].**

Fertilizer treatment	Crop	1994 /1995	1995 /1996	1996 /1997	1997 /1998	1998 /1999	1999 /2000	2000 /2001	Total
SC	Corn	94a	77a	98a	108a	102a	97a	91a	667a
	Chinese cabbage / cabbage[b]	89a	204a	120a	201a	176a	167a	176a	1133a
	Total	183a	281a	218a	309a	278a	264a	267a	1800a
CU	Corn	80ab	57ab	62ab	81b	84ab	74ab	89a	527b
	Chinese cabbage / cabbage	102a	196a	86a	162a	160a	164a	162a	1032a
	Total	182a	253a	148ab	243a	244ab	238ab	251a	1559b
AN	Corn	61b	46ab	32b	62b	45bc	43bc	70b	359c
	Chinese cabbage / cabbage	88a	192a	85a	149a	178a	171a	179a	1042a
	Total	149ab	238a	117b	211a	223b	214b	249a	1401b
NF	Corn	55b	24b	26b	32b	30c	23c	35c	225d
	Chinese cabbage / cabbage	34b	23b	1b	1b	10b	7b	1b	77b
	Total	89b	47b	27c	33b	40c	30c	36b	302c

[a] Mean values within each crop or totals in each year followed by the same letter are not significantly different based on Tukey's multiple-comparison test ($P > 0.05$).
[b] Cabbage was grown in 1997/1998 and Chinese cabbage in the other years.

plot (223 ± 3 kg N ha^{-1} yr^{-1}; 54 %) and the AN plot (200 ± 7 kg N ha^{-1} yr^{-1}; 48 %). The difference between the two chemical fertilizer plots (AN and CU) was not significant ($P >$ 0.05). In the NF plot, 43 ± 5 kg N ha^{-1} yr^{-1} was taken up by crops, which is significantly smaller than those in the other plots ($P < 0.05$). Nishio (2001) reported that Japanese average N recovery rates by sweet corn, Chinese cabbage, and cabbage were computed to be 41%, 41%, and 64%, respectively. The N recovery rates by sweet corn (36% on average for CU; 25% for AN) were lower and those by Chinese cabbage and cabbage (71% for CU; 72% for AN) higher than the national average values.

4.3.2 Changes in N content and δ^{15}N value in topsoil

After 6 yr of fertilization, the total N content in the topsoil increased significantly in the SC plot ($P < 0.05$), remained the same in the CU plot, and decreased in the AN and NF plots (not significantly at $P > 0.05$), compared to the original value (Tables 4.1 and 4.5). The N applied to the AN and CU plots did not appear to accumulate in the topsoil, suggesting the removal of N by crop uptake and gaseous and leaching losses.

In the SC plot, the total N of the topsoil increased by 2.0 g N kg^{-1}. The bulk density of topsoil was 0.9 Mg m^{-3} in the winter of 1999. Assuming that the topsoil was 15 cm deep, the N increment of the topsoil in the SC plot was 2700 kg N ha^{-1}. This value accounts for 54% of N applied to the SC plot during the 6-yr experimental period. In this estimate, soil N mineralization in the SC plot was not considered. On the other hand, if we assume that the amount of N mineralized from soil organic N in the SC plot was the same as that in the NF plot during the 6 yr, the difference in N content between the SC and NF plots (2.5 g N kg^{-1}) can be considered as SC-derived N. Namely, the amount of SC-derived N was 3375 kg N ha^{-1} and 68% of the applied N as SC. These results suggest that a large part of N from SC

Table 4.5.   Total N content, C/N ratio, and $\delta^{15}N$ values in the topsoil[a] after fertilizer treatments (Mean ± SE, $n=2$)[b].

Fertilizer treatment	T-N (g kg^{-1})	C/N	$\delta^{15}N$ (‰)
SC	6.0 ± 0.4*a	8.7 ± 0.1*b	+9.9 ± 0.1*a
CU	3.9 ± 0.1b	11.2 ± 0.1a	+6.3 ± 0.2b
AN	3.4 ± 0.2b	11.1 ± 0.0a	+6.4 ± 0.0b
NF	3.5 ± 0.2 b	11.4 ± 0.1a	+6.8 ± 0.1*b

[a] Topsoils were sampled from a 0-15 cm depth after 6-yr repeated application of fertilizers (1994-1999).
[b] Mean values within each column followed by the same letter are not significantly different based on Tukey's multiple-comparison test ($P > 0.05$).
* Mean values are significantly different from the values of the original soil (Table 4.1) based on Student's t test ($P < 0.05$).

accumulated in the topsoil in organic forms over the 6 yr. Although the C/N ratio of the compost was 6.6, which is low enough to release N (Kuwatsuka, 1984; Janssen, 1996), 54 to 68% of the applied N accumulated in the topsoil. The C/N ratio of the soil in the SC plot became 8.7 after 6 yr of repeated compost application. The repeated application of SC may have caused the lower C/N ratio, resulting in larger N mineralization in the late experimental period. Moreover, 31% of the applied N was taken up by crops during the first 6 yr, suggesting that most part of mineralized N from SC was taken up by crops.

The $\delta^{15}N$ value of the topsoil in the SC plot was significantly higher than those in other plots ($P < 0.05$), probably due to the accumulation of compost N with a high $\delta^{15}N$ value of +14.3‰ (Tables 4.2 and 4.5). The N content of the NF topsoil decreased during the 6 yr while the $\delta^{15}N$ value significantly increased (Tables 4.1 and 4.5), likely owing to preferred loss of light N (^{14}N) from soil (Yoneyama, 1996). The mass balance of topsoil in the SC plot is given by:

$$C_{mix}\delta^{15}N_{mix} = C_{soil}\delta^{15}N_{soil} + C_{SC}\delta^{15}N_{SC} \qquad [4.5]$$

where C_{mix}, C_{soil}, and C_{SC} are N contents of a mixture of soil and SC, soil, and SC-derived N in the mixture (g kg^{-1}), respectively. $\delta^{15}N_{mix}$, $\delta^{15}N_{soil}$, and $\delta^{15}N_{SC}$ refer to $\delta^{15}N$ values (‰) of the mixture, soil, SC, respectively. This equation can be rearranged to calculate C_{SC} as follows:

$$C_{SC} = \frac{C_{mix}\delta^{15}N_{mix} - C_{soil}\delta^{15}N_{soil}}{\delta^{15}N_{SC}}$$

[4.6]

When N loss from the soil was not taken into account, the N content and δ^{15}N value of the original soil sampled before the experiment can be used as C_{soil} (4.0 g kg^{-1}, Table 4.1) and $\delta^{15}N_{soil}$ (+5.9‰), respectively. The SC-derived N of the mixture (C_{mix}=6.0 g kg^{-1}; $\delta^{15}N_{mix}$=9.9‰) of soil and SC ($\delta^{15}N_{SC}$=+14.3‰) was then estimated to be 2.5 g kg^{-1}, which was higher than the N difference between the SC soil and the original soil (2.0 g kg^{-1}). On the other hand, if we consider the N loss from the soil in the SC plot was as much as that in NF plot, the N content and δ^{15}N value of the soil in the NF plot should be used as C_{soil} (3.5 kg kg^{-1}) and $\delta^{15}N_{soil}$ (+6.8‰), respectively. Thus, C_{SC} was calculated to be 2.5 g kg^{-1}, which was consistent with the measured N difference between the SC and NF soils (Table 4.5). This confirms that N loss from the soil also occurred in the SC plot and that the N from SC contributed to the N increment in the topsoil.

4.3.3 Nitrate concentration in soil water at 1-m depth

Nitrate N concentrations in soil water at 1-m depth rose markedly in the summer of the second year (1995/1996) and fluctuated between 30 and 60 mg L^{-1} in the AN and CU plots (Fig. 4.2). Nitrate N concentration in the SC plot began to increase in the fourth year (1997/1998), reaching the same level as in the AN and CU plots in the late period of the experiment. These NO_3-N concentrations were higher than the Japanese standard of groundwater (10 mg L^{-1} NO_3-N), which may be associated with intensive vegetable cropping and high precipitation. In the NF plot, NO_3-N concentration was about 10 mg L^{-1} for the first 4 yr and decreased to 5 mg L^{-1} towards the end of the experiment.

Variations in NO_3-N concentrations in the AN and CU plots showed a similar

temporal pattern, except that NO$_3$-N concentrations in the CU plot was lower than that in the

AN plot by ca. 10 mg L^{-1} throughout the experimental period (Fig. 4.2). This reduction of N

leaching is consistent with Sakata et al. (1995) and Matsumaru (1997), despite the fact that in

those studies, the experimental periods were relatively short and repacked soils were used.
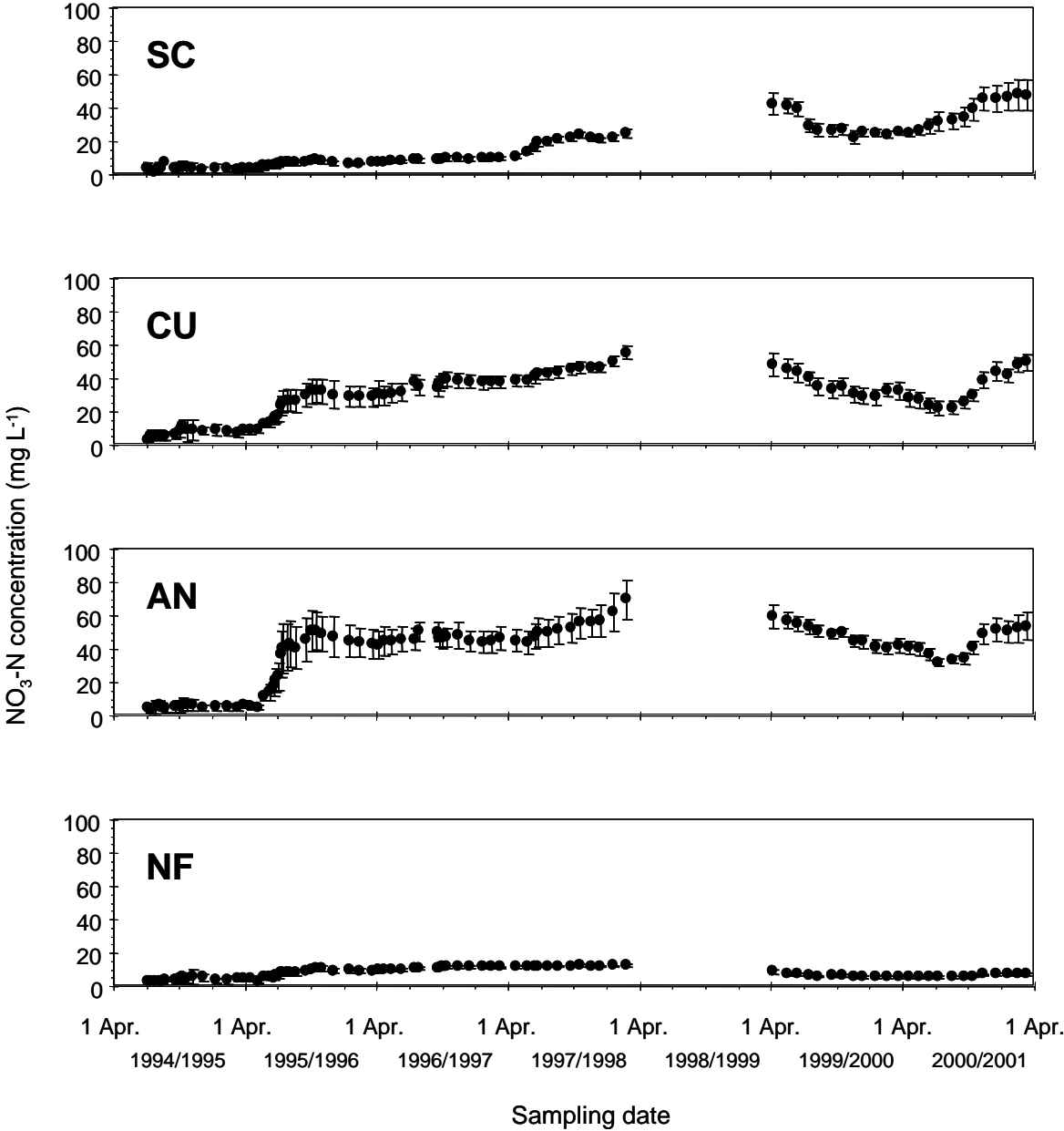
Fig. 4.2. Mean NO$_3$-N concentrations (*n*=5) in soil water at 1-m depth in the four fertilizer
treatments, from 1994 to 2001. SC: swine compost, CU: coated urea fertilizer, AN:
ammonium fertilizer, NF: no fertilizer. Vertical bars indicate standard errors (±SE).

Both of the two reports noted that N derived from coated urea fertilizer remained in the topsoil at the end of the experiments, although its later leaching was not examined. The present study confirmed reduction of N leaching by using coated urea fertilizer over 7 yr. The difference in NO_3-N concentrations in soil water between the CU and AN plots probably resulted from differences in crop uptake of N from respective sources (Table 4.4). While the N application rates in the CU plot were the same as those in the AN plot, N uptake by crops in the CU plot was larger. Therefore, less N application of CU would likely result in the same level of crop yields as in the conventional AN plot accompanying less N leaching than in the AN plot. Owens et al. (1992) examined NO_3-N concentration in subsurface flows in watersheds receiving NH_4NO_3 or slow-release N (methylene urea) for 10 yr. Although NO_3-N concentrations in the area treated with slow-release N area rose more slowly than under the area treated with NH_4NO_3, the concentrations in both areas were still increasing even at the end of the experiment. Owens et al. (1992) could not conclude whether use of slow-release N provides long-term suppression of N leaching. In contrast, the present study showed that, as the whole, NO_3-N concentrations remained at certain levels in the AN and CU plots and the NO_3 leaching was smaller in the CU plot over the 7 yr. The discrepancy between the present results and Owen et al. (1992) may be due to a difference in experimental scales. It may take longer time to elucidate the effects of N fertilization on N loadings at watershed scale as Owen et al. (1992). In other words, a few years may be enough to evaluate the effects of slow-release N fertilizer on N leaching at a depth of about 1 m in small field plots as in the present study.

Nitrate N concentrations in soil water at 1-m depth in the SC plot did not change during the first 3 yr, because a large portion of N applied as SC accumulated in the topsoil. However, the NO_3-N concentrations in the SC plot was continuously increased and became similar to those in the AN and CU plots in the late period of the experiment. Increasing N mineralization owing to the lowered C/N ratio of the soil resulted in an increase in NO_3-N

concentration at 1-m depth in the late period of the experiment (Fig. 4.2). It is also likely to occur that the residual organic N from previously applied manure was mineralized, so that the total amount of mineralized N increased over the years (Angle et al., 1993; Thomsen et al., 1993; Bergstöm and Kirchmann, 1999). Repeated application of composts may simultaneously increase the risk of serious NO_3 leaching, although the level of soil fertility may increase (Addiscott et al., 1991).

Nitrate concentrations and $\delta^{15}N$ values in soil water at 1-m depth were measured in February 1998 when NO_3-N concentration was high in the AN and CU plots and in April 2000 when NO_3-N concentration was low (Table 4.6). Nitrate concentrations in soil water at 1-m depth in the SC and NF plots were significantly lower than in the AN and CU plots in February 1998 ($P < 0.05$). In April 2000, NO_3-N concentration in the SC plot, which was significantly different from in the AN plot ($P < 0.05$) but not significantly from in the CU plot ($P > 0.05$), did not change from February 1998, while the NO_3-N concentrations in the AN and CU plots decreased during the period.

The $\delta^{15}N$ values of soil water in the SC plot were significantly higher than those in the other plots, which ranged from 0.8 to 2.2‰, on both sampling dates ($P < 0.05$). The $\delta^{15}N$

Table 4.6.   Nitrate N concentrations and $\delta^{15}N$ values in soil water at 1-m depth receiving four different fertilizer treatments (Mean ± SE, n=5)[a].

Fertilizer treatment	Sampled on 25 February 1998		Sampled on 18 April 2000	
	NO_3-N (mg L^{-1})	$\delta^{15}N$ (‰)	NO_3-N (mg L^{-1})	$\delta^{15}N$ (‰)
SC	24.3 ± 2.8b	+13.3 ± 0.3a	24.6 ± 1.5b	+12.1 ± 0.1a
CU	55.1 ± 4.1a	+1.7 ± 0.1b	27.8 ± 5.3ab	+1.3 ± 0.1c
AN	69.2 ± 11.6a	+0.8 ± 0.1c	40.8 ± 4.0a	+2.2 ± 0.3b
NF	11.9 ± 0.7c	+2.0 ± 0.2b	5.4 ± 0.7c	+2.0 ± 0.4bc

[a] Mean values within each column followed by the same letter are not significantly different based on Tukey's multiple-comparison test ($P > 0.05$).

values of soil water could be a mixture of those from mineralized soil and compost N, nitrified urea (from CU), ammonium (from AN), and some inputs of deposition (Yoneyama, 1996). The $\delta^{15}N$ values of soil water at 1-m depth (Table 4.6) clearly reflected those of the N sources (Table 4.2). The $\delta^{15}N$ values in the AN- and CU-fertilized plots were slightly higher than those of the fertilizer (+0.7‰ for AN and +0.2‰ for CU). The $\delta^{15}N$ values for the SC plot were slightly lower than that of SC (+14.3‰). These differences are explained by the contribution of mineralized soil N or airborn N. Although the $\delta^{15}N$ value of soil N was +5.9‰ (Table 4.1), that of soil water N in the NF plot was +2‰. The reason for this is that $\delta^{15}N$ of rainfall has generally negative values from -10 to 0‰ (Yoneyama, 1996). Airborn N input is about 10 kg N ha^{-1}yr^{-1} in this region (Tabuchi and Takamura, 1985). Thus, the source of NO$_3$-N in soil water in the NF plot should be a mixture of air-born N and mineralized soil N. Similarly, the contribution of different N sources may cause the change in $\delta^{15}N$ values between fertilizer sources and soil water N. However, we must take a care in the understanding of $\delta^{15}N$ values in soil water N components, since reactions such as nitrification, immobilization, denitrification, and ammonia volatilization may cause the changes in $\delta^{15}N$ values (Yoneyama, 1996).

4.3.4 Effects of precipitation and soil type

The highest NO$_3$-N concentrations were observed in the spring of 1998 and the lowest in the spring and summer of 2000/2001 in the AN and CU plots after the summer of the second year (1995/1996) when the influence of fertilization clearly appeared (Fig. 4.2). The highest precipitation, recorded in 1998/1999, may have caused the lower NO$_3$-N concentration in the following year (Table 4.3 and Fig. 4.1), because the large rainfall resulted in dilution of NO$_3$-N concentrations in soil water and possibly also decrease in NO$_3$-N by denitrification.

The NO_3-N concentrations in the AN and CU plots appreciably decreased from February 1998 to April 2000 while the $\delta^{15}N$ values showed small changes (Table 4.6), indicating that the contribution of denitrification due to high precipitation was probably small.

The retardation of NO_3 transport in soil related with high anion exchange capacity (AEC) was not observed in this experiment, although Katou (2001) estimated the retardation factor of NO_3 was about 2 for a similar Andisol using repacked column experiments. The average water contents of the soil to a depth of 1 m were 700 mm ($0.7 \text{ m}^3 \text{ m}^{-3}$) at 0 kPa and 500 mm ($0.5 \text{ m}^3 \text{ m}^{-3}$) at 10 kPa (Table 4.1), which were large values because of the low bulk density. Field capacity of a similar soil was determined to be ca. 620 mm in the field using TDR (Hasegawa, 2000). On the other hand, EW was only 468 mm (the difference between cumulative precipitation, 1267 mm and evapotranspiration, 799 mm) during the period of May 1994 to July 1995 when the influence of the AN and CU application did not appear on NO_3-N concentration in soil water at 1-m depth. Namely, NO_3 derived from fertilizers reached to a depth of 1 m through the soil before the water stored in the soil to the 1-m depth was completely displaced by new water inputs. Thus the high AEC did not cause the delay in NO_3 leaching. The discrepancy between our result and the estimate by Katou (2001) is possibly explained in terms of uneven water flows caused by the presence of aggregates. Percolating water tends to pass the small intraaggregate pores. Nitrate movement into the intraaggregate pores may be only due to the diffusion (Addiscott, 1991). There is, therefore, less chance for NO_3 to be absorbed onto the soil in the present field experiment, compared to the repacked soil experiment (Katou, 2001).

Nitrogen release by mineralization from the Andisol with a high total N content presumably affected NO_3-N concentration in soil water at 1-m depth in the NF plot. The effect of absence of fertilizer application (NF plot) on NO_3-N concentration appeared in the 6th yr of the experiment, while that of the chemical fertilizer application (AN and CU plots) in the second year (Fig. 4.2). Nitrogen mineralized from the NF soil was not only absorbed by crops

71

but also leached out. Actually, N content of the topsoil in the NF plot decreased from 4.0 to 3.5 g kg^{-1} over the 6 yr (Table 4.5), which is equivalent to 675 kg N ha^{-1}.

4.3.5 Estimation of NO$_3$ concentration with the N and water balance equation

PNCs calculated by using Eq. [4.2] were presented with 6-yr average NO$_3$ concentrations in four treatments in Table 4.7. The *PNCs* satisfactorily predicted the NO$_3$-N concentrations in the AN and CU plots, indicating that excessive N for crops from AN and CU would cause NO$_3$ leaching in due time. The difference in *PNC* between the AN and CU plots (Table 4.7) were due to that in N crop uptake (Table 4.4). This difference in *PNC* was, however, smaller than that in monitored NO$_3$-N concentration (Table 4.7 and Fig. 4.1). On the other hand, the calculated *PNC* in the SC plot was substantially overestimated, presumably because a large part of N from SC accumulated in the topsoil in the organic form during the experimental period. The N available for NO$_3$ leaching in the SC plot were estimated to be 767 kg ha^{-1}

Table 4.7. **Potential NO$_3$-N present in soil (PNP), potential NO$_3$-N concentration (PNC) by the N and water balance equation, and 6-yr average NO$_3$-N concentration in soil water at 1-m depth.**

Fertilizer treatment	*PNP*[a] (kg ha^{-1} yr^{-1})	*PNC*[b] (mg L^{-1})	6-yr average NO$_3$-N[c] (mg L^{-1})
SC	571	99	16
CU	192	33	28
AN	214	37	36
NF	−43	—	7

[a] *PNP* was obtained by subtracting the amount of N uptake, which refers to N of all parts of the crops removed from the fields, from that of N application in a year. Data sets during the period 1994/1995-2000/2001 were used for the calculations.
[b] *PNC* was used as an estimate of NO$_3$-N concentration in soil water at 1-m depth. *EW* was estimated to be 576 mm yr^{-1}.
[c] Data sets during the period 1994/1995-2000/2001 except for 1998/1999 were used for the calculations.

during the 6-yr experimental period 1994/1995 to 1999/2000, which was obtained by subtracting total uptake N (1533 kg ha^{-1}, Table 4.4) and accumulated N in the topsoil (2700 kg ha^{-1}) from total applied N (5000 kg ha^{-1}, Table 4.2), assuming that denitrification and ammonium volatilization were negligible. In this consideration, *PNP* and *PNC* for the SC plot are computed to be 128 kg ha^{-1} yr^{-1} and 24 mg L^{-1}, respectively. This *PNC* is better consistent with the monitored NO$_3$-N concentration than the *PNC* without consideration of N accumulation in soil (Table 4.7).

Even if we know seasonal changes in NO$_3$ concentration, we could not regulate NO$_3$ leaching based on such changes. From this point of view, the N and water balance equation is enough to evaluate chemical fertilizations for NO$_3$ leaching. For compost, however, an increment of total N in topsoil should be taken into account to evaluate NO$_3$ leaching.

4.3.6 Vertical distribution of NO$_3$-N concentration in soil water

Nitrate N concentrations in soil water declined with depth and those at depths more than 300 cm were almost equal to that in groundwater in the AN plots after 6-yr continuous fertilizer application (on 18 April 2000), as shown in Table 4.8. The groundwater table rose to less than 2 m depth a few times in summers (Fig. 4.1), although, on the sampling date, the groundwater table was at 3.6 m below the soil surface. There may be two possible explanations for the decrease in NO$_3$-N concentration in the deep layers. One is that rising groundwater washed away NO$_3$ in the soil solution. The other is that anaerobic conditions resulting from rising groundwater caused denitrification.

Chloride concentrations decreased with depth as well as NO$_3$-N, but the rate of the decline for NO$_3$-N was larger than that for Cl (Table 4.8). Although both anions of Cl and NO$_3$ are mobile in soil systems, Cl does not participate in biological or chemical reactions

Table 4.8. **Nitrate N and Cl concentrations, mole ratios of NO$_3$-N to Cl, and δ^{15}N values in soil water sampled from different soil depths and ground water in plots receiving ammonium nitrogen fertilizer (AN) ($\pm$SD, *n*=2-5).**

Depth	NO$_3$-N	Cl	NO$_3$-N/Cl	δ^{15}N	C_{NO3-N} [b]
(cm)	(mg L^{-1})	(mg L^{-1})	(mol / mol)	(‰)	(mg L^{-1})
100	40.8 $\pm$ 8.9	65.7 $\pm$ 7.6	1.6	+2.2 $\pm$ 0.6	—[c]
200	46.5 $\pm$ 7.5	56.4 $\pm$ 9.0	2.1	-0.7 $\pm$ 0.6	—[d]
250	9.6 $\pm$ 4.0	28.9 $\pm$ 3.1	0.8	-0.5[a]	—[d]
300	3.8 $\pm$ 0.6	23.1 $\pm$ 0.8	0.4	+8.9[a]	27
350	3.2 $\pm$ 0.1	23.1 $\pm$ 0.7	0.4	+7.6[a]	29
400	3.2 $\pm$ 0.0	22.4 $\pm$ 1.5	0.4	+7.6[a]	29
430	3.5 $\pm$ 0.6	22.7 $\pm$ 1.5	0.4	+9.1 $\pm$ 0.6	27
Ground water	3.9 $\pm$ 1.0	23.7 $\pm$ 0.6	0.4	+6.8 $\pm$ 0.6	31

All water samples were obtained on 18 April 2000.
[a] Single sample analysis because of insufficient amount of water.
[b] Nitrate concentration in soil water after denitrification was predicted using the Rayleigh equation [4.4].
[c] Nitrate concentration and δ^{15}N values in soil water at 1-m depth was used as initial values.
[d] Calculations were not treated because δ^{15}N values in soil water were lower than that at 1-m depth.

while NO$_3$ does. The decrease of NO$_3$-N/Cl ratio indicates the occurrence of denitrification in deeper soil.

The δ^{15}N values of soil water deeper than 300 cm showed higher values than those at 100 cm depth (Table 4.8). This fact also suggests the occurrence of denitrification in deeper soil. Böttcher et al. (1990) showed that microbial denitrification in groundwater accorded with the Rayleigh equation with an enrichment factor ε = -15.9‰ (see Eq. [4.3]), although this factor in previous studies ranged from -7.8 to -30‰ (Arai and Tase, 1992). Assuming that ε was -15.9‰ and NO$_3$-N at 1-m depth (40.8 mg L^{-1}, $\delta^{15}N_{ini}$ = +2.2‰) moved to the deeper depths, NO$_3$-N concentrations calculated using Eq. [4.4] are 27-31 mg L^{-1}, which is greater than the measured values 3.2-3.9 mg L^{-1}. This indicates that the contribution of denitrification was not large. Further studies on the dynamics and quality of the groundwater on a larger scale would be helpful to elucidate the mechanisms of the decrease in NO$_3$-N concentrations in soil water with depth.

Nitrate N concentration in groundwater in the AN and NF plots was monitored during the experiment (Fig. 4.3). Nitrate N concentration increased in both plots after 6 yr of repeated fertilizer treatment, since the groundwater in different plots may have been mixed.
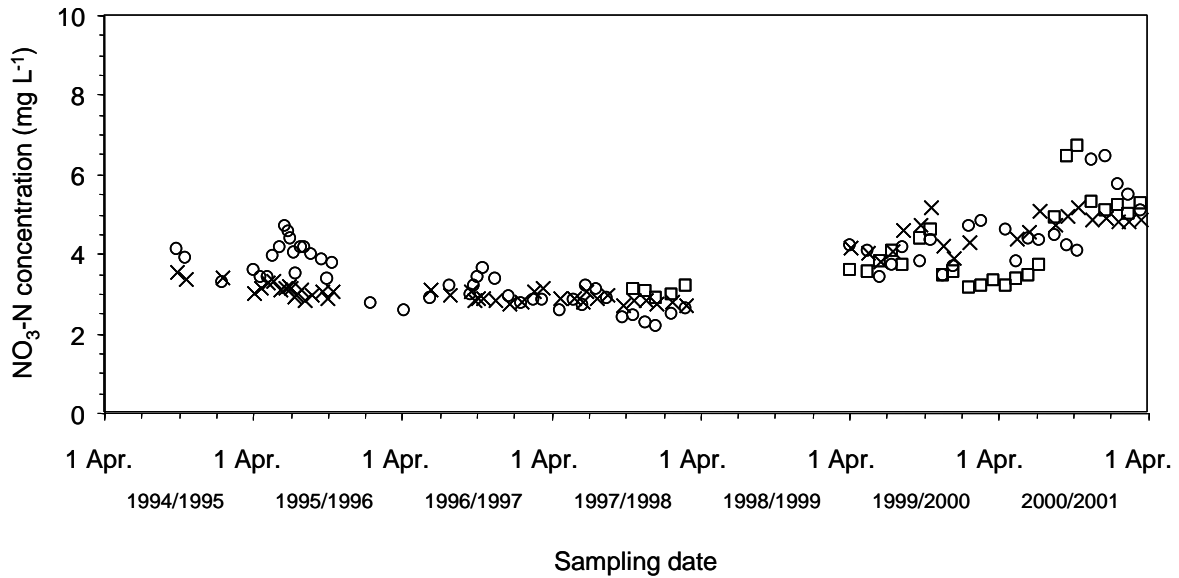
Fig. 4.3. Nitrate N concentration in groundwater in two plots receiving ammonium fertilizer (□; ○) and one plot without fertilizer (×), from 1994 to 2001.

The results indicate a large time lag between agricultural practice and NO_3-N contamination in groundwater.

4.4 CONCLUSIONS

Chemical fertilizers (AN and CU), and compost made by swine waste (SC) were continuously applied on an Andisoil during 6 yr at standard application rates in Ibaraki, Japan. Plots with no fertilizer (NF) were established as a control. Sweet corn and Chinese cabbage / cabbage were grown in the plots.

In the AN and CU plots, NO_3-N concentrations in soil water at 1-m depth started increasing from 15 months after the initiation of the experiment, and reached ca. 40-60 mg L^{-1} in the AN plot and 30-50 mg L^{-1} in the CU plots. Nitrate N concentrations in soil water in the SC plot began to increase in the fourth year, reaching the same level as those in the AN and CU plots in the late experimental period. Organic N from SC first accumulated in the topsoil and mineralized subsequently so as to have NO_3-N concentration similar to those in the AN

75

and CU treatments towards the end of the experiment. Thus, over longer periods, accumulation or changing characters of the organic N may cause substantial N mineralization in soil, resulting in large NO_3 leaching.

The groundwater table rose to less than 2 m depth a few times after heavy rainfall in summer, resulting in a decrease in NO_3-N concentration of soil water at deeper depths. During such events, NO_3 from the soil water would be mixed with groundwater by vertical-transverse dispersion. In addition, rising groundwater may have caused anaerobic conditions in soil resulting in denitrification. Thus, the vertical movement of groundwater played a significant role in NO_3 dissipation in the deep soil layers.

Excessive N from chemical fertilizers applied to Andisols can cause NO_3 leaching at 1-m depth under the Japanese climate (Asian monsoon). Substitution of compost for chemical fertilizer is promising in establishing high yields and low N leaching only during shorter periods. However, continuous application of compost would cause substantial N leaching. Hence, accurate simulation should be conducted to establish the best combination of chemical fertilizer and compost, and to evaluate the effects of groundwater movement on denitrification and dilution of groundwater nitrate.

LEACHING PATTERNS OF NITROGEN AND HEAVY METALS EVALUATED WITH A MODIFIED TANKS-IN-SERIES MODEL

5.1 INTRODUCTION

Management of livestock wastes and sewage sludge has been of large concern during the past decades. In view of recycling such waste products, adequate applications on arable land are recommended. However, these waste products contain not only various nutrients but also high concentrations of heavy metals, especially zinc and copper (McGrath et al., 1994; Harada et al., 1993), which may cause adverse environmental effects.

The mobile fraction of most sludge-applied metals is generally small, unless soils are coarse-textured or very acid (McBride, 1995). However, in some field experiments, evidence of metal leaching at relatively high rates has been found (Richards et al., 1998; Fatta et al., 1997; Campbell and Beckett, 1988). McBride et al. (1997) estimated heavy metal leaching by using the metal/chromium ratio in soil and that in sludge, and thereby indirectly showed that large fractions of heavy metals had migrated out of the topsoil layer. Higher concentrations and leaching losses of heavy metals were measured in sludge amended plots than in control plots, in an experiment in which wick samplers were used (Richards et al., 1998). The relatively high mobility of heavy metals in the above-mentioned examples was

presumably due to preferential flow and movement of organically complexed forms of metals (McBride et al., 1997; Richards et al., 1998). While Richards et al. (1998) suggested the existence of preferential flow by examining dyed flow paths, they did not use any non-reactive tracer to further evaluate the occurrence of preferential flow and the heavy metal leaching. Added to this, measurements of leaching losses by wick samplers are somewhat questionable (Maeda et al., 1999). Overall, very few studies on heavy metal leaching have been conducted, in which the effects of preferential flow have been elucidated. Camobreco et al. (1996) showed that preferential flow, which was evaluated using a non-reactive tracer, could accelerate metal leaching through undisturbed soil columns, but their results were obtained under steady-state flow conditions, which are quite different from natural field situations. Several studies characterizing tracer movement under non-steady state flow conditions have been performed in monolith lysimeters, but most of them have looked at leaching of nitrate (NO_3) and various pesticides (e.g. Bowman, 1988; Bergström and Johansson, 1991), and only a few on heavy metal leaching (Sheppard et al. 1987). In addtion, if non-reactive tracers are not used in such experiments, which is often the case, the effects of preferential flow occurring in soil are difficult to evaluate. One advantage of lysimeters is that lateral flows do not occur and infiltrating water cannot bypass the collection system at the bottom of the lysimeters.

A great deal of information on preferential flow of a non-reactive tracer can be thoroughly evaluated by use of mathematical simulation models. Since the classical combination of Richards' and convection-dispersion equations is not able to describe preferential flow and non-equilibrium transport of solutes (Feyen et al., 1998), new modelling approaches have been developed (Feyen et al., 1998; Jarvis, 1994; Steenhuis et al., 1994). Most of these models are deterministic, which means that an extensive amount of information is required to complete the parameterization. An alternative for modelling preferential flow in soils is a transfer function approach (Jury, 1982; Jury and Gruber, 1989; Utermann et al.,

1990; Grochulska and Kladivko, 1994), whereby the soil system is characterized entirely in terms of a distribution function of non-reactive tracer travel time to a given depth. For this type of approach, only information about application of a tracer on the soil surface, tracer concentrations, and water fluxes at a given depth, are necessary. Probability density functions, such as lognormal functions (Jury, 1982; Vanderborght et al., 1997) and gamma functions (Jury and Gruber, 1989; Grochulska and Kladivko, 1994), have been used as distribution functions to describe non-reactive tracer travel time, because they provide good fit to experimental data. However, the parameters of probability density functions do not have any physical and chemical meanings related to the water flow in soil systems. To overcome this shortcoming, the tanks-in-series model could be an alternative because the meaning of the used parameter is evident (Fogler, 1992). The extremes represented by a completely mixed and a plug-flow reactor are never fully realized in non-ideal reactors. The tanks-in-series model uses a single parameter to account for complex mixing patterns in a non-ideal reactor. The parameter is the number of ideal tanks in series, which gives approximately the same distribution of non-reactive tracer travel time as a non-ideal reactor. The model can be expanded to calculate the conversion and effluent concentrations of chemicals by applying the reaction engineering analysis (Fogler, 1992).

In this study, the author used a modified version of the tanks-in-series model for soil systems to describe a distribution function of non-reactive tracer travel time and validated the model with experimental data obtained in monolith lysimeters. Rainfall intensity may be one of the main factors affecting preferential flow. However, when transfer function models have been used to describe water flow under natural field conditions, tracer travel time to a given depth has been assumed to depend on the amount of water applied (precipitation minus evaporation) or the amount of leachate, regardless of intensity or intermittence of applied water (Jury, 1982; Jury and Gruber, 1989). To test the importance of rainfall intensity for the soil used in our study, the influence of three precipitation regimes was followed. The main

objective was to investigate the influence of preferential flow on leaching of heavy metals and N. For this purpose, Ammonium (NH_4-N) and NO_3-N, zinc (Zn), and copper (Cu) were applied on the surface of monolith lysimeters containing a heavy clay soil, in which preferential flow could have a substantial influence on chemical leaching (Bergström, 1995). The chosen elements are frequently occurring at relatively high concentrations in livestock waste and sewage sludge. Concurrently, bromide (Br) as a non-reactive tracer was applied on the lysimeters to provide information on water movement through the profiles. As mentioned above, the flow behaviour of Br was subsequently characterized with a modified tanks-in-series model.

5.2 THE MODEL

5.2.1 Model description

The theory of the model described here is based on the tanks-in-series model (Fogler, 1992). The distribution of travel time (residence time) of a non-reactive tracer is determined by the injection of the compound into the feedstream entering the reactor, and then the number (*n* (–)) of equally sized and completely mixed flow tanks in series is obtained as a parameter. The parameter *n* shows the degree of mixing of flow in the reactor, and varies from one, for ideal completely mixed flow, to infinity, for ideal plug flow.

This tanks-in-series model was modified for soil systems as described below. The following assumptions were made: (i) when water content in soil exceeds the maximum amount of water held in a freely drained monolith, infiltration occurs and its rate is equal in all tanks; (ii) soil has stagnant flow regions and their ratio to the maximum amount of water in a monolith, when freely drained, does not change during the experiment; and (iii) rainfall does not contain the studied tracer.

80

Assuming that the water flows are completely mixed in each tank, the mass balance of a tracer in the kth tank is given by:

$$\frac{d}{dt}\left(\frac{f_m V}{n} C_k\right) = -C_k R + C_{k-1} R \qquad [5.1]$$

where C (mg L^{-1}) is the tracer concentration, f_m (−) is the ratio between water in mobile regions and the maximum water content in a freely drained monolith, R (mm d^{-1}) is the infiltration rate, t (d) is time, and V (mm) is the maximum water content in the freely drained monolith. The subscript k denotes the order of the tank.

Wierenga (1977) showed, both theoretically and experimentally, that tracer movement in a silty clay loam under transient water flow conditions closely resembles that under steady flow conditions, if tracer concentration was plotted vs. cumulative leachate (Rt) instead of vs. time (t). This assumption for the used soil was confirmed under different precipitation regimes. Normalized time (τ (−)) is defined as the cumulative leachate divided by the field capacity water content, i.e.:

$$\tau = \frac{Rt}{V} \qquad [5.2]$$

Combining Eqs. [5.1] and [5.2] gives:

$$\frac{f_m}{n}\frac{d}{d\tau}(C_k) = -C_k + C_{k-1} \qquad [5.3]$$

Using the Laplace transform, Eq. [5.3] will be transformed as follows:

$$\frac{f_m}{n}\left(sL\ [C_k]\right) = -L\ [C_k] + L\ [C_{k-1}] \qquad [5.4]$$

where s is the Laplace transform parameter. The Laplace transform of C_k is given by:

$$L\ [C_k] = \int_0^\infty C_k(\tau)e^{-s\tau}d\tau \qquad [5.5]$$

Rearrangement of Eq. [5.4] gives the expression:

$$L\ [C_k] = \left(\frac{n}{f_m}\right)\frac{L\ [C_{k-1}]}{\left(s + \dfrac{n}{f_m}\right)} \qquad [5.6]$$

The initial condition on the soil surface is given by the Dirac delta function, namely:

$$C_o = \frac{M}{V}\delta(\tau) \tag{5.7}$$

where M (mg m^{-3}) is the mass of the tracer applied on a lysimeter surface. Accordingly, the Laplace transform solution may be given by:

$$\mathsf{L}\,[C_n] = \left(\frac{n}{f_m}\right)\frac{\mathsf{L}\,[C_{n-1}]}{\left(s+\dfrac{n}{f_m}\right)} = \cdots = \left(\frac{n}{f_m}\right)^n \frac{\dfrac{M}{V}\mathsf{L}\,[\delta(\tau)]}{\left(s+\dfrac{n}{f_m}\right)^n} = \left(\frac{n}{f_m}\right)^n \frac{\dfrac{M}{V}\cdot 1}{\left(s+\dfrac{n}{f_m}\right)^n} \tag{5.8}$$

Inverting the Laplace transform solution of Eq. [5.8] (Ikeda, 1980), the solution of Eq. [5.3] can be written as:

$$C_n = \frac{\dfrac{M}{V}\cdot(\dfrac{n}{f_m})\cdot(\dfrac{n}{f_m}\tau)^{n-1}}{(n-1)!}\,e^{-\frac{n}{f_m}\tau} \tag{5.9}$$

The distribution function of travel time ($E(\tau)$) is obtained by dividing the effluent rate of the tracer by the applied mass, according to:

$$dE(\tau) = \frac{C_n R dt}{M} = \frac{C_n R dt}{M}\frac{V}{R}\frac{d\tau}{dt} = \frac{C_n V}{M}\,d\tau \tag{5.10}$$

$E(\tau)$ can then be derived by:

$$E(\tau) = \frac{C_n V}{M} = \frac{(\dfrac{n}{f_m})\cdot(\dfrac{n}{f_m}\tau)^{n-1}}{\Gamma(n)}\,e^{-\frac{n}{f_m}\tau} \tag{5.11}$$

where Γ is called a gamma function and n will be mathematically expanded to positive numbers. Eq. [5.11] becomes a form of gamma probability density function by itself. Although a gamma probability density function has sometimes been used for $E(\tau)$ (Jury and Gruber, 1989; Grochulska and Kladivko, 1994), the mathematical grounds and relations of the parameters to soil systems have not yet been discussed and theoretically supported by Eq. [5.11].
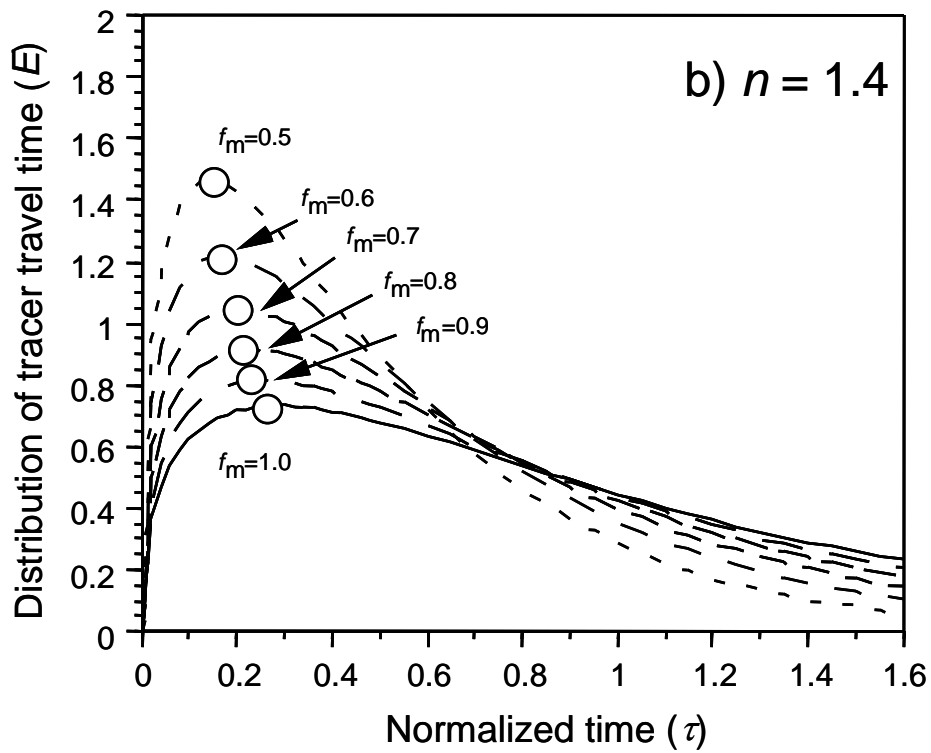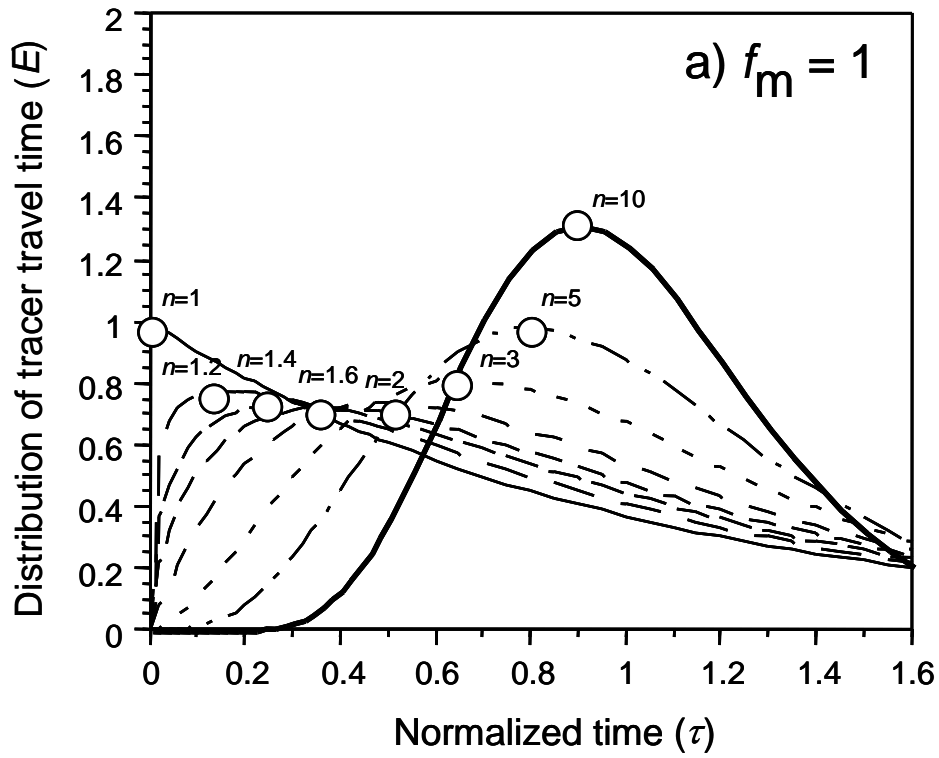
Fig. 5.1. Sensitive analysis of the parameters *n* and f_m used in the modified tanks-in-series model. a) Change of *n* in case of $f_m = 1$; and b) change of f_m in case of *n* = 1.4. The peaks of $E(\tau)$ are marked with a circle.

5.2.2 Model application

In a first step, the sensitivity of the parameters n and f_m was examined (Fig. 5.1). As values on the parameter n became larger, the behaviour of the soil system approached that of a plug-flow reactor. Namely, the peak of $E(\tau)$ moved from $\tau = 0$ to $\tau = 1$ and became larger as the peak approached $\tau = 1$. Smaller values on the parameter f_m, which means larger stagnant regions, made the peak of $E(\tau)$ larger and the maximum value occurred a bit earlier. In addition, Eq. [5.11] shows mathematically that a new graph of $E(\tau)$ is obtained by magnifying that of the original version of $E(\tau)$ (i.e., $f_m = 1$) by the factors $1/f_m$ (vertically) and f_m (horizontally), respectively (Fig. 5.1).

The moment analysis has been used to select the values on parameters for distribution functions, so that the moments of a distribution function are equal to those of the sample data (Toride and Leij, 1996; Utermann et al., 1990; Jury and Gruber, 1989). The mean ($\bar{\tau}$) and variance (σ^2) of tracer travel time in our model were obtained as follows:

$$\bar{\tau} = M_1 = \int_0^\infty \tau E(\tau)d\tau = f_m \qquad [5.12]$$

$$\sigma^2 = M_2 - M_1^2 = \int_0^\infty \tau^2 E(\tau)d\tau - M_1^2 = \frac{f_m^2}{n} \qquad [5.13]$$

where M_1 and M_2 are the first and the second moment of $E(\tau)$. It was necessary for this analysis that the experimental period was long enough. For example, it was necessary for determination of f_m that τ should be more than five in case of $n=1.4$ (Fig. 5.2). In order to avoid this problem, the author focused on the peak of $E(\tau)$ (Fig. 5.1). The coordinate of the peak was obtained by a differential calculation, i.e.:

$$M_{fm,n}(\tau_{max}, E_{max}) = M_{fm,n}(\frac{n-1}{n}f_m, \frac{n(n-1)^{n-1}}{f_m\Gamma(n)}e^{-(n-1)}) \qquad [5.14]$$

where $M_{fm,n}(\tau_{max}, E_{max})$ was the coordinate of the peak of $E(\tau)$. $M_{fm,n}$ was expressed by the combination of the parameters f_m and n (Fig. 5.3). The peak coordinates of the experimental

$n = 1.4$

$f_m = 1.0$
$f_m = 0.9$
$f_m = 0.8$
$f_m = 0.7$
$f_m = 0.6$
$f_m = 0.5$
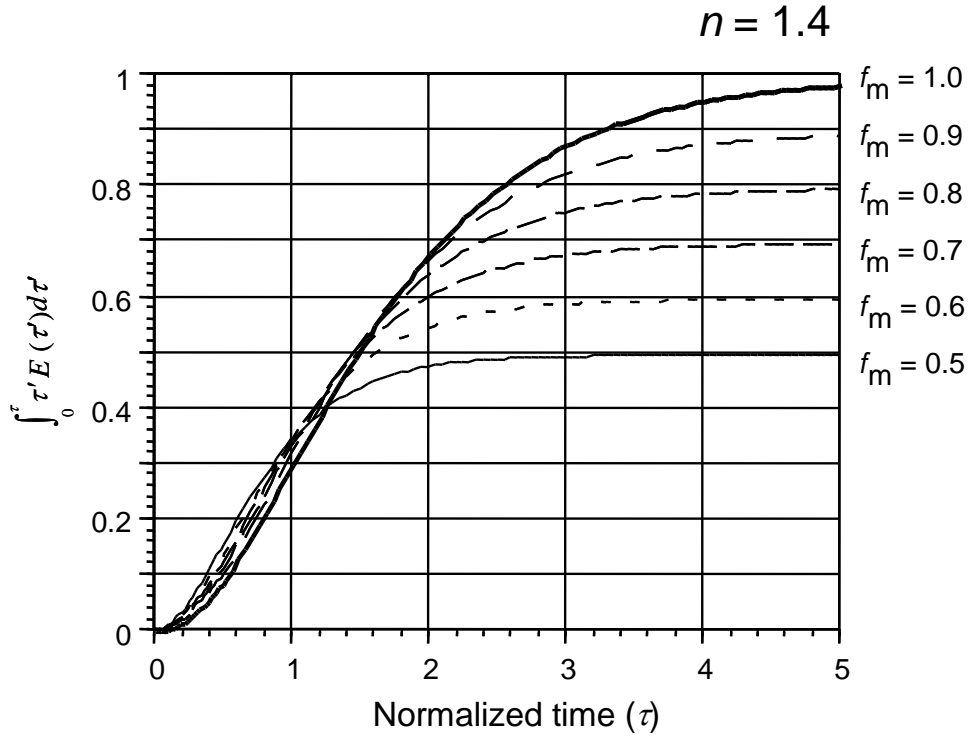
Normalized time (τ)

Fig. 5.2. Integration of the distribution function of tracer travel time multiplied by the moment arm from zero to τ of normalized time.

$f_m = 0.5$ 0.6 0.7 0.8 0.9 1.0

$n = 10$

1 1.2 1.4 1.6 2 3 5
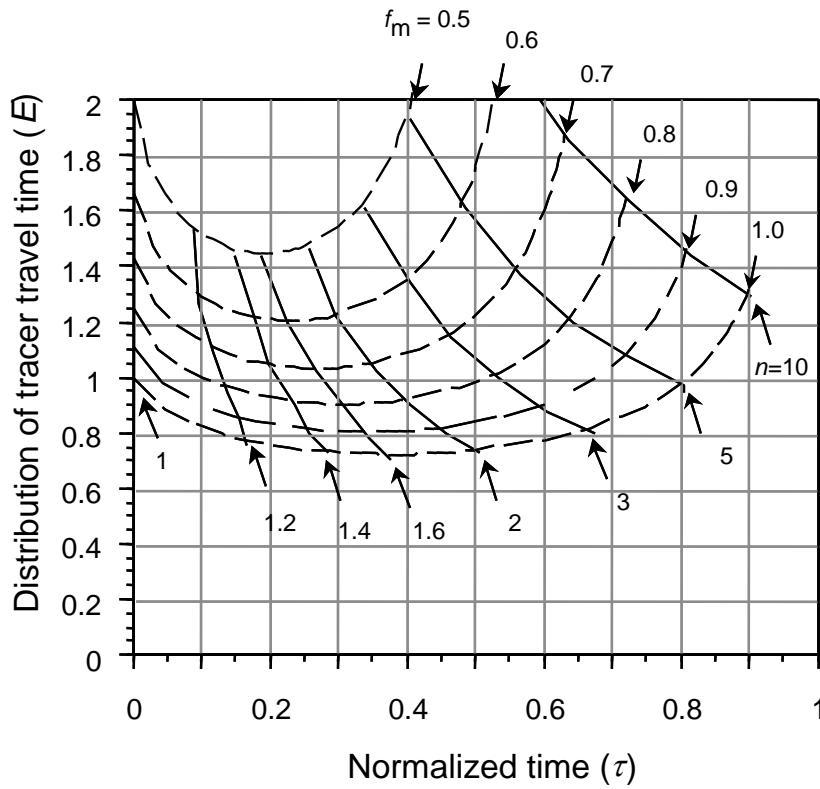
Normalized time (τ)

Fig. 5.3. Relation between the peak of distributions of tracer travel time $(E(\tau))$ and normalized time (τ) for different values on the parameters n and f_m.

85

data ($E(\tau)$) in each lysimeter was visually determined and the corresponding parameters f_m and n were obtained by using the graphs shown in Fig. 5.3. This was done because Eq. [5.14] contains a gamma function and it cannot be solved for f_m and n.

Measured concentrations of bromide were divided by M (10 000 mg m^{-2} = 100 kg ha^{-1}) and multiplied by V (218 mm) according to Eq. [5.11].

5.3 MATERIALS AND METHODS

5.3.1 Soil properties

The soil monoliths were collected at Ultuna, Sweden (59°48'N, 17°39'E) in June, 1998. This soil is a heavy clay soil with a clay content of ca. 40 % throughout the profile, with illite as the dominant clay mineral (Wiklander and Lotse, 1966). It is classified as Fuluventic Eutrochrept according to the USDA soil classification system (Soil Survey Staff, 1975). There are many coarse and fine tubular pores throughout the profile, formed by earthworms and roots. The topsoil structure is moderate/medium to coarse subangular blocky when moist, but becomes massive with cracks when dry (Messing and Jarvis, 1990).

For determination of chemical properties, the soil was air dried for 5 days and sieved (mesh size 2 mm). Soil pH (1:2.5), cation exchange capacity (CEC), and inorganic and organic carbon contents (determined by loss on ignition) were determined in the laboratory. For determination of Cu and Zn concentrations in soil, the soil was digested by 7M HNO_3 at a temperature of 120 ^{O}C for 2 h (Swedish standard SS028311) and then concentrations in the solutions were measured by atomic absorption spectrophotometry (IL551, Instrumentation Laboratory). Bulk density and saturated hydraulic conductivity were measured on cores (72 mm in diameter, 100-mm long) collected in the monoliths used in this study. Some chemical and physical soil properties are listed in Table 5.1.

Table 5.1. Some properties of the Ultuna soil.

Soil property	Soil depth (cm)				
	0–10	10–20	20–30	30–40	40–50
Bulk density (g cm^{-3})	1.35	1.50	1.60	1.65	1.50
Hydraulic conductivity (cm h^{-1})	6.1	1.4×10^{-2}	4.4×10^{-3}	4.4×10^{-3}	4.4×10^{-3}

	0–20 cm	20–50 cm
pH (1:2.5)	7.8	7.8
Zn (mg kg^{-1})	88	106
Cu (mg kg^{-1})	24	24
CEC (cmol$_c$kg^{-1})	19.43	15.03
Inorganic Carbon (%)	0.04	0.03
Organic Carbon (%)	1.33	0.74

To examine sorption of NH$_4$-N, NO$_3$-N, Zn, and Cu to soil, a column experiment was performed to obtain breakthrough curves of the elements under a steady-state flow condition. Sieved topsoil was used for this purpose. The details of the column-flow system followed what has earlier been described by Nishimaki et al. (1994). The column had an inner diameter of 1.9 cm and a length of 9 cm. The column was filled with deionized water, then 20 g of the soil was added, which resulted in a bulk density (ρ) of 0.85 g cm^{-3}. The flow rate through the column was 5.4 cm h^{-1}. The experiment was started by passing 1.0 mol L^{-1} CaCl$_2$ through the column for 24 h, followed by similarly passing deionized water during the next 24 h. Then, the input solution (pH 5.8), including 0.2 mmol L^{-1} KBr, 2 mmol L^{-1} NH$_4$NO$_3$, 0.2 mmol L^{-1} CuCl$_2$, and 0.2 mmol L^{-1} ZnCl, was supplied until ca.130 pore volumes of effluent solution had eluted. Retardation factors R_f (−) were calculated as the pore volumes when the relative concentration was 0.5 (Radioactive waste management center, 1990). Soil-solution distribution coefficients K_d (cm^3 g^{-1}) were calculated by the following equation (Inoue and Kaufman, 1962):

$$K_d = \frac{R_f - 1}{\rho} \theta \qquad [5.15]$$

where θ (−) is the porosity ($\theta = 0.64$).

5.3.2 Collection of monoliths and experimental treatments

Twelve 500-mm deep monoliths, enclosed in polyvinyl chloride (PVC) pipes (295-mm inner diameter and 586-mm long) were collected by use of a coring technique described by Persson and Bergström (1991). After collection, the lysimeters were prepared for gravity drainage by placing a porous plastic sheet over the bottom end of the monoliths. Before installation of the lysimeters in a lysimeter station, all monoliths were slowly filled with tap water from the bottom end until water was ponding on the soil surface. After saturation, the monoliths were allowed to drain freely for 1 week to reach a moisture content close to field capacity. The lysimeters were then placed in pipes permanently installed (below ground level) at the lysimeter station in Uppsala, Sweden. Before installation, all lysimeters were weighed to determine the field-capacity water content in each monolith. The change of water content in soil over the experimental period was also measured by weighing. The maximum amount of water in a monolith, after being freely drained, was 218 mm.

Three precipitation regimes were used in triplicate: (i) N-C and N-A, which were exposed to natural precipitation during the period 22 July 1998 to 25 January 1999; (ii) D-A, which was exposed to 'double' natural precipitation from 22 July to 9 November 1998, and then natural precipitation only until 25 January 1999; and (iii) T-A, which was exposed to 'triple' natural precipitation from 22 July to 9 November 1998, and then natural precipitation until 25 January 1999. Weekly supplemental irrigation for D-A and T-A was calculated as the difference between the target value and the cumulative natural precipitation during the week, which was then applied on the soil surface during one or two days (< 20 mm d^{-1}) in the following week. Rainfall simulators (giving a rainfall intensity of ca. 4 mm h^{-1}) filled with tap water were used for irrigation. The amounts of water added in each treatment are listed in Table 5.2. The pH of tap water was 7.4.

Nitrogen and heavy metals, dissolved in 100 mL of water, were uniformly applied

on each monolith by using an atomizer (Atomizer No.163, Devilbiss). Nitrogen was applied as NH_4NO_3 at a rate of 100 kg N ha^{-1} (50 kg NO_3-N ha^{-1} and 50 kg NH_4-N ha^{-1}), zinc as $ZnCl$ at a rate of 100 kg Zn ha^{-1}, and copper as $CuCl_2$ at a rate of 40 kg Cu ha^{-1}. The used N rate represents the normal dose for barley under Swedish conditions. The selected Zn and Cu application rates were determined so that the concentration of metals in the topsoil would likely be within the maximum concentrations of metals allowed in agricultural soils treated with sewage sludge in countries within the European Community (150-300 mg Zn kg^{-1}; 50-140 mg Cu kg^{-1}) (McGrath et al., 1994). Simultaneously, bromide was applied as KBr at a rate of 100 kg Br ha^{-1}. During application, the chemicals were mixed with the upper 5 cm of soil with a trowel. All chemicals were applied on 22 July 1998. No application was done on three control lysimeters (N-C), of which one was destructively sampled on 22 December, to determine bulk density and saturated hydraulic conductivity. All control lysimeters were exposed to natural precipitation only (see above), during the entire period.

5.3.3 Leachate sampling and water analysis.

Water leaching through the monoliths was led in plastic (polyethylene) pipes to glass sampling bottles placed in the belowground measuring station. The bottles were weighed after every rainfall event to determine the leachate volumes. Simultaneously, subsamples were taken for chemical analysis.

Concentrations of NO_3-N, NH_4-N, and Br were determined by flow-injection analysis (Fiastat 5010 Analyzer, Tecator AB) according to colorimetric methods; NO_3-N, according to the Cd-reduction method (APHA, 1985), NH_4-N, with a combined flow-injector gas-diffusion method (Tecator, 1984), and Br, according to the phenol red method (Anfält and Twengström, 1986). Concentrations of Zn and Cu were measured by inductively coupled

plasma spectroscopy (ICP-AES JY70 PLUS, Jobin Yuon), and pH was determined by use of a

pH meter (PHM82 Standard pH meter, Bergman & Beving).

5.4 RESULTS AND DISCUSSION

5.4.1 Sorption of NH$_4$-N, NO$_3$-N, Zn, and Cu to soil

The relative concentration of the elements was calculated as a ratio between the concentration

in the effluent of the packed soil column and that in the input solution (Fig. 5.4). The

retardation of the breakthrough curves of the elements to that of a non-reactive tracer results

from sorption of the elements to soil (Radioactive waste management center, 1990). NO$_3$-N

was not sorbed to soil because the behaviour of NO$_3$-N was similar to that of a non-reactive
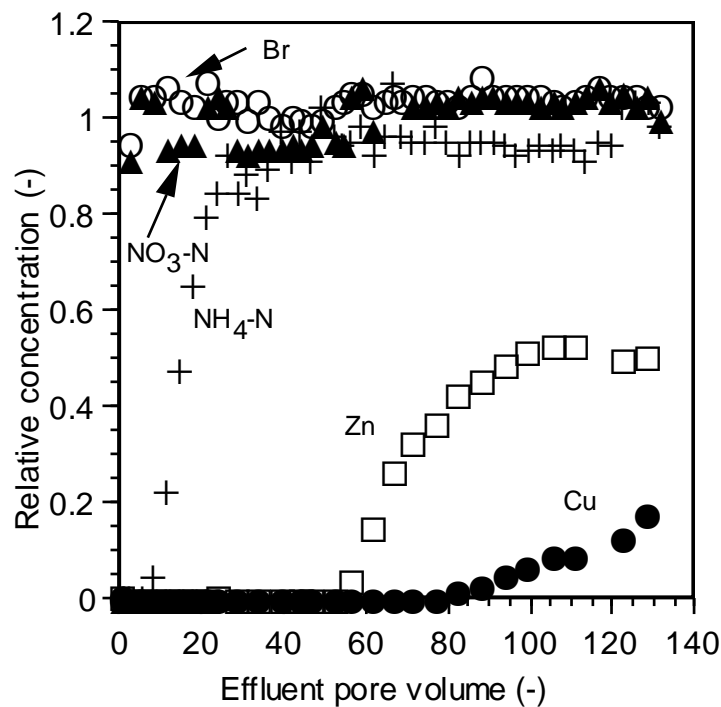
Fig. 5.4. **Breakthrough curves of NO$_3$-N, NH$_4$-N, Zn, and Cu through a soil column under a steady-state flow condition.**

tracer, in this case, Br (Fig. 5.4). The relative concentrations of Cu did not reach 0.5 during the period, which means that the R_f value for Cu must have exceeded 130. The K_d values for NH$_4$-N, Zn, and Cu in soil were 11, 75, and over 97 mL g^{-1}, respectively.

5.4.2 Weather and drainage conditions

The total precipitation was 252 mm during the experimental period (22 July 1998 - 25 January 1999), which is about 60 mm less than the 30-yr normal precipitation during the same period. The supplemental irrigation made the total water inputs 396 and 540 mm, for D-A and T-A, respectively (Table 5.2 and Fig. 5.5).

Table 5.2.   Water inputs in the three irrigation treatments.

	Water inputs (mm)	
Treatment	July 22-Nov. 9	Nov. 10 - Jan. 25
N-C	154 mm	98 mm
N-A	154 mm	98 mm
D-A	298 mm	98 mm
T-A	442 mm	98 mm
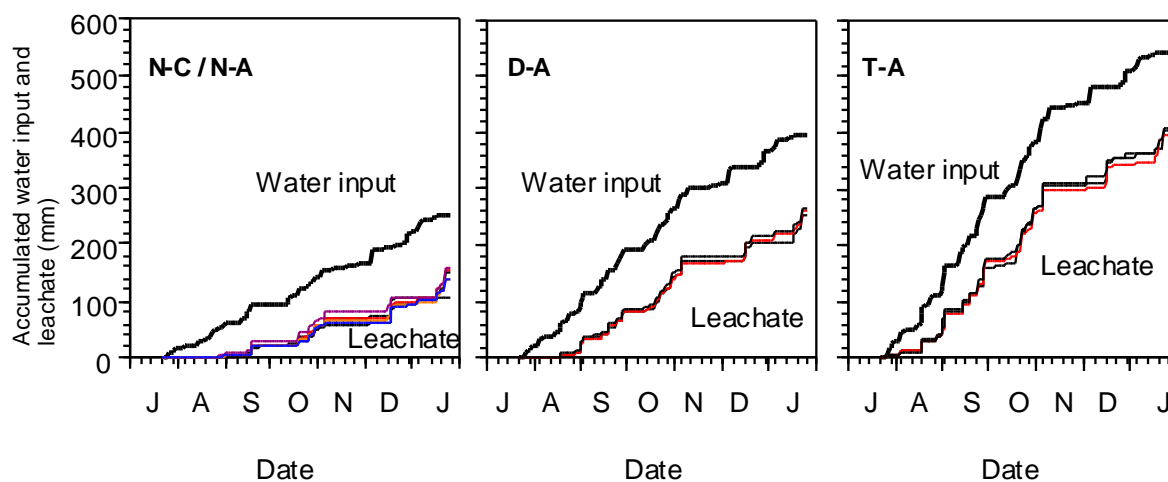
Fig. 5.5.   Accumulated amounts of precipitation and leachate during the period 22 July 1998 to 25 January 1999.

The soil was, more or less, frozen from 10 November onwards, and precipitation thereafter often occurred as snow. Still, the accumulated snow occasionally melted and water sometimes infiltrated in December and January when the temperature continued to be above freezing for several days. During such periods, water from the melted snow was typically ponding on the soil surface for a few days because the soil was still frozen. The average total amounts of leachate were 148 mm for N-C and N-A, 261 mm for D-A, and 403 mm for T-A (Fig. 5.5). These values accounted for 59 %, 66 %, and 75 % of the total water inputs, respectively. The differences in water content of the soil monoliths before and after the experiment were 5.2 mm (2 % of the input) for N-C and N-A, 3.2 mm (1% of the input) for D-A, and 8.2 mm (2 % of the input) for T-A. Accordingly, the amounts of evaporation during the experiment were 99 mm for N-C and N-A, 132 mm for D-A, and 129 mm for T-A.

At the end of October for T-A and in the middle of January for D-A, the cumulative amounts of leachate reached a level, which was equivalent to the amount of water (218 mm) that was present in each monolith after being freely drained. The N-C and N-A monoliths did not reach this water saturation level during the period (i.e., it was only 68 % of the field capacity moisture content at the end of the experiment).

5.4.3 Bromide leaching

Br recoveries in leachate were, on the average, 40 % for N-A, 61 % for D-A, and 74 % for T-A during the experiment (Table 5.3). Br concentrations for D-A and T-A reached about 40 mg L^{-1} in the beginning of the experiment and then decreased below 10 mg L^{-1} towards the end (Fig. 5.6). Br concentrations for N-A also increased to about 40 mg L^{-1}, although, a bit later than D-A and T-A, and then decreased to the same level as D-A and T-A. In other words, Br concentrations in the peak of the breakthrough curves were quite similar for all treatments

Table 5.3. Inputs and leaching (Mean±SD, n=3) of Br, N, Zn, and Cu (kg ha^{-1}).

Treatment	Br	NO$_3$-N	NH$_4$-N	Zn	Cu
		Inputs (Application + in rainfall and irrigation)			
N-C	0 + 0	0 + 1	0 + 1	0 + 0	0 + 0
N-A	100 + 0	50 + 1	50 + 1	100 + 0	40 + 0
D-A	100 + 0	50 + 3	50 + 1	100 + 0	40 + 0
T-A	100 + 0	50 + 5	50 + 1	100 + 0	40 + 0
		Leaching			
N-C	1.0 ± 0.3	9.1 ± 6.0	0.5 ± 0.4	0.18 ± 0.15	0.02 ± 0.01
N-A	40.0 ± 3.3	32.9 ± 10.3	0.7 ± 0.2	0.48 ± 0.10	0.03 ± 0.00
D-A	60.7 ± 5.7	55.2 ± 12.8	1.0 ± 0.3	1.27 ± 0.42	0.05 ± 0.00
T-A	74.4 ± 4.0	62.5 ± 5.6	1.6 ± 0.2	1.24 ± 0.77	0.08 ± 0.02

which had received Br, and the peaks appeared in the order of the water input rates, such that the decrease in Br concentrations after the peak was more rapid when water inputs were larger. If the water entering the soil moved downwards as matrix flow, the Br peak concentration would appear when the accumulated leachate reached an amount of water corresponding to the water content at field capacity in a monolith. However, in all treatments the Br peaks eluted before the accumulated leachate reached this level, which is a clear indication of preferential flow.

A common problem with lysimeters is that water and water-carried chemicals may flow along the lysimeter wall, thereby affecting solute movement in the same way as preferential flow. The extent of this problem for the type of lysimeter used in this study was assessed in an experiment presented by Bergström et al. (1994) in which monoliths of a clay and a sandy soil were treated with two non-reactive tracers (^{36}Cl and tritiated water). One was applied in the center of the monolith surfaces and the other along the wall. In each soil, both tracers appeared simultaneously in leachate, which show that 'sidewall flow' is not a problem for this type of lysimeter.
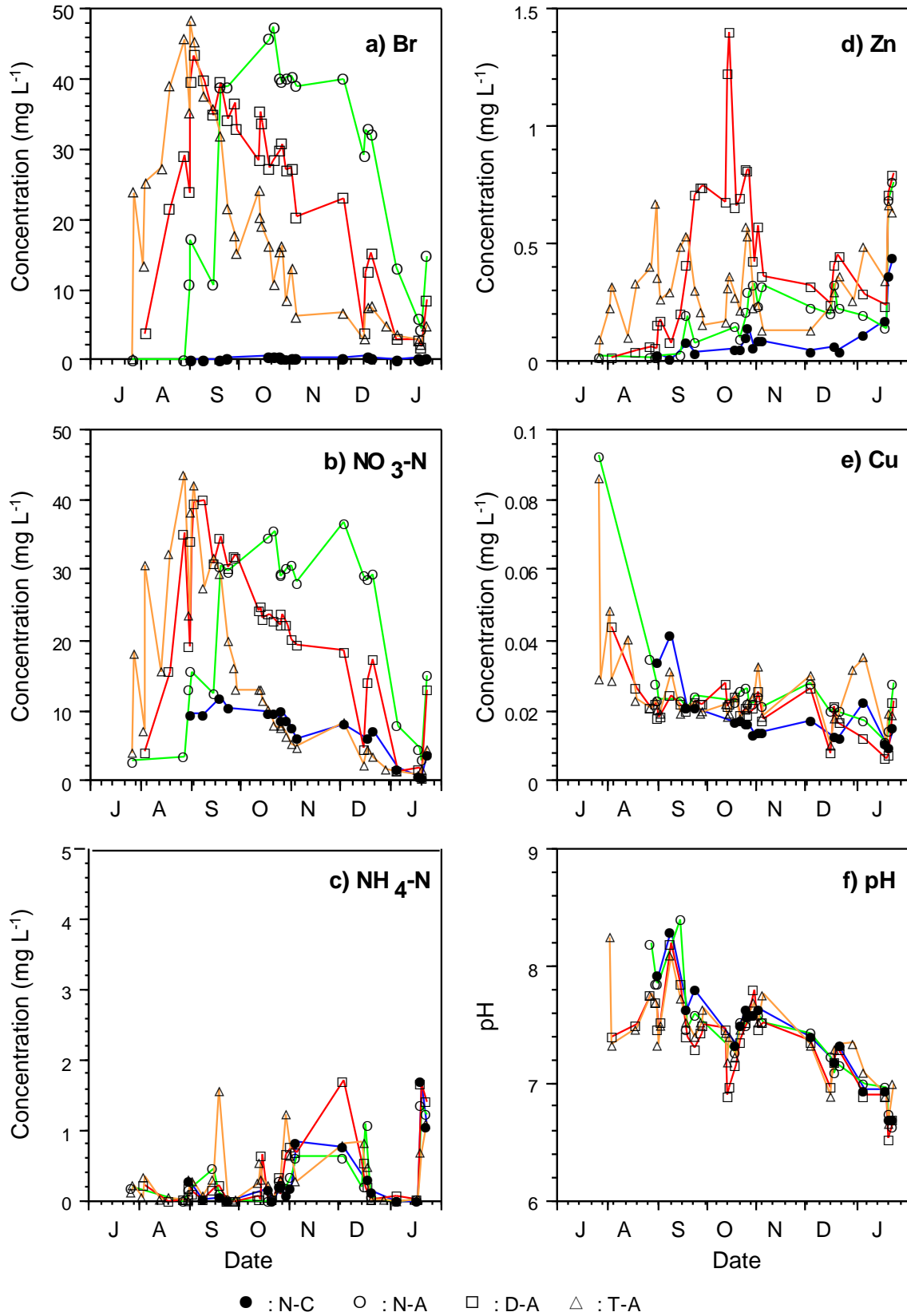
Fig. 5.6. **Concentrations of a) Br, b) NO₃-N, c) NH₄-N, d) Zn, and e) Cu, and f) pH values in leachate during the period 22 July 1998 to 25 January 1999. Each value represents the mean of three replicates.**

94

5.4.4 Model results

Preferential flow is caused mainly by two mechanisms. One is the existence of stagnant regions (dead space). This mechanism can be expressed in terms of the parameter f_m. The other is due to uneven water-flow rates. Some regions with rapid flow rates, such as macropores, and matrix flow regions will result in a large variability of flow rates. This condition may be expressed in terms of the parameter n.

Experimental results are plotted in Fig. 5.7, together with fitting curves for different values on the parameters f_m and n used in the model. Generally, experimental data was well predicted by the modified tanks-in-series model. The values on f_m ranged from 0.6 to 1.0 and those of n are from 1.1 to 2.0. These results suggest that the heavy clay soil used in this study might have 0-40% of stagnant regions in the profile. If the degree of mixing and stagnant regions were smaller without preferential flow, the peak of $E(\tau)$ would appear at $\tau = 1$ (Fig. 5.1). The peaks of $E(\tau)$ were, however, observed far earlier than $\tau = 1$ in all treatments (Fig. 5.7). In other words, the mixing conditions in the monoliths were pronounced. This high degree of mixing suggests that matrix flow, and different kinds of preferential flow, occurred simultaneously in this clay soil. The values of f_m increased with those of n for N-A and D-A, although, the values of n were constant for T-A (Fig. 5.8). It is possible that a high degree of mixing occurred in small mobile regions. No clear relationships between the two parameters and the precipitation regimes could be seen (Fig. 5.8). Therefore, it may be safely assumed for this heavy clay soil that $E(\tau)$ can be expressed in terms of the cumulative leachate, regardless of precipitation regime. In other words, these results showed that the precipitation regime did not affect the degree of preferential flow in the studied columns.

During later periods of the experiment, measured values of tracer travel time were lower than simulated values in all monoliths (Fig. 5.7). These periods coincide with freeze-thaw periods. The flow conditions during such periods seemed to be quite different
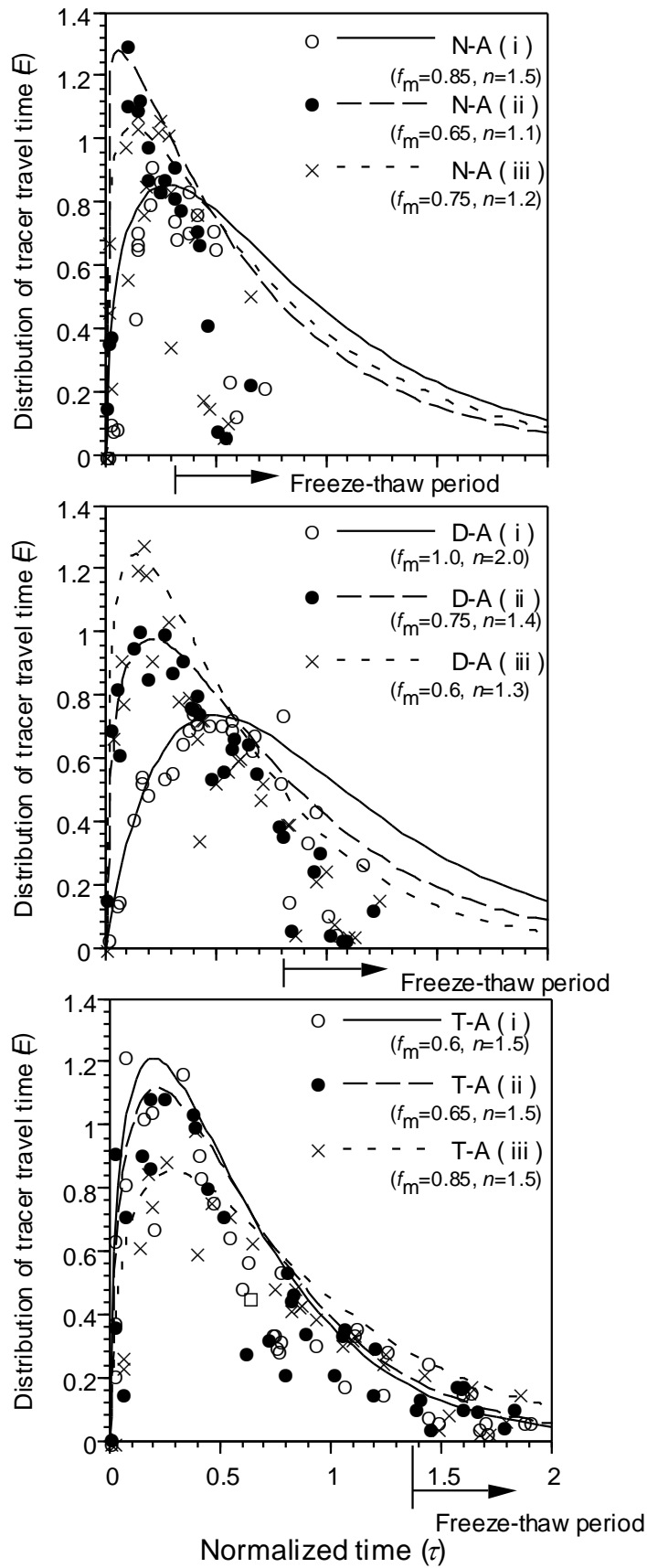
Fig. 5.7. Measured and simulated distributions of tracer travel time ($E(\tau)$) vs. normalized time (τ). (i), (ii), and (iii) represent the three respective replicates.
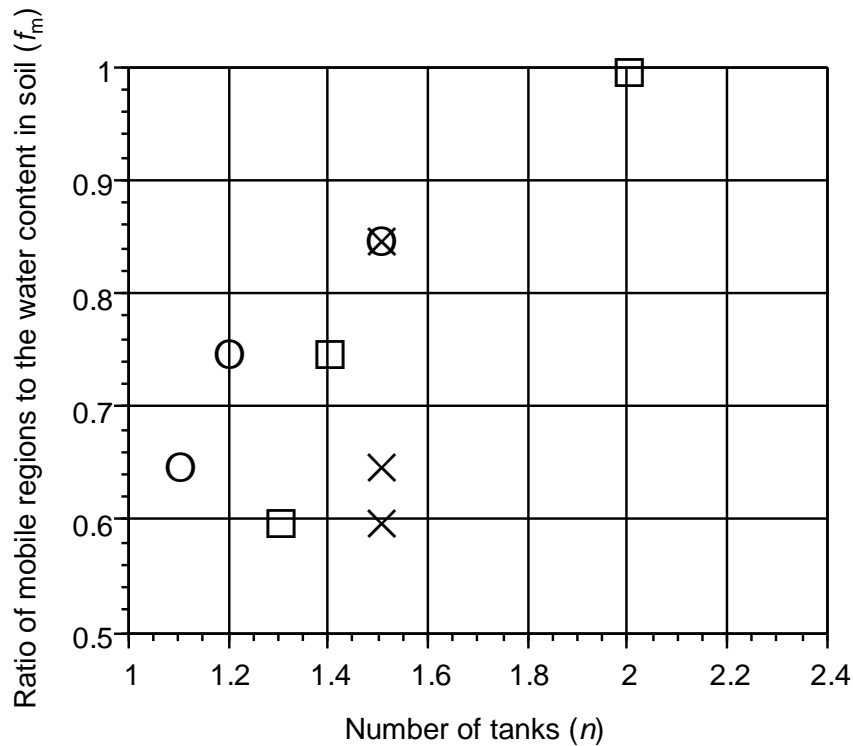
Fig. 5.8. Values of *n* and f_m in the three precipitation regimes (N-A: ○, D-A: □, T-A: ×).

from those occurring during the summer months. Low concentrations of Br (low distributions of normalized tracer travel time) were seen in the first discharge after a long period of snow accumulation, which is similar to an observation by Bergström and Jarvis (1993). They explained this in terms of redistribution of the tracer to smaller unfrozen pores on freezing, and that, upon melting, percolating water would be practically free from the tracer.

5.4.5 Nitrogen leaching

Total leaching losses of inorganic N (NO_3-N and NH_4-N) for N-C was about 10 kg ha^{-1} (Table 5.3). Nitrate leaching losses increased with increasing water inputs and accounted for 66, 110 and 125 % of the total inputs of NO_3-N in the N-A, D-A, and T-A treatment, respectively.

Despite the fact that NO_3-N was applied at a rate which was only half that of Br, the pattern by which NO_3-N appeared in leachate was similar to that of Br, except that the background concentrations of NO_3-N (cf. the N-C treatment) were higher and NO_3-N peak concentrations were slightly lower than the corresponding Br concentrations (Fig. 5.6). Over the experimental period, NO_3-N concentrations in the treatments that received N (N-A, D-A, and T-A) were higher than what is recommended for drainage water leaving agricultural soils in Sweden (5.0 mg L^{-1}). NO_3-N concentrations for N-C were about 10 mg L^{-1} in the beginning of the period and then decreased to 2 mg L^{-1} towards the end. Such concentrations are typical for Swedish clays soils similar to this one, which are exposed to agricultural practices (Bergström and Johansson, 1991). In terms of NO_3-N leaching, the N-C load accounted for about 20 % of the input of the other treatments.

The similar leaching pattern of NO_3-N and Br, means that NO_3-N presumably also moved through the soil profiles by preferential flow. In contrast, Bergström (1995) stated that preferential flow appeared to be of little significance for NO_3-N transport; at least, it did not increase leaching in a similar soil. This was explained in terms of an even distribution of N in the soil matrix, and water rapidly flowing through preferential flow paths should therefore not carry significant amounts of NO_3-N. A similar explanation was given by Larsson (1999). In the treatments receiving supplemental irrigation in this study, NO_3-N leaching losses were higher than the input of NO_3-N with fertilizer, indicating high background concentrations and NO_3-N formation in soil (Table 5.3). It is also important to note that there was no crop growing in the monoliths used here, which is normally the largest N-sink in agricultural soils.

The occurrence of NH_4-N in leachate was quite different from those of NO_3-N and Br (Fig. 5.6). Also, the difference in NH_4-N concentrations between the treatment that did not receive N (N-C) and those that received N (N-A, D-A, and T-A) was not clear. NH_4-N leaching accounted for 1.4-3.2 % of the total inputs of NH_4-N. One of the reasons for this is sorption of NH_4-N in the topsoil, which was shown to occur in the sorption test (see Section

4.1). Some of NH_4-N may have been discharged as NO_3-N after nitrification (Table 5.3).

5.4.6 Leaching of heavy metals

Heavy metal leaching accounted for minor parts of their inputs. The leaching losses generally increased with increasing water input rates, but there was no difference in Zn leaching losses between D-A and T-A (Table 5.3). Volume weighted mean concentrations of Zn were 0.12 mg L^{-1} for N-C, 0.32 mg L^{-1} for N-A ($P < 0.05$, t-test), 0.49 mg L^{-1} for D-A ($P < 0.05$), and 0.31 mg L^{-1} for T-A. The corresponding values for Cu were 0.016 mg L^{-1} for N-C, 0.023 mg L^{-1} for N-A ($P < 0.05$), 0.020 mg L^{-1} for D-A, and 0.021 mg L^{-1} for T-A. Zn and Cu concentrations in the treatments, which received the element, were higher than those in the control. An increase of Cu leaching losses with water input rates was largely due to an increase of the accumulated leachate.

Zn concentrations increased over time (Fig. 5.6), starting with those of the T-A treatment, followed by the D-A treatment. The highest Zn concentrations occurred in the D-A treatment, with a peak value of 1.4 mg L^{-1} in October. After a decrease in November/December, the Zn concentrations for all treatments were, again, relatively high in January. In contrast to the development of Zn concentrations over time, Cu concentrations were high in the beginning of the period, but decreased relatively soon after application and leveled out towards the end of the period (Fig. 5.6). There was no clear difference in Cu concentrations among the treatments. A comparison of the K_d values (see Section 4.1) for Cu and Zn, revealed that more Cu was sorbed to soil than Zn. The volume weighted average Zn concentrations in leachate of the monoliths, which received the element, exceeded the Swedish standard for drinking water (0.3 mg L^{-1}). The peak concentrations of Zn were quite different among the irrigation treatments, in contrast to the peak concentrations of Br and

NO$_3$-N, which were similar among the treatments (Fig. 5.6).

The Zn concentrations in leachate of all monoliths are shown in Fig. 5.9 to examine the relation to preferential flow in more detail. Zn concentrations for D-A (iii), T-A (i), and T-A (ii) were consistently high, with the maximum concentration shown for D-A (iii) (Fig. 5.9). Concentrations for D-A (iii) and T-A (i) were high in the beginning and then decreased. High concentrations, followed by rapid decreases, are highly related to low values of f_m (Figs.
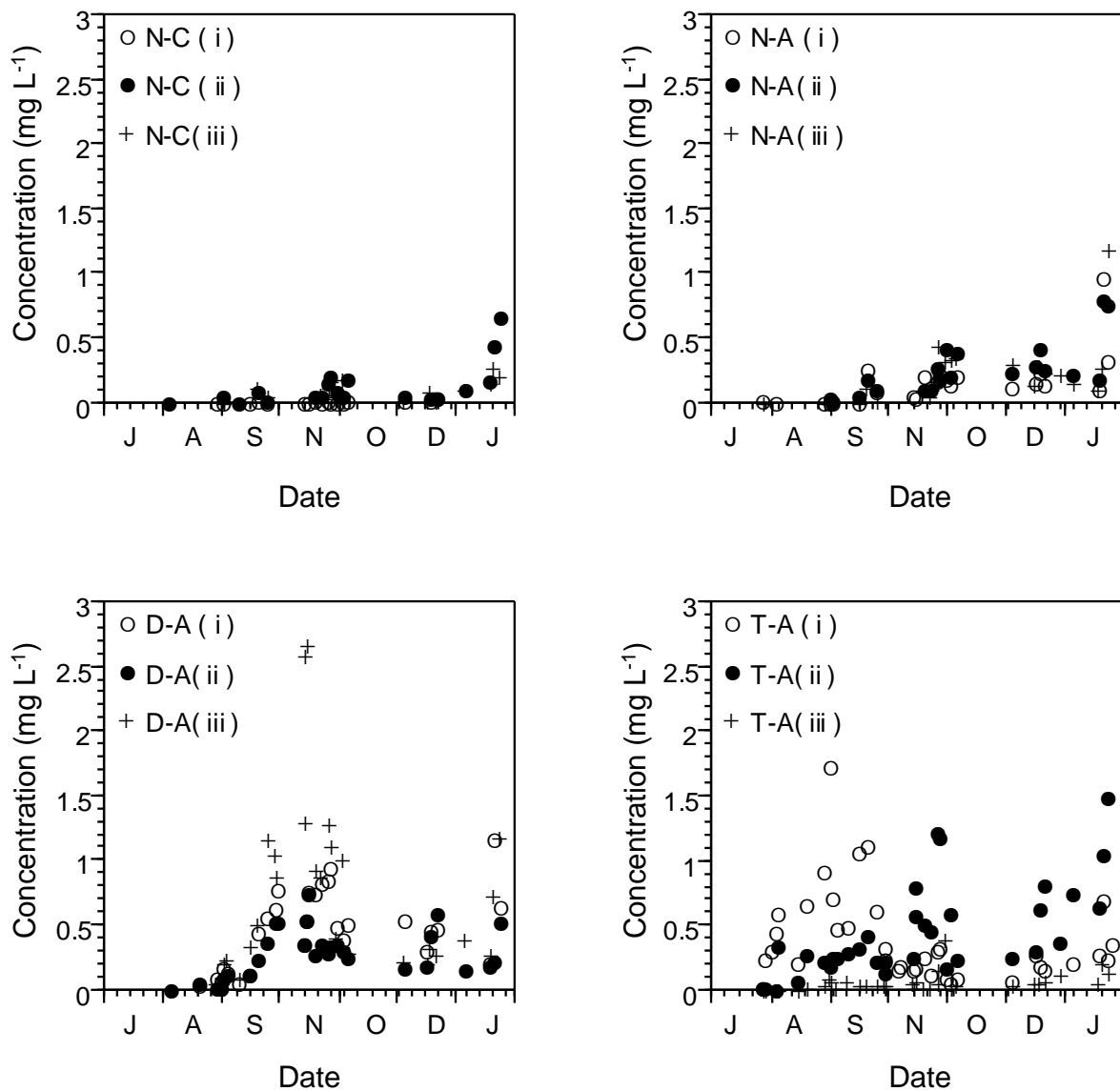
Fig. 5.9. Zn concentrations in leachate of all monoliths during the period from 22 July 1998 to 25 January 1999. (i), (ii), and (iii) represent the three respective replicates.

5.7 and 5.9). Low values of f_m and n are indicative of more pronounced preferential flow; i.e., an earlier appearance and a higher peak of $E(\tau)$ (Fig. 5.1). Preferential flow did not necessarily cause high concentration of Zn, as seen for T-A (iii). However, it was quite clear that preferential flow enhanced heavy metal leaching.

The heavy metal concentrations before the metal applications were 88 mg Zn kg^{-1} and 24 mg Cu kg^{-1} in the topsoil (Table 5.1). If these metals, which were applied at rates of 100 kg Zn ha^{-1} and 40 kg Cu ha^{-1}, were distributed equally in the top 5 cm of soil, the concentrations of heavy metals in this layer would be 236 mg Zn kg^{-1} and 83 mg Cu kg^{-1}, respectively, which is within the range of the EC limits. Nevertheless, Zn concentrations in leachate were quite high, whereas Cu leaching was negligible in this experiment. This could be explained not only in terms of differences in sorption behaviour (see Section 4.1), but also because of the low concentration of organic carbon in the used soil (Table 5.1). Organic matter forms complexes with metals by exchange and chemisorption reactions. Cu has a high affinity for organic matter and moves through soil bound to organic colloids (del Catilho et al., 1993). In other words, mobility of Cu would increase with increasing organic matter content in soil.

The pH of leachate decreased from about 8 to 6.5 during the period (Fig. 5.6). Average pH of precipitation was 6.7 and that of tap water was 7.4. The decrease in pH, which enhances the mobility of heavy metals (McBride, 1995), may be a contributing factor to the high concentrations of Zn during winter. If pH in supplemental irrigation water was similar to that of natural precipitation, leaching of heavy metals would have been higher than what our results showed.

5.5 CONCLUSIONS

By use of a non-reactive tracer (Br), the author confirmed that preferential flow through the 500-mm deep clay monoliths is an important flow pattern. Preferential flow Br in the monoliths was well described by the modified tanks-in-series model with the parameters n and f_m; that is, in terms of the degree of mixing of water in soil and the ratio between mobile regions and the maximum amount of water in a monolith, when freely drained. When determining parameter values, the required experimental period was made shorter by using a peak coordinate of distribution of Br travel time, instead of the moment analysis. In the soil used here, the model could use the cumulative leachate as the only variable in the distribution function of tracer travel time under non-steady flow conditions. Accordingly, the modified tanks-in-series model for a non-reactive tracer may enable us to consider a soil monolith as a non-ideal reactor characterized by the parameters n and f_m. This approach can be a helpful tool when chemical leaching through soils with different preferential flow process are compared. Combining the model for a non-reactive tracer with chemical reaction models (including sorption, transformation, and biodegradation) will then contribute to give us a complete picture of chemical leaching. Leaching of N occurred in the form of NO_3-N, which was also largely displaced through preferential flow, as was the case for Zn, which occurred at relatively high concentrations in leachate, whereas leaching of Cu was negligible. Further studies are necessary to examine leaching of N and heavy metals from real organic amendments, over prolonged periods.

SUMMARY AND CONCLUSIONS

6.1 THEMES

The final goal of the studies undertaken in this thesis was to prevent groundwater contamination by NO_3 from agricultural sources. Although N fertilizer is essential for crop production, excessive N could leach out of arable soils and eventually cause NO_3 contamination of groundwater. Therefore, the mechanisms of NO_3 leaching under environmental conditions must be better understood for the prediction of groundwater contamination and establishment of sustainable agricultural systems.

For this purpose, the author selected and took up three research themes in this thesis: (i) awareness of the NO_3 problem, (ii) development of methods for monitoring NO_3 leaching, (iii) analysis of the effects of various methods of fertilizer application and preferential flow on NO_3 leaching. The author presents the summary of the preceding chapters and the conclusions of this thesis. Finally, the author proposes future needs to expand the results of the thesis to a general understanding of NO_3 leaching processes.

6.2 SUMMARY

In Chapter 2, the relation between NO_3 contamination of groundwater and agricultural

activities was reviewed.

The Japanese Government set the environmental quality standard for NO_3-N in groundwater at 10 mg N L^{-1} in 1998, based on the admissible level for avoiding infant methemoglobinemia. In Japan, 6.3% of groundwater contained NO_3 exceeding 10 mg L^{-1} in 1998 and agriculture is a leading source of NO_3 in groundwater.

Excessive N in soil may lead to large N gaseous and leaching losses from arable land, unless the patterns of N uptake by crops match N available in soil. However, conversely, excessive N is necessary as insurance in some cases. One reason for this is that rainfall, which can not be predicted and controlled, would bring NO_3 in soil to deeper vadose zones, particularly immediately after fertilization. Another is that some vegetables physiologically require a high content of N in soil even at harvest. Besides, the N mineralization rate of manure, which should be applied to arable land, is difficult to predict under natural conditions.

The magnitude of the adverse impact of the factors influencing NO_3 leaching must be evaluated to improve agricultural management, resulting in the maintenance of crop yields while reducing NO_3 leaching. These factors include fertilizer management, cropping systems, soil types, and climatic conditions. The main concept of preventive measures is to match available-N in soil to crop demand-N all the time.

In Chapter 3, methods for monitoring NO_3 leaching in upland fields were introduced and the practical use of wick samplers and monolith lysimeters was discussed.

The monitoring methods must be accurate, easy to use, and inexpensive, in order to evaluate many agricultural measures for preventing groundwater contamination under various environmental conditions. There is no perfect method of determining NO_3 leaching in fields at present. It much depends mainly on the soils studied and the available resources. Conventional lysimeter facilities have drawbacks in limiting the number of experimental

treatments or replicates because of the high cost. In situ lysimeters such as wick samplers, which are installed in actual fields, are promising alternatives. However, the in situ lysimeters are not fully satisfactory. On fairly uniform unstructured soil, porous suction cup samplers are the best choice to determine the NO_3 concentration in soil water while other tools are necessary to determine the NO_3 fluxes. Monolith lysimeters containing undisturbed soil are suitable for structured or sandy soils where preferential water flow often occurs. The monolith lysimeters are recommended for studies where a large number of treatments or replicates are needed. Drainage collection systems can be used where impermeable clay subsoil exists under the system.

In the second section, the performance of wick samplers was investigated in terms of water collection efficiency. Water collection efficiency of wick samplers, defined as the volume of water collected by a sampler divided by the water flux from the root zone, should be close to 100%. The author used three wick samplers differing in wall height in an Andisol (Hydric Hapludand) under constant rainfall intensity and examined the effects of the rainfall intensity and wall height on the water collection efficiency based on experimental data and a numerical analysis. The water collection efficiency of wick samplers increased with the rainfall intensity and wall height because the increase in both rainfall intensity and wall height resulted in a distribution of the total potential inside the wick sampler close to that outside the wick sampler. Furthermore, the ratio of the cross-sectional area of the drain hole to that of the cylinder must be taken into account in the design of a wick sampler. The performance of the wick samplers in an actual field showed a similar trend to that in laboratory tests. Nitrogen leaching was measured in the sweet corn field treated with chemical fertilizer at 200 kg N ha^{-1} using the wick samplers. Nitrogen leaching in the field was estimated at 30-70 kg ha^{-1} during the test period from 5 May to 6 August 1997.

In the third section, a drilling system for the collection of soil monoliths was developed. This unique model can be attached to the three-point hitch system, which is a

standard for all tractors, on the rear of a tractor. 'Sidewall flow', which refers to the process that water or solute runs along the lysimeter wall, was not observed for an Andisol monolith sampled using this drilling system.

In Chapter 4, NO_3 leaching was studied in an Andisol (Hydric Hapludand) treated with three types of N fertilizers in addition to a control (SC: swine compost, CU: coated urea, AN: ammonium N, or NF: no fertilizer) for 7 yr. Sweet corn (*Zea mays* L.) was grown in summer, followed by Chinese cabbage (*Brassica rapa* L. var. *amplexicaulis*) or cabbage (*Brassica oleracea* L. var. *capitata*) in autumn each year. In the chemical fertilizer plots treated with AN or CU, the NO_3-N concentration in soil water at 1-m depth increased markedly in the summer of the second year and fluctuated between 30 and 60 mg L^{-1}. In the SC plot, the NO_3-N concentration started increasing in the fourth year, reaching the same level as in the AN and CU plots in the late period of the experiment. In the NF plot, the NO_3-N concentration was about 10 mg L^{-1} for the first 4 yr and decreased to 5 mg L^{-1}. The potential NO_3-N concentrations determined by an N and water balance equation satisfactorily predicted the NO_3-N concentration in the AN and CU plots, but substantially overestimated that in the SC plot, presumably because a large portion of N from SC first accumulated in soil in the organic form. Nitrate N concentration in the soil water decreased with depth from 1 to 4.3 m. The groundwater table rose to less than 2-m depth in summer. The rising groundwater washed away soil NO_3 and induced anaerobic conditions in soil, resulting in denitrification. The latter was supported by the fact that the NO_3-N/Cl ratios of soil water at depths of more than 3 m were lower and those $\delta^{15}N$ values were higher than at 1 m in the AN plot, although the contribution of denitrification may be small. Our results indicate that, under the Japanese climate (Asian monsoon), excessive N from chemical fertilizers applied to Andisols can cause substantial NO_3 leaching, while compost application may enable to achieve high yields and low N leaching during a few years but would lead to the same level of NO_3

leaching as in chemically fertilized plots over longer periods of time.

In Chapter 5, the leaching rates of N and heavy metals (zinc and copper) were measured in 500-mm deep monolith lysimeters containing a heavy clay soil (Fuluventic Eutrochrept). The purpose was to investigate the influence of preferential flow on the leaching of these chemicals under different precipitation regimes. Nitrogen was applied at a rate of 100 kg ha^{-1} (50 kg NO$_3$-N ha^{-1} and 50 kg NH$_4$-N ha^{-1}), Zn at a rate of 100 kg ha^{-1}, and Cu at a rate of 40 kg ha^{-1}. Simultaneously, Br was applied at a rate of 100 kg ha^{-1} to provide information on water movement through the profiles. A modified version of the 'tank-in-series model' was used to describe a distribution function of non-reactive tracer (Br) travel time and compare the results with experimental data obtained in the lysimeters. Rapid discharge of Br in the monoliths was taken as clear evidence for preferential flow. This flow behaviour was well described by the model through the parameters n and f_m; that is, in terms of the degree of mixing of water in soil and the ratio between mobile regions and the maximum amount of water in a monolith, when freely drained. When determining parameter values, the required experimental period was made shorter by using a peak coordinate of distribution of non-reactive tracer travel time, instead of the moment analysis. The model could use the cumulative leachate as the only variable in the distribution function of tracer travel time under non-steady flow conditions. Nitrogen leaching occurred in the form of NO$_3$-N, which was also largely displaced through preferential flow. Zinc leaching was also enhanced by preferential flow, whereas Cu leaching was negligible. Concentrations of NO$_3$-N and Zn in the leachate in the treatments, which received the element, often exceeded the Swedish or Japanese drinking water guidelines. The results obtained in this study show that preferential flow may have a substantial influence on the leaching of heavy metals and N, and the combination of monolith lysimeters and the modified tanks-in-series model may be used to classify soils in terms of the occurrence of such flow behaviour.

6.3 CONCLUSIONS

The present study addressed the above three themes through critical reviews, field experiments, and theoretical discussions.

For the first theme, the author pointed out that balancing both effects of nitrogenous fertilizer, namely crop growth promotion and human health concern, should be considered at any levels and suggested that the mechanisms of NO_3 leaching must be understood to propose optimum balanced practices in a field.

For the second themes, the author suggested that the use of wick samplers and monolith lysimeters was the most suitable method. Wick samplers are not fully satisfactory at present but could be improved based on the findings of this thesis. Monolith lysimeters have a large potential to evaluate NO_3 leaching in structured soils and enable to carry out studies where a large number of treatments or replicates are needed. The developed drill system, which can be attached to the three-point hitch system of a tractor, was found to be a useful and convenient device to collect soil monoliths.

For the last themes, NO_3 leaching from different fertilizers and in structured soil where preferential flow would occur was monitored and the data obtained in the experiments were well evaluated with approaches based on simple mathematics. Although precise prediction of N fate in the environment is required in some cases, the risk evaluation of agricultural management for NO_3 leaching should also provide sufficient information for policy making or regulation.

6.4 FURTHER NEEDS

This study presented the performance of wick samplers and monolith lysimeters for NO_3

leaching monitoring. For practical use of wick samplers, selection of materials for wicks is the most important issue. We need to develop wicks that provide the same matric potentials at the top of the wick, as those at the corresponding soil depth outside the sampler, regardless of the water conditions, so that water entering the collection vessel can be the same as infiltrating water. As for monolith lysimeters, we need to test sidewall flow for different soils and the effects of the surface area of a monolith on crop growth.

The author demonstrated that the N and water balance equation proposed by OECD could predict NO_3 leaching for chemical fertilizers but not for composts. The fate of manure-N applied to fields must be farther examined using ^{15}N-labeled manure. Only one kind of compost was used in this study. Due to the diversity of the kinds of manure, different manures may show different results from that in the present study.

Lateral flow of groundwater was not considered in this study. Analysis of three-dimensional flow of groundwater may enable to analyze the quality changes of groundwater on a large scale and over a prolonged period.

The modified tanks-in-series model was used to evaluate the preferential flow of a non-reactive tracer in a structured soil. This model should be validated in different soils for expansion of the use. Combining the model with chemical reaction models (including sorption, transformation, and biodegradation) should enable to obtain a complete picture of NO_3 leaching.

Leaching processes of phosphorus and pesticides have not been investigated in Japan, because these chemicals are more absorbed on soil or organic matter than nitrate. However, presently, phosphorus losses should not occur to avoid eutrophication of waters and also due to the limiting resources of phosphate rock. Because some pesticides may function as environmental endocrine disrupters, the dynamics of such pesticides with trace concentration must be studied under environmental conditions.

REFERENCES

Abe K., M. Maeda, and K. Matsumori. 1999. Decrease in N loadings by a linkage system of upland and paddy fields. (In Japanese.) p. 256. *In* Abstract of the Annual Meeting, Japanese Society of Soil Sci. Plant Nutr. Vol. 45. Sapporo, 30 July-1 August 1999.

Adams, P.L., T.C. Daniel, D.R. Edwards, D.J. Nichols, D.H. Pote, and H.D. Scott. 1994. Poultry litter and manure contributions to nitrate leaching through the vadose zone. Soil Sci. Soc. Am. J. 58:1206-1211.

Addiscott, T.M., A.P. Whitmore, and D.S. Powlson. 1991. Farming, fertilizers and the nitrate problem. CAB International, Wallingford, UK.

Andraski, T.W., L.G. Bundy, and K.R. Brye. 2000. Crop management and corn nitrogen rate effects on nitrate leaching. J. Environ. Qual. 29:1095-1103.

Anfält, T., and S. Twengström. 1986. The determination of bromide in natural waters by flow injection analysis. Analitica Chimica Acta. 179:453-457.

Angle, J.S., C.M. Gross, R.L. Hill, and M.S. McIntosh. 1993. Soil nitrate concentrations under corn as affected by tillage, manure, and fertilizer applications. J. Environ. Qual. 22:141-147.

APHA. 1985. Standard methods for examination of water and waste water, 16th ed. American Public Health Association, Washinton DC, USA.

Arai, H., and N. Tase. 1992. Evaluation of self-purification in Tamagawa Jousui channel by using ^{15}N natural isotope. (In Japanese, with English abstract.) Environ. Sci. 5:249-258.

Arimitsu, K. 1982. Studies on the dynamic aspects of water in forest soils II. Movement of soil water and solute elements. (In Japanese, with English abstract.) Bull. For. & For. Prod. Res. Inst. 318:11-78.

Aronsson, H., and G. Torstensson. 1998. Measured and simulated availability and leaching of nitrogen associated with frequent use of catch crops. Soil Use Manage. 14:6-13.

Beckwith, C.P., J. Cooper, K.A. Smith, M.A. Shepherd. 1998. Nitrate leaching loss following application of organic manures to sandy soils in arable cropping: I. Effects of application time, manure type, overwinter crop cover and nitrification inhibition. Soil Use Manage. 14:123-130.

Bergström, L. 1987. Nitrate leaching and drainage from annual and perennial crops in tile-drained plots and lysimeters. J. Environ. Qual. 16:11-18.

Bergström, L. 1990. Use of lysimeters to estimate leaching of pesticides in agricultural soils. Environ. Pollut. 67:325-347.

Bergström, L. 1995. Leaching of dichlorprop and nitrate in structured soil. Environ. Pollut. 87:189-195.

Bergström, L.F., and N.J. Jarvis. 1993. Leaching of dichlorprop, bentazon, and ^{36}Cl in undisturbed field lysimeters of different agricultural soils. Weed Sci. 41:251-261.

Bergström, L., N. Jarvis, and J. Stenström. 1994. Pesticide leaching data to validate simulation models for registration purposes. J. Environ. Sci. Health (Part A). 29:1073-1104.

Bergström, L., and R. Johansson. 1991. Leaching of nitrate from monolith lysimeters of different types of agricultural soils. J. Environ. Qual. 20:801-807.

Bergström, L.F., and H. Kirchmann. 1999. Leaching of total nitrogen from nitrogen-15-labeled poultry manure and inorganic nitrogen fertilizer. J. Environ. Qual. 28:1283-1290.

Boll, J., T.S. Steenhuis, and J.S. Selker. 1992. Fiberglass wicks for sampling of water and solutes in the vadose zone. Soil Sc. Soc. Am. J. 56:701-707.

Böttcher, J., O. Strebel, S. Voerkelius, and H.L. Schmidt. 1990. Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer. J. Hydrol. 114:413-424.

Bowman, B.T. 1988. Mobility and persistence of metolachlor and aldicarb in field lysimeters.

J. Environ. Qual. 17:689-694.

Brandi-Dohrn, F.M., R.P. Dick, M. Hess, and J.S. Selker. 1996. Field evaluation of passive capillary samplers. Soil Sc. Soc. Am. J. 60:1705-1713.

Brown, L.R. 1999. State of the world 1999-2000: A Worldwatch Institute report on progress toward a sustainable society. (In Japanese, translated by H. Hamanaka et al.) Diamond, Tokyo.

Burart, M.R., and D.W. Kolpin. 1992. Hydrologic and land-use factors associated with herbicides and nitrate in near-surface aquifers. J. Environ. Qual. 22:646-656.

Camobreco, V.J., B.K. Richards, T.S. Steenhuis, J.H. Peverly, and M.B. McBride. 1996. Movement of heavy metals through undisturbed and homogenized soil columns. Soil Sci. 161:740-750.

Campbell, D.J., and P.H.T.Beckett. 1988. The soil solution in a soil treated with digested sewage sludge. J. Soil Sci. 39:283-298.

Canter, L.W. 1996. Nitrates in groundwater. CRC Press LLC, New York.

Chang, C., and T. Entz. 1996. Nitrate leaching losses under repeated cattle feedlot manure applications in Southern Alberta. J. Environ. Qual. 25:145-153.

del Catilho P., W.J. Chardon, and W. Salomoms. 1993. Influence of cattle-manure slurry application on the solubility of cadmium, copper, and zinc in a manured acidic, loamy-sand soil. J. Environ. Qual. 22:689-697.

de Rooij, G.H., and K.E. Wit. 1996. Taking large undisturbed soil cores for use in monolith lysimeters. p. 127-136. *In* G.H. de Rooij. Preferential flow in water-repellent sandy soils: Model development and lysimeter experients. ph.D. diss. Wageningen Agric. Univ., The Netherlands.

Douglas, B.F., and F.R. Magdoff. 1991. An evaluation of nitrogen mineralization indices for organic residues. J. Environ. Qual. 20:386-372.

Environment Agency, Japan 1993. Handbook of measures to groundwater pollution by nitrate.

(In Japanese.) Research Center for Prevention of Industrial Pollution. Tokyo.

Environment Agency, Japan. 1999. Annual report on the environment (Details) 2000. (In Japanese.) Gyousei, Tokyo, Japan.

Eriksen, J., M. Askegaard, and K. Kristensen. 1999. Nitrate leaching in an organic dairy/crop rotation as affected by organic manure type, livestock density and crop. Soil Use Manage. 15:176-182.

FAO. 2001. FAOSTAT Agriculture data [Online]. Available at http://apps.fao.org/page /collections (verified 16 August 2001).

Fatta, D., C. Voscos, A.J. Haralambous, and M. Loizidou. 1997. A study on the groundwater quality in the surroundings of a landfill. J. Environ. Sci. Health. A32:2275-2287.

Feyen, J., D. Jacques, A. Timmerman, and J. Vanderborght. 1998. Modelling water flow and solute transport in heterogeneous soils: A review of recent approaches. J. Agric. Eng. Res. 70:231-256.

Fogler, H.S. (Editor). 1992. Elements of chemical reaction engineering, 2nd ed. Prentice-Hall International, Elglewood Cliffs, NJ.

Fried, J.J. 1991. Nitrates and their control in the EEC aquatic environment. *In* I. Bogárdi and R.D. Kuzelka (ed.) Nitrate contamination: Exposure, consequences, and control. NATO ASI Ser. G: Ecological Science 30. Spring-Verlag, Berlin.

Gerke, H.H., M. Arning, and H. Stöppler-Zimmer. 1999. Modeling long-term compost application effects on nitrate leaching. Plant Soil 213: 75-92.

Grochulska, J., and E.J. Kladivko. 1994. A two-region model of preferential flow of chemicals using a transfer function approach. J. Environ. Qual. 23:498-507.

Hallberg, G.R. 1986. From hoes to herbicides. J. Soil Water Conserv. 41:357-364.

Hallberg, G.R., and D.R. Keeney. 1993. Nitrate. *In* W.M. Alley (ed.) Regional ground-water quality. Van Norstrand Reinhold, New York.

Harada, Y. 1997. Application rates of livestock manure. (In Japanese.) p. 68-73. *In* K. Haga et

al. (ed.) Manual for treatment and utilization of livestock wastes. Livestock Industry's Environmental Improvement Organization, Tokyo, Japan.

Harada, Y., K. Haga, T. Osada, and M. Koshino. 1993. Quality of compost produced from animal wastes. Jpn. Agric. Res. Q. 26: 238-246.

Harada, Y., and T. Yamaguchi. 1998. Properties of animal waste composts in Japan. p. 49-54. *In* T. Matsunaka (ed.) Proc. Int. Workshop on Environmentally Friendly Manage. of Farm Animal Waste. Sapporo, Japan. 25-29 November 1997. Kikanshi Insatsu, Japan.

Hasegawa, S. 2000. Field capacity of a volcanic ash soil – the real conditions. (In Japanese, with English abstract.) J. Jpn. Soc. Soil Phys. 83:41-46.

Hasegawa, S., S. Osozawa, and H. Ueno. 1994. Measurement of soil water flux in Andisols at a depth below a root zone of about 1 meter. Soil Sci. Plant Nutr. 40:137-147.

Haverkamp, R., M. Vaucilin, J. Touma, P.J. Wierenga, and G. Vachaud. 1977. A comparison of numerical simulation models for one-dimensional infiltration. Soil Sc. Soc. Am. J. 41:285-294.

Hayami, T. 1993. Determination of new environmental quality standards for water. (In Japanese.) J. Water Environ. 16:224-230.

Hayashi, Y., and R. Hatano. 1999. Annual nitrogen leaching to subsurface drainage water from a clayey aquic soil cultivated with onions in Hokkaido, Japan. Soil Sci. Plant Nutr. 45:451-459.

Hirata, T. 1996. Present state of groundwater issue due to nitrate-nitrogen. (In Japanese.) J. Water Environ. 19:950-955.

Holder, M., K.W. Brown, J.C. Thomas, D. Zabcik, and H.E. Murray. 1991. Capillary-wick unsaturated zone soil pore water sampler. Soil Sc. Soc. Am. J. 55:1195-1202.

House of Lords. 1989. Select committee on the European communities: Nitrate in water with evidence. Her Majesty's Stationery Office. London.

Ibaraki Agricultural Center. 1998. Guidelines for vegetable production. (In Japanese.) Ibaraki

Agricultural Center, Mito, Japan.

Ikeda, M. 1980. Basic applied mathematics. (In Japanese.) Hirokawa Publishing, Tokyo, Japan.

Inoue, Y., and W.J. Kaufman. 1962. Prediction of movement of radionuclides in solution through porous media, Health Phys. 9:705-715.

Janssen, B.H. 1996. Nitrogen mineralization in relation to C:N ratio and decomposability of organic materials. Plant Soil 181:39-45.

Japan Meteorological Agency, 2001. Normals for the period 1971-2001 [CD-ROM]. (In Japanese.) Japan Meteorological Agency, Tokyo, Japan.

Jarvis, N.J. 1994. The MACRO MODEL Version 3.1 - Technical description and sample simulations. Rep. Dissertations 19, Dep. Soil Sci., Swedish Univ. Agric. Sci. Uppsala, Sweden.

Jinno, Y., and T. Honna. 1999. Nitrate leaching and nitrogen balance in turfgrass field by lysimeters. (In Japanese, with English abstract.) Jpn. J. Soil Sci. Plant Nutr. 70:297-305.

Jury, W.A., and J. Gruber. 1989. A stochastic analysis of the influence of soil and climatic variability on the estimate of pesticide groundwater pollution potential. Water Resour. Res. 25:2465-2474.

Jury, W.A. 1982. Simulation of solute transport using a transfer function model. Water Resour. Res. 18:363-368.

Kamewada, K. 1997. CEC and AEC. (In Japanese.) p. 208-211. *In* Japanese Society of Soil Science and Plant Nutrition (ed.) Analysis of soil environment. Hakuyu-sha, Tokyo, Japan.

Kaneko, F., and Y. Yamamoto. 1999. Nitrogen balance on the sandy field by using the pan lysimeter method. (In Japanese.) Jpn. J. Soil Sci. Plant Nutr. 70:190-193.

Katou, H. 1997. Hydraulic conductivity. (In Japanese.) p. 66-69. *In* Japanese Society of Soil Science and Plant Nutrition (ed.) Analysis of soil environment. Hakuyu-sha, Tokyo, Japan.

Katou, H., 2001. Time scale for nitrate transport in soil. (In Japanese.) p. 35-39. *In*

Proceedings of the 21st Symposium on Agro-Environmental Science: Agricultural Activities and the Carbon and Nitrogen Cycling in the Global Area. Tsukuba, Japan.

Kawanishi, T., H. Kawashima, and Y. Ozaki. 1991. Increase in nitrate concentrations of groundwater and agricultural production: case studies in foreign countries and future tasks. (In Japanese.) J. Water and Waste. 33:725-736.

Kimble, J.M., C.L. Ping, M.E. Sumner, and L.P. Wilding. 2000. Andisols. p. E209-242. *In* M.E. Sumner (ed.) Handbook of soil science. CRC Press, Boca Raton, FL.

Kobayashi, S. 1989. Evapotranspiration. (In Japanese.) p. 848-853. *In* The Japanese Society of Irrigation, Drainage and Reclamation Engineering (ed.) Handbook of agricultural engineering. Shin-Nihon-Insatsu, Tokyo, Japan.

Kobayashi, Y. (ed.). 1994. Source protection of drinking water supply. Gihoudou, Tokyo.

Koshino, M. 1976. Loadings of nutrients from arable land and eutrophication. (In Japanese.) p. 149-191. *In* T. Hayase, J. Ando, and M. Koshino (ed.) Fertilizer and environmental protection: Effects of chemical fertilizer and manuring of wastes. Soft Science, Tokyo.

Kumazawa, K. 1999. Present status of nitrate pollution in groundwater. (In Japanese.) Jpn. J. Soil Sci. Plant Nutr. 70:207-213.

Kuwabara, H. 1989. Hydrological cycle. (In Japanese.) p. 842. *In* The Japanese Society of Irrigation, Drainage and Reclamation Engineering (ed.) Handbook of agricultural engineering. Shin-Nihon-Insatsu, Tokyo, Japan.

Kuwatsuka, S. 1984. Organic components in soil. (In Japanese.) p. 39-54. *In* K. Kyuma, S. Shoji, S. Kuwatsuka, T. Hattori, K. Wada, Y. Katou, H. Wada, Y. Ooba, H. Okajima, Y. Takai. (ed.) New soil science. Asakura-shoten Tokyo, Japan.

Larsson, M. 1999. Quantifying macropore flow effects on nitrate and pesticide leaching in astructured clay soil. PhD diss. Swedish Univ. Agric. Sci., Uppsala, Sweden.

Maeda, M. 2000. Monitoring methods of nitrate leaching and their problems. (In Japanese.) p. 2-8. *In* Workshop on Soil and Fertilizer Management, Zentsuji, Japan. 3-4 February 2000.

Shikoku Natl. Agric. Exp. Sta., Japan.

Maeda, M., and L.F. Bergström. 2000. Leaching patterns of heavy metals and nitrogen evaluated with a modified tanks-in-series model, J. Contam. Hydrol. 43:165-185.

Maeda, M., B. Liyanage, and Y. Ozaki. 1999. Water collection efficiency of wick sampler under steady state flow conditions. Soil Sci. Plant Nutr. 45: 485-492.

Maeda, M., and Y. Ozaki. 1994. Optimization of local agro-ecosystem (I): Water quality purification in paddy fields. (In Japanese.) Environ. Sanitary Eng. Res. 8:264-269.

Maeda, M., and Y. Ozaki. 1998. Design of an in situ small lysimeter by artificial rainfall system and numerical simulation. Vol. 1 p. 164. *In* Proc. 16th World Cong. Soil Sci. Montpellier, France. 20-26 August 1998.

Maeda, M., B. Zhao, Y. Ozaki, T. Yoneyama. in press. Nitrate leaching in an Andisol treated with different types of fertilizers. Environ. Pollut. in press.

MAFF (ed.) 1998. Pocket Bulletin of Fertilizer. (In Japanese.) Association of Agriculture and Forest Statistics, Tokyo.

Mariotti, A., J.C. Germon, P. Hubert, P. Kaiser, R. Letolle, A. Tardieux, and P. Tardieux. 1981. Experimental determination of nitrogen kinetic isotope fractionation: Some principles; illustration for the denitrificiation and nitrification processes. Plant Soil 62:413-430.

Matsumaru, T. 1997a. Evaluation of nitrate leaching in Ando and sandy soils by lysimeters. (In Japanese, with English abstract.) Jpn. J. Soil Sci. Plant Nutr. 68:423-429.

Matsumaru, T. 1997b. Suppression of nitrate leaching in upland fields by use of coated fertilizer. (In Japanese, with English abstract.) Jpn. J. Soil Sci. Plant Nutr. 68:430-434.

McBride, M.B. 1995. Toxic Metal accumulation from agricultural use of sludge: Are USEPA regulations protective? J. Environ. Qual. 24:5-18.

McBride, M.B., B.K. Richards, T. Steenhuis, J.J. Russo, and S. Sauvé. 1997. Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. Soil Sci.

162:487-500.

McGrath, S.P., A.C. Chang, A.L. Page, and E. Witter. 1994. Land application of sewage sludge: scientific perspectives of heavy metal loading limits in Europe and the United States. Environ. Rev. 2:108-118.

Messing, I., and N.J. Javis. 1990. Seasonal variation in field-saturated hydraulic conductivity in two swelling clay soils in Sweden. J. Soil Sci. 41:229-237.

Mishima, S., N. Matsumoto, and K. Oda. 1999. Nitrogen flow associated with agricultural practices and environmental risk in Japan. Soil Sci. Plant Nutr. 45:881-889.

Mizuno, N., and M. Minami. 1980. The use of $H_2SO_4-H_2O_2$ for the destruction of plant matter as a preliminary to determination of N, K, Mg, Ca, Fe, and Mn. (In Japanese.) Jpn. J. Soil Sci. Plant Nutr. 51:418-420.

Moyer, J.W., L.S. Saporito, R.R. Janke. 1996. Design, construction, and installation of an intact soil core ysimeter. Agron. J. 88:253- 256.

Nagai, S. 1991. An hydrochemical approach to groundwater pollution: Status and problems of inorganic pollution. (In Japanese.) J. Groundwater Hydrol. 33:145-154.

National Agriculture Research Center (ed. Water Quality Control Laboratory). 1999. Workshop on practical problems for monitoring of NO_3 leaching in upland fields. (In Japanese.) Asahi-Insatsu, Tsukuba, Japan.

Neumann, S.P. 1973. Saturated-unsaturated seepage by the finite elements. Proc., ASCE HY. 99:2233-2250.

Nishimaki, K., N. Satta, and M.Maeda. 1994. Sorption and migration of radioiodine in saturated sandy soil. J. Nucl. Sci. Tech. 31:828-838.

Nishio, M. 2001. Analysis of the actual state of nitrogen application in arable farming in Japan. (In Japanese, with English abstract.) Jpn. J. Soil Sci. Plant Nutr. 72:513-521.

Nonaka, M., and T. Kamura. 1995. Nitrate leaching and nitrogen balance in sand dune upland soil by lysimeters. (In Japanese, with English abstract.) Jpn. J. Soil Sci. Plant Nutr.

66:372-380.

OECD. 1999. Environmental indicators for agriculture, Volume 2: Issues and design, "The York workshop". OECD Publ., Paris.

Ogawa, Y. 2000. Nitrate pollution of groundwater and a turning point of agricultural practices: Analysis of runoff mechanisms and regeneration of nitrogen cycle. (In Japanese.) Nousan-gyoson-bunka-kyoukai, Tokyo.

Ooe, T., I. Nakamura, and K. Yoshida. 1999. Health impacts and water pollution by nitrite and nitrate. (In Japanese.) The St. Marianna Medical J. 27:1-10.

Owens, L.B., W.M. Edwards, and R.W. van Keuren. 1992. Nitrate levels in shallow groundwater under pastures receiving ammonium nitrate or slow-release nitrogen fertilizer. J. Environ. Qual. 21:607-613.

Persson, L., and L. Bergström. 1991. Drilling method for collection of undisturbed soil monoliths. Soil Sc. Soc. Am. J., 55:285-287.

Power, J. F., R. Wiese, and D. Flowerday. 2000, Managing nitrogen for water quality ─ lessons from management systems evaluation area. J. Environ. Qual. 29:355-366.

Radioactive waste management center, 1990. Radionuclides distribution coefficient of soil to soil-solution. (In Japanese.) Environmental Parameters Series 2. Radioactive Waste Management Center, Tokyo, Japan.

Radulovich, R., and P. Sollins. 1987. Improved performance of zero-tension lysimeters. Soil Sc. Soc. Am. J., 51:1386-1388.

Randall, G.W., D.R. Huggins, M.P. Russelle, D.J. Fuchs, W.W. Nelson, and J.L. Anderson. 1997. Nitrate losses through subsurface tile drainage in conservation reserve program, alfalfa, and row crop systems. J. Environ. Qual. 26:1240-1247.

Richards, B.K., T.S. Steenhuis, J.H. Peverly, and M.B. McBride. 1998. Metal mobility at an old, heavily loaded sludge application site. Environ. Pollut. 99:365-377.

Richards, L.A. 1931. Capillary conduction of liquids through porous mediums. Physics.

1:318-333.

Rowell, D.L., 1994. Soil Science: Methods and Applications. Addison Wesley Longman, Edinburgh, UK.

Saigusa, M., H. Kodama, K. Shibuya, and T. Abe. 1993. Single basal application of nitrogen fertilizer on dent corn cultivation using controlled release urea. (In Japanese, with English abstract.) J. Jpn. Grassland Sci. 39:44-50.

Sakata, N., K. Yamamoto, H. Nakahara, and T. Marumoto. 1995. Moving of nitrogen from coating fertilizer in soil. (In Japanese, with English abstract.) Jpn. J. Soil Sci. Plant Nutr. 66:253-258.

SAS Institute Japan, 1993. SAS/STAT user's guide version 6. (In Japanese.) SAS Institute Japan, Tokyo, Japan.

Sheppard, M.I., D.H. Thibault, and J.H. Mitchell. 1987. Element leaching and capillary rinse in sandy soil cores: experimental results. J. Environ. Qual. 16:273-284.

Shipitalo, M.J., and W.M. Edwards. 1993. Seasonal patterns of Water and chemical movement in tilled and no-till column lysimeters. Soil Sci. Soc. Am. J. 57:218-223.

Shoji, S., M. Nanzyo, and R.A. Dahlgren 1993. Volcanic ash soils: genesis, properties and utilization. Elsevier Sci. Publ., Amsterdam, the Netherlands.

Soil Conservation Survey Conference. (ed.) 1991. Surveys and measures on Japanese upland soils. (In Japanese.) Hakuyu-Sha, Tokyo, Japan.

Soil Survey Staff. 1975. Soil taxonomy. A basic system of soil classification for making and interpreting soil surveys. USDA. Soil Conserv. Serv. Agric. Handb. 436, Washington DC.

Soil Survey Staff. 1990. Keys to soil taxonomy, 4th ed., p.144, SMSS Technical Monograph no. 6. Blacksburg, Virginia.

Soil Survey Staff. 1999. Soil taxonomy. A basic system of soil classification for making and interpreting soil surveys. USDA. Soil Conserv. Serv. Agric. Handb. 436, Washington DC.

Souma, S. 1988. Fertilizer application for improving the quality of vegetables. (In Japanese.)

Nousanson-Bunaka-Kyoukai, Tokyo.

Spalding R.F., and M.E. Exner. 1993. Occurrence of nitrate in groundwater – a review. J. Environ. Qual. 22:392-402.

Steenhuis, T.S., J. Boll, E. Jolles, and J.S. Selker. 1995. Field evaluation of wick and gravity pan samplers. *In* L.G. Willson, L.G. Everett, S.J. Cullen (ed.) Handbook of vadose zone characterization and monitoring. Lewis Publishers, Boca Ranton, FL.

Steenhuis, T.S., J. Boll, G. Shalit, J.S. Selker, and I.A. Merwin. 1994. A simple equation for predicting preferential flow solute concentrations. J. Environ. Qual. 23:1058-1064.

Steenhuis, T.S., J. -Yves Parlange, and S.A. Aburime. 1995. Preferential flow in structured and sandy soils: consequences for modeling and monitoring. p. 61-77. L.G. Willson, L.G. Everett, S.J. Cullen (ed.) Handbook of vadose zone characterization and monitoring. Lewis Publishers, Boca Ranton, FL.

Tabuchi, T. 2001.The fate of nitrogen in aqua-soil sphere. (In Japanese.) J. Water and Waste. 41: 886-890.

Tabuchi, T., and Y. Takamura, 1985. Runoff of nitrogen and phosphorus from watersheds. (In Japanese.) Tokyo-Daigaku Shuppankai, Tokyo, Japan.

Tecator, 1984. Tecator Application Note, ASN 50.01/84.

Thomsen, I.K., J.F. Hansen, V. Kjellerup, and B.T. Christensen. 1993. Effects of cropping system and rates of nitrogen in animal slurry and mineral fertilizer on nitrate leaching from a sandy loam. Soil Use Manage. 9:53-58.

Thornthwaite, C.W. 1948. An approach toward a rational classification of climate. Geographical Rev. 38:55-94.

Toride, N., and F.J. Leij. 1996. Convective-dispersive stream tube model for field-scale solute transport. I. Moment analysis. Soil Sci. Soc. Am. J. 60:342-352.

U.S. EPA. 1992. Another look: National survey of pesticide in drinking water wells – Phase II Report, EPA 579/09-91-020, January, Office Water, Washington, D.C.

U.S. Geological Survey. 1999. The quality of our nation's waters: Nutrients and pesticides. U.S. Geological Survey Circular 1225.

Utermann, J., E.J. Kladivko, and W.A. Jury. 1990. Evaluating pesticide migration in tile-drained soils with a transfer function model. J Environ. Qual. 19:707-714.

Vanderborght, J., C. Gonzalez, M. Vanclooster, D. Mallants, and J. Feyen. 1997. Effects of soil type and water flux on solute transport. Soil Sci. Soc. Am. J. 61:372-389.

Vinten, A.J.A., and K.A. Smith. 1993. Nitrogen cycling in agricultural soils. p.39-74. *In* T.P. Burt, A.L. Heathwaite, and S.T. Trudgill (ed.) Nitrate: Processes, patterns, and management. John Wiley and Sons, West Sussex, UK.

Wierenga, P.J. 1977. Solute distribution profiles computed with steady-state and transient water movement models. Soil Sci. Soc. Am. J. 41:1050-1055.

Wiklander, L., and E. Lotse. 1966. Mineralogical and physico-chemical studies on clay fractions of Swedish cultivated soils. Lantbrukshögskolans Annaler. 32:439-475.

Wilson, L.G., and D.W. Dorrance. 1995. In situ pore-liquid sampling in saturated regions of the vadose zone. p. 605-616. *In* L.G. Willson, L.G. Everett, S.J. Cullen (ed.) Handbook of vadose zone characterization and monitoring. Lewis Publishers, Boca Ranton, FL.

Yoneyama, T. 1996. Characterization of natural ^{15}N abundance of soils. p. 205-223. *In* T.W. Boutton and S. Yamasaki (ed.) Mass spectrometry of soils. Marcel Dekker, New York.

Yoneyama, T., and M. Yoshida 2000. δ^{13}C and δ^{15}N values of tephra profiles at three sites in southern Kyushu, Japan. (In Japanese, with English abstract.) Jpn. J. Soil Sci. Plant Nutr. 71:834-839.