Measurement of Nutrient Availability and Solute Transport in Soils with Ion Exchange Resin Capsules[1]

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Contents

I. GENERAL INTRODUCTION

Assessment of nutrient availability in soils is important to enhance crop growth and provide efficient management of agricultural resources. Likewise, detection of solute transport or leaching of agricultural chemicals is necessary in improving crop production but its impact on the quality of surface water or groundwater (i.e. possible pollution) is of utmost consideration.

There are several ways of measuring nutrient or element concentrations in the soil. Standard or conventional methods of soil testing are done by treating the soil with chemical solutions that are often nutrient-specific, requiring the use of different solutions for different elements. Thus, a method that could provide "universal" or simultaneous extraction of nutrients would be more convenient and efficient.

Extraction with ion exchange resin is a process that has more analogy with plant uptake of nutrients than any other extractant [46]. The resin capsule method makes use of spherical capsules of mixed-bed cation and anion exchange resins and provides a "universal" extraction for all nutrients[38]. Resin capsules are inserted directly into saturated and homogenized soil samples without soil drying and grinding[38] or installed in the field in situ[34,14]. Unlike batch-equilibrated resins, the use of mixed-bed resin capsules does not require subsequent shaking or stirring action, thereby allowing the resin to serve as a sink, simulating nutrient movement to a plant root. This method is sensitive to nutrient diffusion, a governing factor in plant availability of most nutrients[49]. As such, the resin capsule method (compared to other methods) cannot be used as a rapid soil test.

Several methods of measuring solute transport are available, but depending

on the target solute and type of soil, their usefulness varies. The common methods are the use of porous or suction cups, pan samplers or lysimeters, and destructive soil sampling. Sampling of soil solution with suction cups and destructive soil sampling offer ease of sampling but they may not be suitable under conditions of bypass or preferential flow, where the use of pan samplers may be more useful.

Resin capsules used in soil columns as well as in field plots (with and without crops subjected to different water regimes) yielded results that indicate the utility of these capsules for solute transport studies[21]. With the use of access tubes, repeated sampling or monitoring of nutrients or solute at the same point in the field is possible. Solutes can be accumulated even under soil moisture conditions that may no longer allow collection of soil solution with suction cups[34]. Water or soil solution moves through the resin capsule at the same rate as in the soil due to the presence of large pores between the resin beads[21].

To compare the use of resin capsules with conventional soil tests in assessing soil nutrient availability, a laboratory incubation study (chapter III) was conducted. At the same time, the transport of solutes (nitrate, cations, and phosphorus) in a clayey soil grown to onion was monitored using pan lysimeters, suction cups, and resin capsules. Results of the nitrate leaching experiment are presented in chapter IV, while those of the cations (K, Ca, Mg, and Na) and phosphorus, in chapter V.

II. REVIEW OF LITERATURE

A. Characteristics of the Resin Capsule Method

The resin capsule method simulates processes of soil-root systems in which roots absorb nutrients from soil solution by releasing counter ions such as H^+, OH^-, and HCO_3^-, with both diffusion and mass flow contributing to the availability of most nutrients[49]. The resin capsule has a spherical shape (2-cm diameter, UNIBEST, Inc. MT) and is composed of strongly acidic cation (H^+) and strongly basic anion (OH^-) exchange resins with a 2.2 $mmol_c$ of cation + anion exchange capacity. The resin capsule will accumulate all solutes that can diffuse to the capsule from the medium in which it is inserted[34]. The resin capsule is inserted into the soil without subsequent mixing or stirring action. Because of its high affinity to anions and cations, the capsule adsorbs all ions from the surrounding film layer of soil solution, and in exchange, releases counter ions (H^+, OH^-).

Potentially the resin capsule method, often referred to as the Phytoavailability Soil Test or PST in most literature, provides information about the initial concentration of the nutrient in soil solution, the dynamics of ion release from solid phases, and ion diffusion through the soil[35].

B. The Use of Resin Capsules for Assessing Soil Nutrient Supplying Capacity
a. Kinetics of resin adsorption and its interpretation

The amount of nutrient or element adsorbed on the resin as a function of time is described well by the power function $RAQ_i = a_i t^{b_i}$. The resin adsorption quantity (RAQ) is the amount of nutrient i adsorbed per unit surface area of the capsule (μmol cm^{-2} or mol m^{-2}) at time t (d), and a and b are rate coefficients used to describe the adsorption kinetics of the anion or cation on the resin. Using this equation as a standard approach to characterize the soil nutrient status, quantitative (RAQ) as well as kinetic parameters (a, b) are obtained. In contrast to conventional soil tests, the resin capsule method not only measures the overall fertility level in terms of a particular nutrient pool, but also describes short-term and long-term availability of a nutrient to a sink[13].

Short-term availability as expressed by rapid adsorption during the first day (coefficient a) is mainly associated with release processes from pools of readily available nutrients in soil[12]. In this phase, the adsorption rate is primarily limited by film diffusion (i.e., the counter movement of ions to and from the liquid surrounding the resin beads and the surface of the resin beads) and ion exchange at the capsule and from soil solids.

Moderately available pools, processes of their depletion and diffusion to the sink as the major transport mechanism, are accounted for by a second kinetic constant b. Several processes dominating the rate coefficient b for different nutrients are the following[12] :

(1) ion diffusion (transport of ions through the bulk soil to the capsule),
(2) cation exchange (NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Na^+),
(3) mineralization of soil organic matter (N, P, S),
(4) solubilization and mobilization of inorganic and organic nutrient pools (P, Fe, Mn),
(5) release of specifically bound cations from the interlayers or wedge positions of clay minerals (NH_4^+ and K^+),
(6) release of structural cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) from soil minerals by dissolution,
(7) anion exchange, and
(8) reduction-oxidation (Fe, Mn, P, S).

Thus, coefficient b characterizes the capability of a soil to maintain a nutrient flux to a strong sink like a resin or a plant root. It integrates the potential delivery rate from different nutrient pools as well as the physico-chemical characteristics of a soil that control diffusive solute transport.

Both coefficients a and b determine the total amount of a nutrient that is available during a given time. A high b value alone does not necessarily mean a large cumulative release, because a may be very low, and vice versa. Results of such a kinetic approach indicate 1) the overall level of cumulative nutrient release (RAQ_i), 2) short-term availability of a nutrient (a_i), and 3) the nutrient long-term supply rate (b_i).

b. Examples and observations

Results of resin capsules installed in situ showed the spatial and temporal variation of nutrients at critical growth stages of transplanted rice[9]. The resin capsule method also showed sensitivity to past fertilizer history and the resulting build-up or depletion of soil P and K reserves in rice soils. Clear long-term treatment effects on the soil P status were measured with a significantly higher P release in +P treatments (+NP, +NPK) and the greatest P depletion in the + NK (−P) treatments[11]. Likewise, treatments that did not receive fertilizer K but with N or both N and P addition were depleted in K reserves as indicated by the low values of a_K and b_K coefficients in those treatments suggesting a continuous exhaustion of extractable and non-exchangeable K[10]. In a pot experiment with soybean where resin capsules were inserted directly into potted soils, increased resin P and K adsorption were observed in soils with increasing P and K fertilizer rates[28].

C. The Resin Capsule Method, Conventional Soil Tests, and Plant Uptake
a. Nitrogen

Incubation of resin capsules in saturated soil condition (soil paste) of 24 surface samples from arable soils which represented nine orders of the Soil Taxonomy showed that the correlation between coefficient a_N and soil organic C was not significant[13]. Highly significant correlations between a_N and characteristics of the sorption complex (e.g., clay, CEC, and exch. Mg) occurred, however, supporting the hypothesis that N accumulation on the resin during the first day is supplied mainly by labile mineral pools (solution N and exchangeable NH_4^+).

A comparison of different soil N tests and the resin capsule method (incubation study using soils taken before transplanting) on assessing the nitrogen supplying capacity of lowland rice soils in southern India[44] revealed that RAQ N at 1d and 14d were highly correlated with $KMnO_4$-N and initial extractable NH_4 -N (2M KCl). The relationship between RAQ N (NH_4-N) and organic C or total N, however, was clustered. The best relationship was obtained between RAQ 14d and alkaline $KMnO_4$-N ($r^2 = 0.72$, $p < 0.001$), indicating similar N pools measured with both methods. Correlation with crop N uptake at panicle initiation was higher for RAQ N at 14 d than in the other soil N tests, but at first flowering and active tillering, correlations between the other soil N tests and N uptake were higher.

b. Phosphorus

A study using 24 surface soils showed that the resin P coefficient a_P of the function $RAQ_P = a_P t^{b_P}$ was not strongly related to Olsen P ($r = 0.60$, $p < 0.01$)[13]. The resin capsule method has an acidifying effect on the interfacial solution as the resin adsorbs cations in exchange for H^+, which also results in increased P solubility[49]. On the other hand, Olsen P uses alkaline extractants. Thus, the two methods measure different P pools. A much closer correlation ($r = 0.82$, $p < 0.01$) was obtained between resin a_P and the Bray II procedure using acid P

extraction[13].

Across ten sites with very different soil characteristics, a regression model explained 38% of the variation in P uptake in the NK and NPK treatments as a function of a_P and b_P, taking into account that the fertilizer N level increased the prediction accuracy for plant uptake ($r^2 = 0.64$)[11]. Greenhouse studies indicated that the correlation between P uptake by sorghum-Sudan grass and resin capsule (PST) results were as good or better than those with the Olsen P soil test (PST: $r = 0.91$; Olsen: $r = 0.87$)[31]. There was no significant correlation between P uptake by soybean and resin P (in a pot experiment of four soils), however, although there was an increase in resin P as P concentration in plant increased[28].

c. Potassium

In a study conducted on lowland rice soils across ten sites in Asia[10], it was found that extractable K alone (1M NH_4OAc) explained only 53 % of the variation in total K uptake in the NP and NPK treatments. After introducing a term that combined several static soil properties to the regression model, however, the coefficient of determination (r^2) increased from 0.72 to 0.75. Similar to conventional soil tests, the initial resin K adsorption rate coefficient (a_K) was not a sufficient measure of K uptake across all sites. However, the b_K coefficient alone explained 63% of the variation in K uptake. Combining both kinetic parameters into a regression model explained 82% of the K uptake in NP and NPK treatments.

Significant correlations ($r = 0.45$–0.59, $p < 0.07$) between soybean K uptake and resin K adsorption after 35 days of resin incubation and plant growth were obtained in a pot experiment conducted on four soils of silty to clayey texture, under approximately moist field conditions[28].

D. The Resin Capsule as a Tool for Monitoring Solute Transport

In a leaching experiment conducted on packed soil columns[21], bromide leaching patterns (BLPs) under continuous unsaturated water flow were similar to both the resin capsule and vacuum extraction (or suction cup) methods except for the time for peak concentrations to occur at the upper and lower sampling depths. The discrepancy in the appearance of BLPs was attributed to fundamental differences in the manner by which ions are removed from the soil. A "channeling" effect or a higher rate of water flow due to applied suction may cause an earlier appearance of BLPs with the suction cup method. In the case of the resin capsule, however, water moves through the capsule at the same rate as in the soil.

Under intermittent water flow, distinct spikes of BLPs were measured by resin capsules, which corresponded to changes in soil water potential. On the other hand, only broad plateaus for BLPs were measured by vacuum extraction, implying greater sensitivity of the resin capsule method to soil moisture changes. The authors[21] of that study explained that at low moisture contents, applied

suction (vacuum extraction method) probably resulted in extraction of soil solution from only the larger pores where the water potential was lowest. Thus, to obtain a similar amount of soil solution from drier soil, the same size pores may have been extracted, but at greater distances from the porous candle.

In the same study[21] resin capsules were also used to monitor the movement of Br⁻ tracer in a field experiment, and results showed the utility of resin capsules for detecting Br⁻ transport as affected by irrigation intensity, plant water use, and plant Br⁻ uptake.

III. EXPERIMENT 1 : USE OF RESIN CAPSULES FOR MEASURING P, K, AND N OF TWO SOILS UNDER TWO MOISTURE CONDITIONS

A. Introduction

The use of resin capsules under saturated soil conditions has been well studied (chapter II), except in particular upland conditions where the soil is unsaturated most of the time. Nevertheless, evidences indicating the use of resin capsules under such conditions are also available[34,21].

Since diffusion processes largely control the adsorption of ions on the resin[49], I assumed that the soil properties affecting ion diffusion in soils under upland conditions such as soil water content and texture would also affect resin accumulation of soil nutrients. Thus, a laboratory incubation study was conducted to: 1) determine the effect of soil moisture on the resin adsorption of N, P, and K in a sandy and a silty soil, 2) compare the use of conventional soil tests with the resin capsule method in measuring N, P, and K contents, and 3) analyze the nutrient release kinetics of a silt loam and a sandy loam using resin capsules.

B. Materials and Methods
a. Preparation and benchmark analysis of soils

Samples of soils with a silty (Mollic Fluvaquents,) and sandy (Aquic, Humic Udivitrands,) texture were collected from the plow layer of two upland fields in Hokkaido, Japan. The silty soil was taken from the Hokkaido University Faculty of Agriculture Experimental Farm in Sapporo and the sandy soil, from the crop field of Hokkaido University Livestock Farm in Shizunai. Some physical and chemical properties of the sieved, air-dried soils are listed in Table 1.
b. Treatments

The study was conducted using samples of sieved (<2 mm), air-dried silt loam (SiL) and sandy loam (SL) soils, at two levels of soil gravimetric water content (0.32 kg kg⁻¹ and 0.65 kg kg⁻¹). The 0.65 kg kg⁻¹ moisture content represented saturated conditions (SAT) and, 0.32 kg kg⁻¹, unsaturated conditions (UNSAT). To obtain an accurate comparison between the conventional soil test (i.e., 2M KCl extraction) and the resin capsule method in the measurement of NH_4^+ and NO_3^- concentrations, nitrogen was added at concentrations of 0, 10, 20,

Table 1. Some physical and chemical properties of the sieved (<2 mm), air-dried soils used in the incubation study.

Soil Property	Method	Unit	Silt loam[1]	Sandy loam[2]
Clay	Pipette	kg kg^{-1}	0.105	0.128
Silt	Pipette	kg kg^{-1}	0.548	0.108
Sand	Pipette	kg kg^{-1}	0.346	0.764
Organic Carbon	Acid-dichromate oxidation	kg kg^{-1}	0.031	0.031
Total N	Kjeldahl	kg kg^{-1}	0.003	0.003
Available P	Bray II	mg kg^{-1}	147	150
Exchangeable K	1M NH$_4$OAc, pH 7	cmol$_c$ kg^{-1}	2.21	0.24
CEC	NH$_4$OAc/KCl extraction	cmol$_c$ kg^{-1}	35.60	14.00
Exch. Ca	1M NH$_4$OAc, pH 7	cmol$_c$ kg^{-1}	21.80	4.10
Exch. Mg	1M NH$_4$OAc, pH 7	cmol$_c$ kg^{-1}	4.54	0.86
Exch. Na	1M NH$_4$OAc, pH 7	cmol$_c$ kg^{-1}	0.21	0.07
pH	H$_2$O (1:2.5)		6.13	5.58
pH	1M KCl (1:2.5)		4.73	4.34

[1] Hokkaido University Experimental Farm, Sapporo
[2] Maize field, Hokkaido University Livestock Farm, Shizunai

40, and 60 mg N kg soil^{-1} as (NH$_4$)$_2$SO$_4$. Each treatment was triplicated.

c. Soil preparation for the 0.32 kg kg^{-1} (UNSAT) moisture content

Ammonium sulfate solution was added (in small portions through a hand-held sprayer) to samples of air-dried soil in a plastic bag to supply the amount of N required at each N level and reach UNSAT conditions. The bag was sealed and kept overnight at a constant temperature (4°C) after which portions (about 50 g, dry wt.) of the soil were transferred to 100 ml hard plastic cups for incubation.

d. Soil preparation for the 0.65 kg kg^{-1} (SAT) moisture content

Samples of air-dried soils were weighed into buckets, with one bucket for each N level, and sufficient amounts of water were added to reach SAT conditions. The soil mixtures were puddled and allowed to stand (covered) for 4 days at 25°C. Immediately before incubation, (NH$_4$)$_2$SO$_4$ was added to the soil paste and about 70 ml portions were transferred into cups for incubation.

e. Resin capsule incubation and analysis of resin N, P, and K

One resin capsule was inserted into the center of each cup until it was completely covered with soil. To ensure contact between the surface of the capsule and the soil, the cup was either tapped (for SAT conditions) or slightly pressed from the surface (for UNSAT conditions). The cups were tightly covered and kept at 25°C. Resin capsules were retrieved after 1, 7, 14, and 28 days and immediately washed with deionized water until all adhering soil particles were removed. All resin capsules were stored at 4°C until extraction of adsorbed ions by shaking the capsules with 30 ml 2M HCl twice, 30 min each time[37]. The extracts were analyzed using colorimetric or photometric methods for NH$_4^+$ [20], NO$_3^-$ [24], and HPO$_4^{2-}$ [23]. The amount of K in the extracts was determined by flame photometry.

f. Soil incubation and analysis of N, P, and K using conventional methods

From the same soil used for the incubation of resin capsules, samples were taken and incubated at 25°C for 7 days. NH_4^+ and NO_3^- from all the samples were extracted using 2M KCl at the onset (0d) and end (7d) of incubation. Contents of soil P and K were measured only from 7d samples of the +0 and + 60mg N kg soil^{-1} treatments.   Available P was analyzed with the Bray II method, and K was extracted with 1M NH_4OAc, pH 7 and the amount measured by flame photometry.   The concentrations of NH_4^+ and NO_3^- in the KCl extracts were determined by the same methods as those used for the resin capsule extracts.

g. Statistical analyses and interpretation of resin kinetic constants

Linear regression analysis was performed to determine the relationship between the contents of resin N and KCl–extractable N.   Since available N was predominantly in the form of NH_4^+ under SAT conditions, the concentration of resin NH_4–N at different times was compared with that of the soil initial (0d) KCl –extractable NH_4–N.   On the other hand, since available N under UNSAT conditions consisted mainly of NO_3^- after 7d of incubation, the concentration of resin NO_3–N was compared with that of 7d soil NO_3–N under UNSAT conditions.

Release kinetics of N, P, and K for each soil in the +0N treatment at each soil moisture level was determined by the power function, $RAQ_{i,t} = a_i t^{b_i}$, where $RAQ_{i,t}$ is the resin adsorption quantity or amount of nutrient i adsorbed per unit surface area of the capsule (mol m^{-2}) at time t (d), and a and b are rate coefficients used to describe the adsorption kinetics of the anion or cation on the resin. Coefficient a is an indicator of the magnitude of the readily available nutrient fractions while coefficient b characterizes the ability of a soil to maintain a nutrient flux to a strong sink like a resin or a plant root[13].

C. Results
a. Effect of soil moisture and texture on P, K, and N measurements

Adsorption of P on the resin (resin P) at 28d was much smaller in SL than in SiL (Fig. 1a), although the two soils contained the same amounts of Bray II P.   In addition, the reduction of soil moisture from 0.65 kg kg^{-1} (SAT) to 0.32 kg kg^{-1} (UNSAT) caused an 80% reduction of resin P in SiL and 94% in SL.   For both soils, resin K under UNSAT conditions was 78% lower than that of resin K under SAT conditions (Fig. 1b).

Bray II P values were lower under UNSAT than under SAT conditions for both SiL and SL.   The difference in soil moisture, however, did not affect the amount of exchangeable K (by 1M NH_4OAc) in either soil.

Using 2M KCl, the content of extractable N ($NH_4^+ + NO_3^-$) in SL was the same under both soil moisture conditions, but with the use of resin capsules, the N content was higher under SAT than under UNSAT conditions (Fig. 1c).   In SiL, however, both methods showed higher values of N under UNSAT than under

(a) Phosphorus

(b) Potassium

(c) Nitrogen

Soil moisture content (kg kg⁻¹)
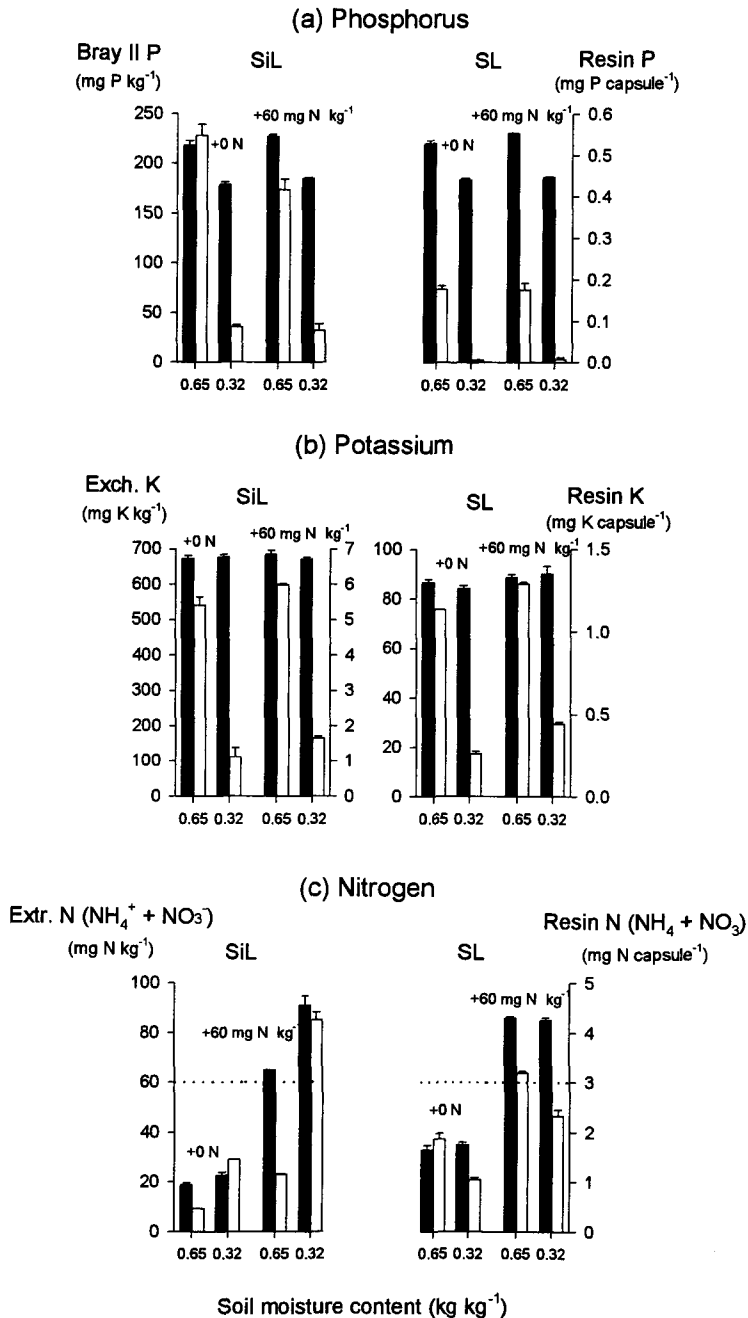
Fig. 1. Measurements of P, K, and N ($NH_4^+ + NO_3^-$) in Hokkaido silt loam (SiL) and
sandy loam (SL) soils using conventional soil tests after 7d of incubation (■)
and resin capsules after 28d of incubation (□) at 0.32 kg kg⁻¹ and 0.65 kg kg⁻¹
soil moisture contents. Error bars show standard deviation of three replicates.
The amount of extractable N was measured using 2M KCl and that of
exchangeable K using 1M NH_4OAc, pH 7.

SAT conditions, with a greater difference in the amount of resin N. An increase in the amount of KCl-extractable N after 7d of soil incubation was observed both under SAT and UNSAT conditions in SL, but only under UNSAT conditions in SiL (Fig. 2).

After 7d of soil incubation under UNSAT conditions, the amount of NO_3^- in SiL was 94% of that of KCl-extractable N ($NH_4^+ + NO_3^-$) and 88% in SL; but under SAT conditions, the amount of NH_4^+ was 82 and 90% for SiL and SL, respectively. The results of linear regression analyses between resin adsorption and KCl-extraction of N (NO_3^- under UNSAT conditions and NH_4^+ under SAT conditions) are shown in Table 2. Under UNSAT conditions, the regression between resin NO_3-N (28d) and soil KCl-extractable NO_3-N (7d) in SiL yielded a high r^2 (0.991) with the regression line being very close to the 1:1 line (i.e., 50 g dry soil, as the basis of comparison) (Table 2a, Fig. 3a). Regression between the two methods for all the incubation times except for 1d yielded significant r^2 values $\geq$ 0.936. In the case of SL, r^2 values between the two methods were lower and significant relationships were obtained only at 14d and 28d (Table 2a). Resin NO_3^- was also lower than KCl-extractable NO_3^- (Fig. 3a). On the other hand, resin NH_4-N was higher in SL than in SiL under SAT conditions (Fig. 3b),

Fig. 2. Soil N ($NH_4^+ + NO_3^-$) extracted with 2M KCl after 0 (●, ■) and 7 (O, □) days of incubation in the sandy loam (SL) and silt loam (SiL) soils at 0.65 kg kg^{-1} and 0.32 kg kg^{-1} moisture contents. Error bars show standard deviation of three replicates.

Table 2. Linear regression analyses[3] ($y = y_0 + ax$) between KCl-extractable N (mg kg^{-1}) and resin N (mg capsule^{-1}).

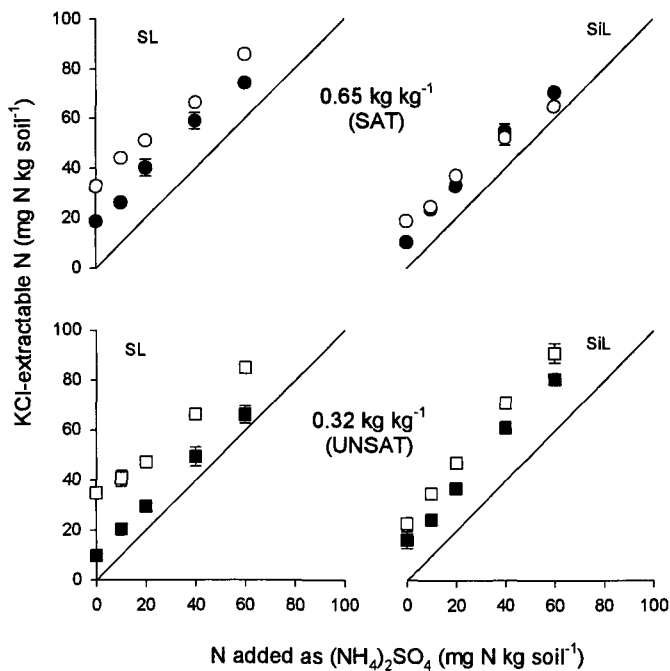| Resin Incubation Time (d)	y_0		a		r^2	
a) NO$_3$-N at 0.32 kg kg^{-1} (UNSAT): x = soil NO$_3$-N after 7days; y = resin NO$_3$-N						
Silt loam soil						
1	0.062	ns	0.0005	ns	0.333	ns
7	0.259	*	0.0095	**	0.941	**
14	−0.184	ns	0.0379	**	0.936	**
28	0.461	*	0.0445	**	0.991	**
Sandy loam soil						
1	0.023	**	−0.0001	ns	0.231	ns
7	0.094	*	0.0009	ns	0.583	ns
14	0.215	*	0.0039	*	0.788	*
28	0.082	ns	0.0247	*	0.828	*
b) NH$_4$-N at 0.65 kg kg^{-1} (SAT): x = initial soil NH$_4$-N; y = resin NH$_4$-N						
Silt loam soil						
1	−0.004	ns	0.0029	**	0.989	**
7	0.018	ns	0.0068	**	0.997	**
14	0.048	**	0.0096	**	0.999	**
28	0.125	**	0.0128	**	0.996	**
Sandy loam soil						
1	−0.067	*	0.0071	**	0.989	**
7	−0.035	ns	0.0185	**	0.999	**
14	0.072	ns	0.0254	**	0.983	**
28	0.413	*	0.0296	**	0.976	**

*, ** Significant at 5% and 1% level, respectively; [3]The number of samples was five for all incubation times

although significant relationships were obtained between the two methods in both soils regardless of the duration of the period of resin incubation (Table 2b).

b. Resin adsorption kinetics of P, K, and N in unfertilized (+0N) soils

1. Phosphate. Under SAT conditions, the values of the P-supplying capacity index, b_P (in $RAQ_P = a_P t^{b_P}$), were moderate[13] (compared to values obtained in previous studies) both soils but the value of the readily available P index, a_P, was much higher in SiL than in SL, resulting in a higher accumulation of P (RAQ_P) in SiL (Fig. 4a). Under UNSAT conditions, the RAQ_P value was low in SiL and very low in SL, resulting in a low or non-significant fit to the power function under these soil moisture conditions.

2. Potassium. Under SAT conditions, the values of b_K (in $RAQ_K = a_K t^{b_K}$) were almost similar in the two soils but the a_K values were much higher in SiL than in SL, yielding a very high RAQ_K value in SiL (Fig. 4b). The values of a_K under UNSAT conditions were much lower than under SAT conditions, but the values of b_K did not seem to be affected by moisture conditions.

3. Nitrogen. RAQ_N (NH$_4$$^+$ + NO$_3$$^-$) under UNSAT conditions in SiL were comparable to those of RAQ_N under SAT conditions in SL (Fig. 4c). Values of a_N and b_N (in $RAQ_N = a_N t^{b_N}$) were higher under UNSAT conditions in SiL,

(a) NO$_3^-$ at 0.32 kg kg^{-1}(UNSAT)

KCl-extractable NO$_3$-N after 7d of incubation (mg N kg^{-1})

(b) NH$_4^+$ at 0.65 kg kg^{-1}(SAT)

Initial KCl-extractable NH$_4$-N (mg N kg^{-1})
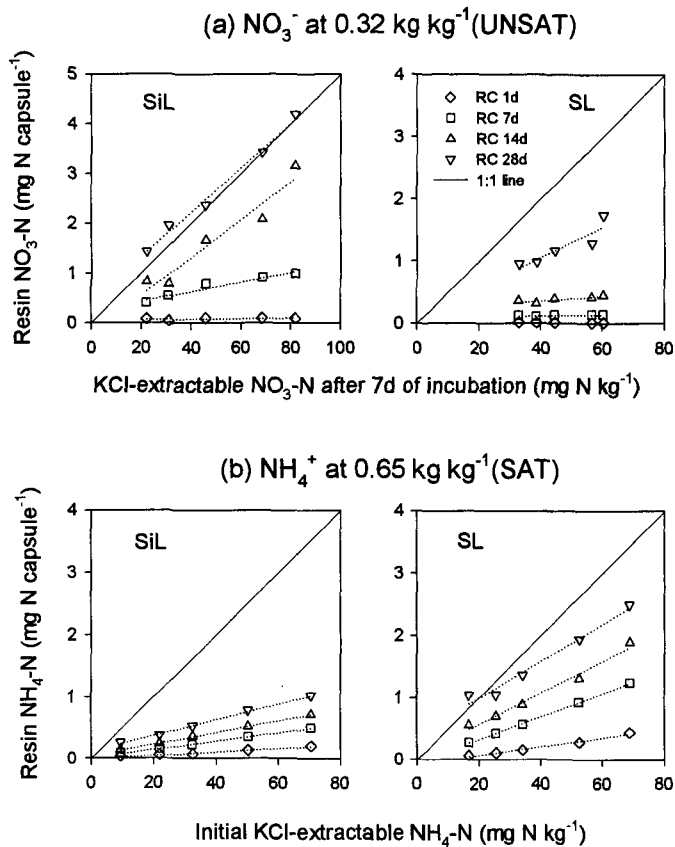
Fig. 3. Relationship between soil extraction with 2M KCl and incubation with resin capsules (RC) in measuring (a) NO$_3^-$ concentration at a moisture content of 0.32 kg kg^{-1} and (b) NH$_4^+$ concentration at 0.65 kg kg^{-1} in silt loam (SiL) and sandy loam (SL) soils. The 1:1 line represents equivalent amounts of resin N and KCl-extractable N when the amount of soil used for incubation was 50 g.

whereas they were higher under SAT conditions in SL. Furthermore, the a_N values were higher in SiL while the b_N values were higher in SL.

D. Discussion
a. Effect of soil moisture and texture on P, K, and N measurements
1. Phosphorus. Decrease of P adsorption on the resin due to reduced soil moisture was similar to the decrease of P absorption by plant roots under conditions of low soil water availability[26]. The lower content of resin P at a low soil moisture content indicated that P diffusion decreased probably due to increased tortuosity[18]. Likewise, the lower Bray II P values under UNSAT conditions (as compared with those under SAT) indicated that the amount of
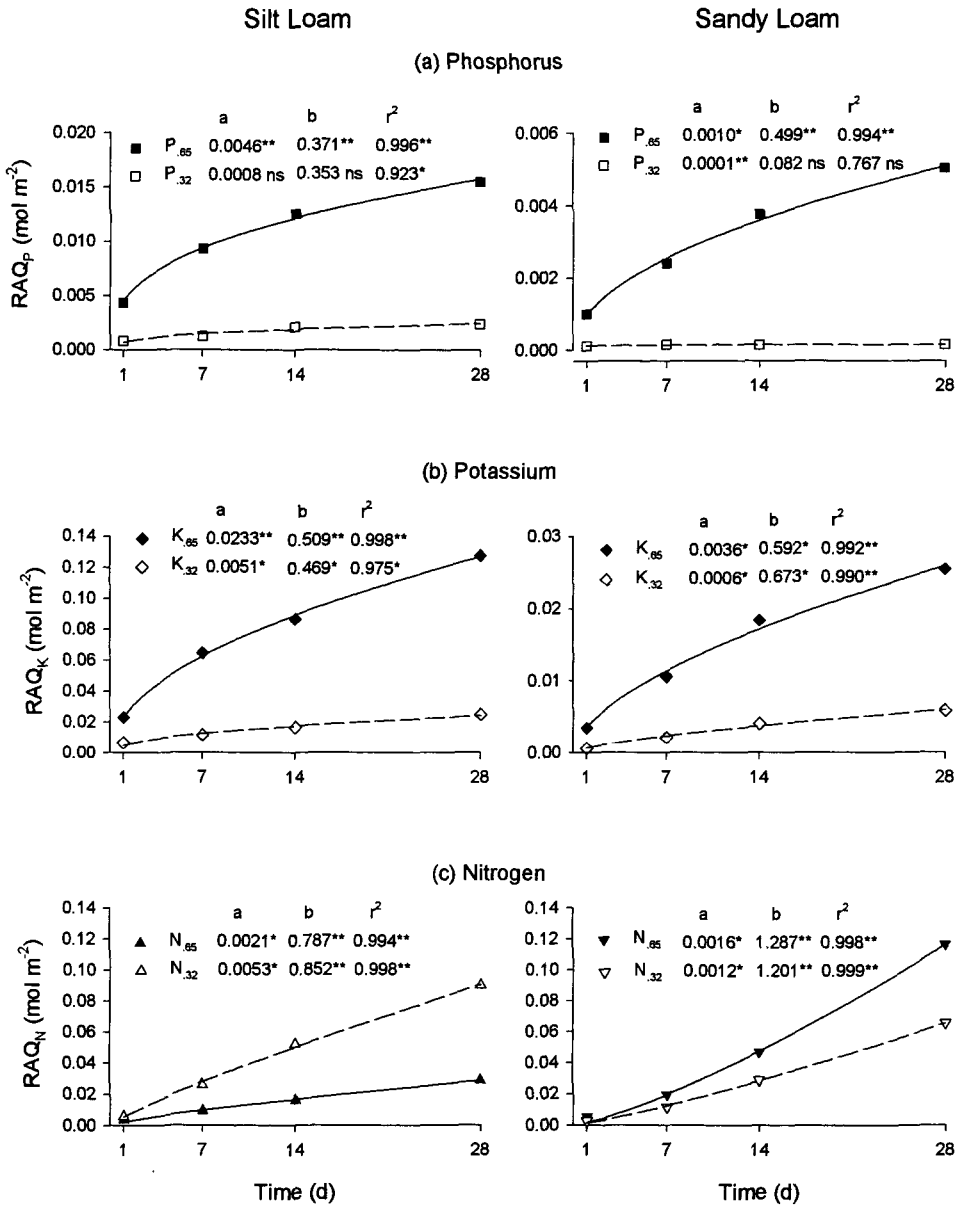
Fig. 4. Resin adsorption kinetics of P, K, and N ($NH_4^+ + NO_3^-$) in Hokkaido silt loam
(SiL) and sandy loam (SL) soils at 0.65 kg kg^{-1} and 0.32 kg kg^{-1} moisture
contents. Regression lines were obtained from non-linear estimation with the
power function, $RAQ_i = a_i t^{b_i}$, where RAQ is the amount of resin adsorption
of ion i at time t (d) and a and b are rate coefficients used to describe the
adsorption kinetics of the ion on the resin. Data shown were taken from $+0N$
treatments only.

*, ** Significant at 5% and 1% level, respectively

available P was less under unsaturated conditions, suggesting that the lower resin P values observed under low soil moisture conditions were partly due to a lower amount of available P.

The aggravating effect of a coarse or sandy soil texture on P diffusion revealed by a greater reduction of the amount of resin P in SL than in SiL, could be related to the effect of the bulk density on P diffusion. A soil with coarse texture shows a higher bulk density than a fine-textured soil[18]. In a previous study, it was observed that at a high bulk density, changes in the water content affected the self-diffusion coefficient of P in both sandy loam and silty clay loam to a greater extent than at a low bulk density[19]. In addition, separate and discontinuous pockets of water may be formed under unsaturated conditions in the sandy soil[18], further leading to an increase in the tortuosity and decrease of P diffusion.

2. Potassium. The present study showed a 4.7-fold increase in the content of resin K when soil moisture increased from 0.32 kg kg^{-1} to 0.65 kg kg^{-1} (Fig. 1b), while other workers[30] observed a 2.8-fold increase (in an H-saturated resin sink in Bozeman silt loam) when the soil moisture increased from 10 to 28%. Such an increase was attributed mainly to a decreased tortuosity of the diffusion path when soil moisture increased[30]. The textural difference between SiL and SL soils did not seem to cause a difference in resin K content, probably due to the almost similar amounts of clay content and organic carbon in the two soils. Exchangeable K is held by the negative charges of organic matter and clay minerals[43]. The contribution of clay to exchangeable K was in the range of 73 -83%, and to non-exchangeable K, in the range of 35-74 %[51].

3. Nitrogen. Under SAT conditions, extractable N was represented predominantly by NH_4^+ (Fig. 3). A decrease in KCl-extractable N at 60 mg N kg soil^{-1} after 7d of soil incubation in SiL (Fig. 2), however, suggested the occurrence of N loss, presumably through denitrification. Higher rates of denitrification have been reported in finer-textured soils[22]. On the other hand, net N mineralization was observed in SL after 7d (Fig. 2), which may account for higher resin N content in SL than in SiL under SAT conditions. Another important factor might be the high amount of exchangeable K in SiL (Table 1, Figs. 1b, 4b) which could have inhibited the adsorption of NH_4^+ on the resin, since K^+ has a stronger affinity to the cation exchange resin than NH_4^+ [35].

Under UNSAT conditions, the increase in the amount of KCl-extractable N after 7d of soil incubation in the two soils (Fig. 2) indicated the occurrence of net N mineralization in both soils. The higher content of resin N in SiL than in SL (Fig. 1c), however, suggests that NO_3^- adsorption on the resin was faster and more efficient in a finer-textured soil (Fig. 3a).

b. Kinetics of resin P, K, and N in unfertilized (+0N) soils

1. Phosphorus. The higher a_P value in SiL than in SL suggests a greater supply of readily available P in SiL despite the similarity of Bray II P values between the

two soils. The values of the coefficient b_P obtained from soils in this study (0.499 and 0.371 for SL and SiL, respectively; Fig. 4a) were similar to or higher than those obtained in P-fertilized rice soils in long-term fertility experiments in Asia (i.e., China, India, Indonesia, Philippines, and Vietnam)[11]. Large b_P values may indicate the presence of significant amounts of residual fertilizer P, which is likely in the case of soils sampled in the present study, since both had been used for growing upland crops with regular fertilizer application over a period of several years. The high Bray II P values in both soils (Table 1) corresponded to the high b_P values recorded in these soils.

2. Potassium. The higher a_K value, which contributed to the higher RAQ_K value in SiL, indicates the presence of a considerable amount of readily available K and corresponded to the greater amount of NH_4OAc-extractable K in SiL than in SL (Table 1). A previous study reported that the a_K values of soils differing in texture and origin were positively correlated ($r = 0.78$, $p < 0.01$) with the content of exchangeable K determined by 1M NH_4OAc[13]. The similarly high values of b_K in the two soils may be partly due to the same amount of total carbon and clay content in these soils. A positive correlation between the b_K values and the content of organic carbon was reported[13].

3. Nitrogen. Results of resin N ($NH_4^+ + NO_3^-$) kinetics suggest that the N-supplying capacity of the two soils was comparable, although the availability and form of N varied with moisture content and soil texture. The similarity of cumulative RAQ_N after 28d in the two soils was in agreement with similar amounts of total N as well as organic C in them (Table 1).

The higher value of a_N in SiL than in SL may be related to the higher values of CEC and exchangeable bases in SiL. A high and positive correlation between a_N and soil properties related to the sorption complex of a given soil was report-ed[13]. However, the higher values of b_N in SL than in SiL for both moisture contents are in sharp contrast to previous findings[13] that b_N was positively correlated with silt content and negatively correlated with sand content. Such a discrepancy might be due to differences in the patterns of mineralization between a volcanic ash soil (SL) and an alluvial soil (SiL). Andisols were reported to show lower N mineralization rates than those of nonandic soils, although they have a higher mineralization potential[27]. Our results revealed a slow release of N in the andic SL initially, but a sharp increase was observed after two weeks of incubation, resulting in a high b_N value for the kinetic curve.

E. Conclusions

Adsorption of P and K on resin capsules were much lower under unsaturated soil conditions as compared with the saturated, showing a similarity to a general absorption tendency of P and K by plant roots. Soils with the same P content according to Bray II method but of different texture (proportion of sand, silt, and clay particles) had different amounts of readily available P (a_P), but their long-

term supplying capacity (b_P) was the same.   The amount of NH_4OAc-extractable K corresponded with the amount of readily available K (a_K) in the soil but not with its long-term supplying capacity (b_K).

Resin N adsorption kinetics (amount of N adsorbed on the resin as a function of time) in soils with identical total N and organic C contents differed according to soil moisture, texture, or soil type (e.g. alluvial soil, volcanic ash soil).   Under UNSAT conditions, diffusion or transport of N (mostly NO_3^-) to the resin in a fine-textured soil was faster than in a coarse-textured soil.   Under SAT conditions, however, the transport of N (primarily as NH_4^+) to resin was faster and more efficient in the SL than in the SiL.

IV. EXPERIMENT 2: DETECTION OF NITRATE LEACHING THROUGH BYPASS USING PAN LYSIMETER, SUCTION CUP, AND RESIN CAPSULE

A. Introduction
Nitrate leaching from agricultural fields is one of the major factors contributing to groundwater contamination or pollution of the water environment. Numerous studies have been conducted to analyze nitrate transport or movement in the soil, not only because of its impact on the environment but also on the economic aspects of agriculture.

The present study was conducted to determine the differences between the use of suction cups, pan lysimeters, resin capsules, and subsurface drainage for analyzing nitrate transport in a clayey soil.

B. Materials and Methods
a. Experimental site
The study was conducted in an upland field cultivated with onion (*Allium cepa* L.) in Mikasa, Hokkaido, Japan (43°14′ N, 141°50′ E), from May to November 1999 (Fig. 5).   Fertilizer nitrogen (322 kg N/ha) was applied only once at the end of April, shortly before transplanting.   The crop was harvested during the second week of September 1999.   The groundwater table lay at 70-80 cm depth throughout the year.   Subsurface drains installed at 80-100 cm depth at 12-m intervals were connected to the same effluent exit, draining about 0.95 ha (125m × 76m).

b. Soil
The soil at the site was classified as fine, mesic, mollic Fluvaquent[41].   The physical and chemical properties of the different horizons were reported elsewhere[16].   Soil texture consisted of silty clay or heavy clay from the Ap layer (0 -28 cm) down to the C horizons (48-100+ cm).   Saturated hydraulic conductivity in the Ap horizon was low (1.0×10^{-7} m s^{-1}) but the C horizons showed high conductivities (4.6×10^{-6} and 2.2×10^{-4} m s^{-1}) due to the presence of macropores[16].
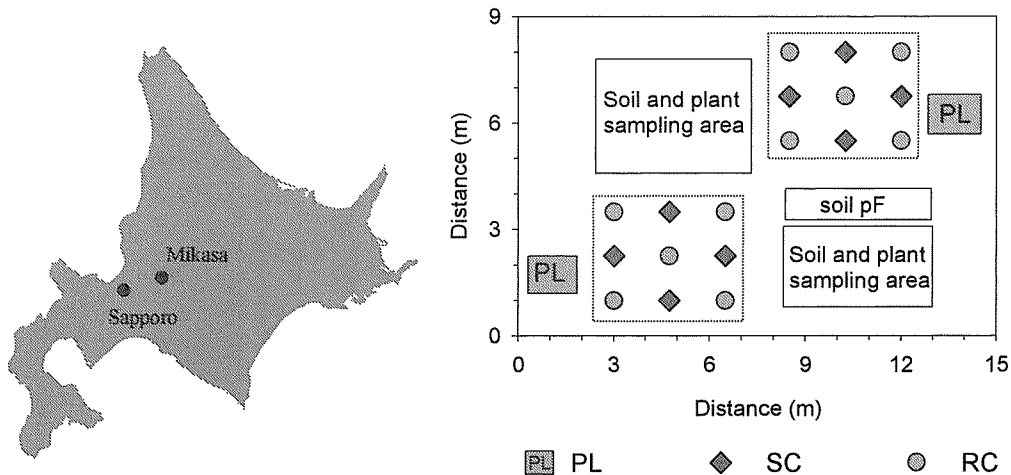
Fig. 5. Layout of the measurement plot showing locations of pan lysimeters (PL, holes for installation), suction cups (SC), and resin capsules (RC) in an onion field at Mikasa, Hokkaido, Japan. The broken lines outline the subplots for RC and SC installation.
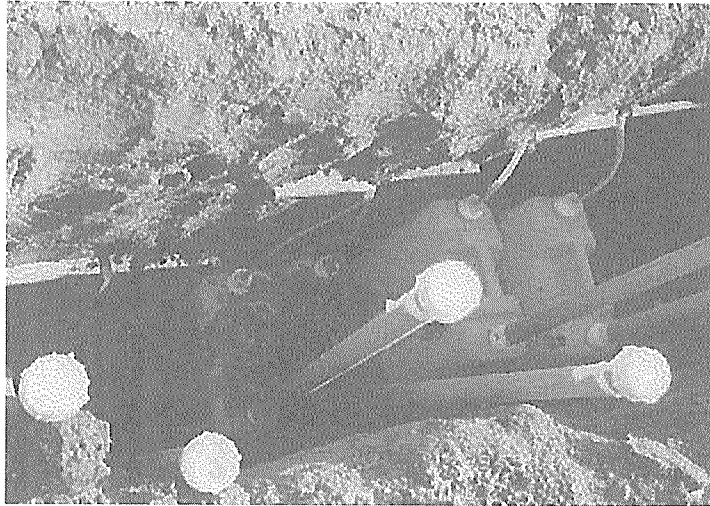
c. Installation of suction cups, pan lysimeters, and resin capsules

Figure 5 illustrates the layout of the measurement plot. Immediately after transplanting, a 15m x 9m plot was marked where two subplots (3.5m x 2.5m each) were setup for the installation of suction cups (SC) and resin capsules (RC) at different depths (15, 30, 50, 80 cm for SC; 15 and 50 cm for RC). In each subplot, four SC and five RC were inserted at each depth. For the installation of pan lysimeters (PL) at different depths (30, 50, 80 cm), a hole (1.5m × 1m × 1m) was dug outside each subplot. At each depth and location, two pan samplers (stainless steel, 20cm × 30cm) were carefully inserted by jacking to minimize the disturbance of the soil profile, and slightly inclined from the horizontal plane to enable the collection of drainage water (Fig. 6). The drainage water intercepted by the pan sampler was conveyed to a 20-L bucket through a plastic tube (1-cm diameter) that connected the end of the pan to the bucket.

For the installation of resin capsules, access tubes, made of polyvinyl chloride (PVC, outer diameter = 4.2cm and inner diameter = 3.4cm), were set at a 30° angle from the vertical line (Fig. 6) to prevent interference to vertical flow at the point of sampling[21]. The access tube was equipped with a cap to prevent the entry of water from the surface (e.g. rainfall). One resin capsule was attached to the end of a smaller tube (2-cm diameter) and inserted into the access tube. The inner tube was pulled out every time (two weeks) the resin capsule was retrieved and replaced. Resin capsules were washed thoroughly with deionized water on the same day that they were retrieved from the field.

d. Collection and analysis of samples

(a)

(b)
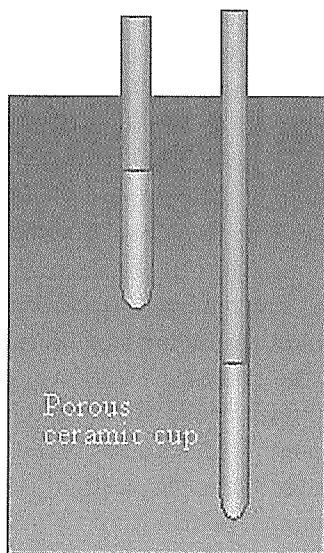
(c)

(Adapted from WECSA)

Fig. 6. Installation of a) pan lysimeters (PL), b) suction cups (SC), and c) resin capsules (RC).

Soil solution samples from suction cups were collected 1-2 times per week by applying a suction of approximately -70kPa immediately after the collection of the samples from previous pumping. Samples from PL as well as subsurface drainage (DR) were also collected at the same time. Drainage flow and rainfall data were monitored through a data logger. Soil matric potential at different depths was measured through tensiometers every time samples were collected.

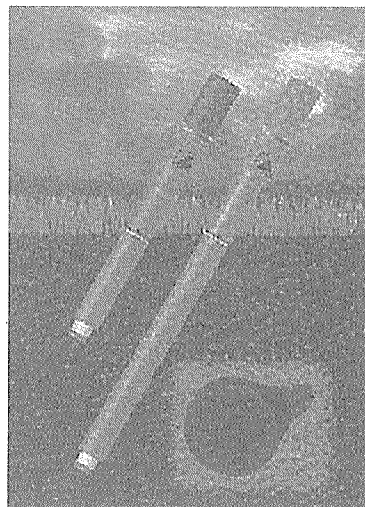Water samples were taken to the laboratory and kept in a refrigerator until the analysis of NO_3^- by ion chromatography. Procedures for handling of resin capsules, extraction of adsorbed ions, and analysis of NO_3^- were the same as those described in Chapter III.

e. Presentation and statistical analysis of results

For the RC method, the means of 10 replicates (from the two subplots) for each soil depth were used in presenting the results. For SC, results were included in the analysis only if the samples collected consisted of at least three replicates out of eight possible samples for each sampling date at a certain depth.

For correlation analysis, RC data were compared with those from the other methods by using the mean concentration of the non-RC parameter (i.e. SC, PL, and DR) during the RC installation period. Furthermore, comparison was performed only when at least two consecutive data were available (from the non-RC parameter during the RC installation period), and when the RC installation period covered 13-16 days.

Nitrate concentration (mg N/L) in the samples obtained by SC, PL, and DR will be referred to as SC NO_3^-, PL NO_3^-, and DR NO_3^-, and the amount of NO_3^- adsorbed on RC (mg N/capsule) will be referred to as RC NO_3^-.

C. Results and Discussion

a. Rainfall and drainage patterns

During the study period (May-Nov 1999), the total rainfall was 663mm and total drainage was 315mm (Fig. 7a). The drainage pattern corresponded closely to the rainfall pattern (Fig. 7b); both rainfall and drainage revealed a large increase from the end of July to early August.

b. Nitrate in suction cup, pan lysimeter, and subsurface drainage samples

At the topsoil level, SC NO_3^- was always higher than PL NO_3^- (Fig. 8). At a 15-cm depth, SC NO_3^- decreased with time while it showed increasing trends at 30- and 50-cm depths. On the other hand, PL NO_3^- fluctuated at all depths. The decreasing trend of SC NO_3^- at the 15-cm depth (i.e., from June to August and from October to November) may be attributed to leaching, plant uptake, and gaseous losses (e.g. denitrification), while the increasing trends of SC NO_3^- at 30 - and 50-cm depths after August, to internal catchment where water accumulated at the bottom of discontinuous macropores[47,6,7].

At the groundwater level (80-cm depth), SC NO_3^- showed a steady decrease with time where the initial (first two months) values were >12 mg N L^{-1} and

Mirasol F. PAMPOLINO

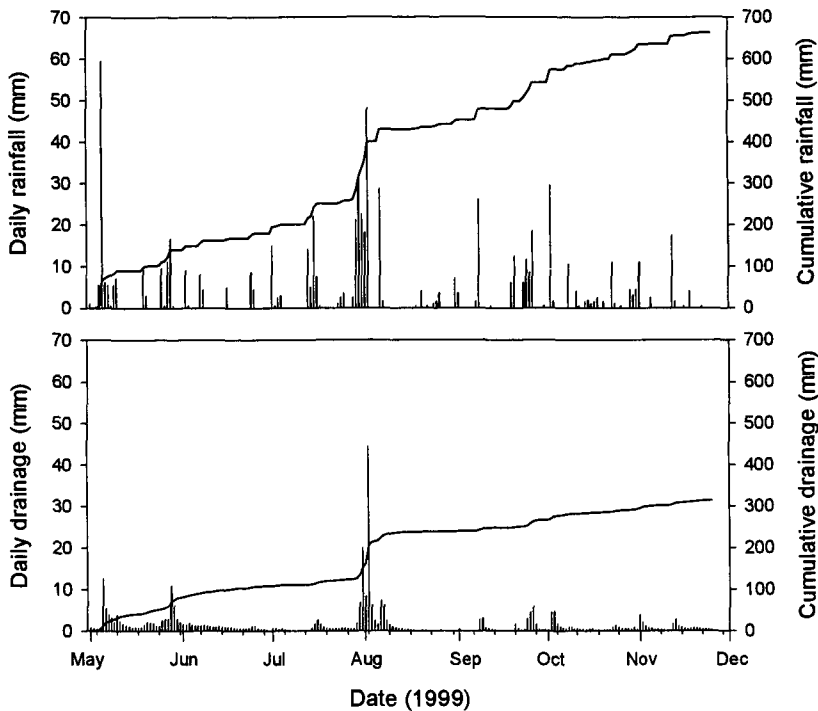**Fig. 7.** Rainfall and drainage patterns at the experimental site (Mikasa, Hokkaido, Japan) from May to November 1999.

latter values were <5 mg N L^{-1} (Fig. 9). PL and DR NO_3^- exhibited fluctuating temporal patterns, however, mostly affected by fluxes of drainage. PL NO_3^- was always higher $(>10$ mg N $L^{-1})$ than SC NO_3^- except on three consecutive sampling dates (late June to mid-July) when the drainage rate and volume were so low that the PL NO_3^- decreased to <2.5 mg N L^{-1}. Likewise, DR NO_3^- was consistently higher than that of SC NO_3^- at the 80-cm depth. DR NO_3^- tended to be low when the rate of drainage flow was low, especially during no (or minimal) rainfall several days before sampling.

The higher concentrations of NO_3^- in DR and PL samples (as compared with those of SC) at the 80-cm depth indicated that bypass or macropore flow was the primary mechanism for NO_3^- transport to subsurface drainage or groundwater, and suggested that the solutions collected by the SC method were largely representative of those inside soil aggregates. The suction cups are usually bypassed by water flowing through macropores, especially in structured clay soils[15,1]. It was observed that the concentration of solutes obtained from ceramic solution samplers was neither representative of the total solute quantity contained in the soil volume nor the flux concentration where preferential flow occurred[25]. Moreover, the results of SC at an 80-cm depth revealed a depletion of nitrate over

(a) Suction Cup Method

◇ 15-cm depth
△ 30-cm depth
○ 50-cm depth
□ 80-cm depth

(b) Pan Lysimeter Method

Sampling Date (1999)
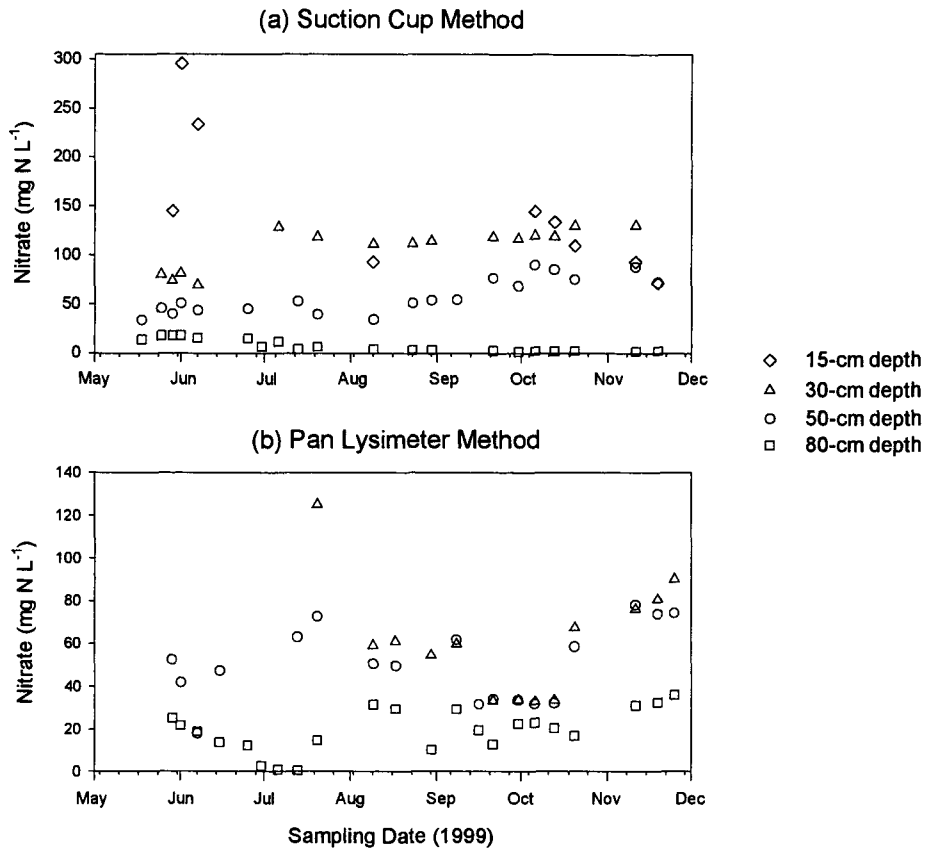
Fig. 8. Temporal variation of nitrate concentration at different soil depths measured
from samples collected using a) suction cups (SC) and b) pan lysimeters (PL).
Values of samples obtained by the suction cup method represent means of 3-8
replicates, while those for pan lysimeters 1-4 replicates.

○ SC
□ PL
+ DR

Sampling Date (1999)

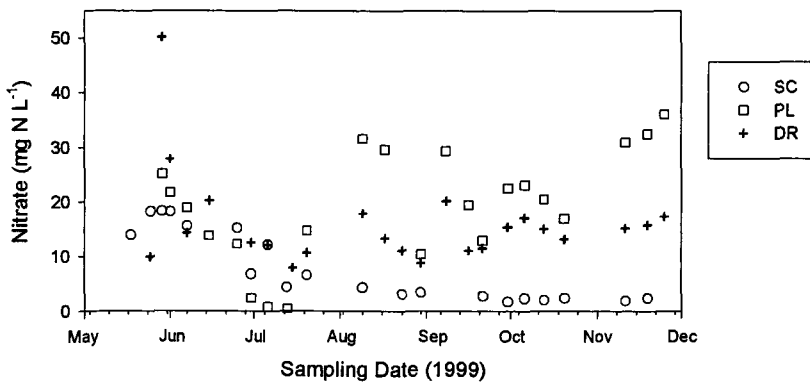**Fig. 9.** Nitrate concentration measured from samples collected at 80-cm depth using
suction cups (SC), pan lysimeters (PL), and subsurface drainage (DR). Values
represent means of 3-8 replicates for SC, 1-4 replicates for PL and one replicate
for DR.

time without apparent recharge, suggesting that the higher concentrations at the observation period onset have been associated with the presence of residual nitrate. The continuous decrease in SC NO_3^- at the 80-cm depth also indicated that most nitrate transported to this depth was drained through subsurface drainage or leached into groundwater rather than being diffused to or adsorbed on the soil matrix. The results further suggest that most nitrate leaching (transport) occurred due to the rapid vertical movement of water or bypass flow. It was suggested that preferential flow plays an important role in rainfall-leaching patterns, and results of a previous study indicated that bypass flow was the only major mechanism for water and solute flow in a highly structured clay soil[42]. Other researchers also obtained results suggesting the existence of preferential or bypass flow of solutes in clayey soils[3,1,5,6,42,50,32].

c. Nitrate adsorbed on the resin capsule

The use of the RC method resulted in a larger amount of NO_3^- at 15- than at 50-cm in depth initially, but the trend was reversed after sufficient leaching (235mm drainage) and plant uptake, i.e., after a five-day high intensity rainfall three months following fertilizer application and transplanting (Fig. 10). At the 15-cm depth, the concentration of RC NO_3^- ranged from 0.15 to 2.3 mg N/capsule and in 75% of the observations the value was <1 mg N/capsule. Highest values were recorded during the first two installation periods and a high value (>1 mg N/capsule) was again obtained in the late October to early November installation (i.e., more than one month after harvest), probably due to N mineralization associated with decomposition of plant residues in the topsoil. The range of RC NO_3^- at the 50-cm depth was 0.26-2.25 mg N/capsule and 66% of the values were >1 mg N/capsule. High values (>2 mg N/capsule) were observed in early August (RC installed during continuous high intensity rainfall) and after harvest (early November).
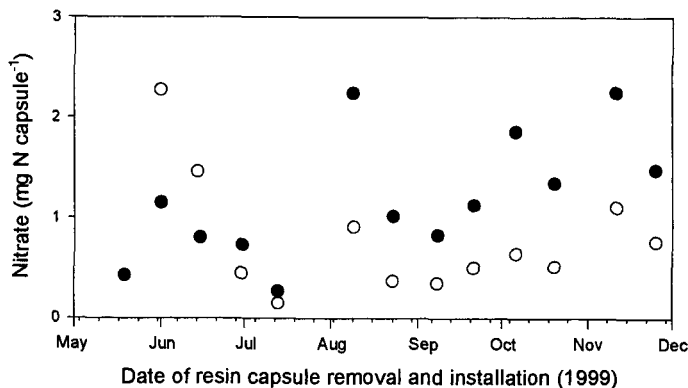
Fig. 10. Temporal variation in the amount of nitrate adsorbed on the resin capsules at 15- (O) and 50-cm (●) depths. Values shown are means of 10 replicates.

d. Comparison of the resin capsule method with drainage, pan lysimeter, and suction cup methods

RC NO_3^- showed a positive correlation with the mean DR and PL NO_3^- during the RC installation period (Fig. 11). Correlation between the RC NO_3^- at a 15-cm depth and the mean DR NO_3^- yielded an r value of 0.987 ($p < 0.01$, $n = 10$) and that between the RC NO_3^- at 50cm and mean PL NO_3^- at 80cm gave an
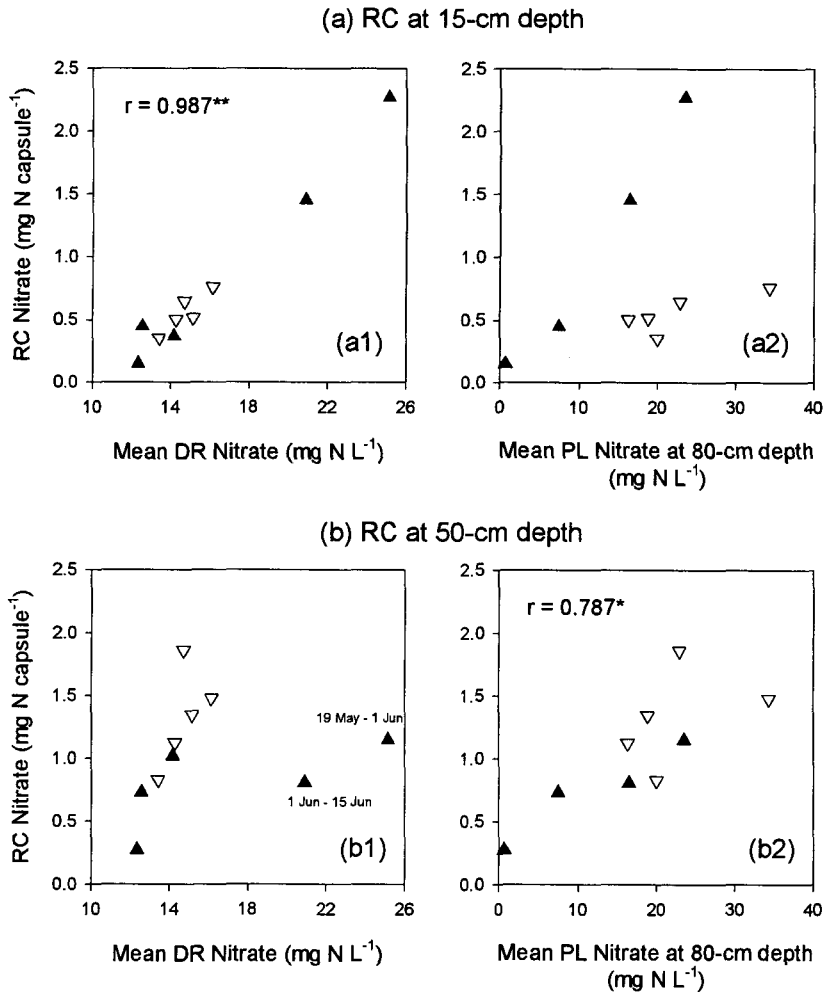
Fig. 11. Relationship of the amount of nitrate adsorbed on the resin capsules (RC) at (a) 15- and (b) 50-cm depths to the mean concentration of nitrate in the subsurface drainage (DR) and pan lysimeter (PL) samples during the RC installation period (approximately two weeks). Filled symbols (▲) show data during the crop growing period (May-July) and unfilled symbols (▽), from crop maturity to the post harvest period (Aug-Nov).
*, ** Significant at 5% and 1% level, respectively

r value of 0.787 ($p < 0.05$, $n = 9$). These observations show that the resin capsule was able to intercept continuously a representative amount of nitrate moving through macropore or even bypass flow. There was no clear relationship between RC NO_3^- and SC NO_3^- at any depth, indicating that the amount of NO_3^- adsorbed on the RC was primarily affected by rapidly moving water rather than matrix flow or diffusion.

A high correlation ($r = 0.834$, $p < 0.01$, n = 8) between the RC NO_3^- at a depth of 50cm and the mean DR NO_3^- was also obtained when data from the first month of observation were excluded. During the early period, DR NO_3^- values were highest, and although the RC results at 15cm reflected these high values, the RC data at 50cm failed to give the same results. Such a discrepancy is not easy to explain, but it might have been due to the presence of cracks or a high variability of water flow in the subsoil during this time causing a highly preferential flow of nitrate, which bypassed the capsules. A positive correlation was also observed between RC NO_3^- at 15cm and PL NO_3^- at 80cm. Two groups could be differentiated, however, one group during the active crop growth period (May–July) and another group from crop maturity to the post-harvest period (Aug–Nov) (Fig. 11a2). This difference indicates the availability of NO_3^- in the topsoil during these periods with a high value during the crop-growing period (mostly from applied fertilizer), but a decrease in the topsoil after substantial plant uptake and leaching. These observations also reflect the differences between the DR and PL methods, even though both methods enabled the collection of soil solution moving through macropore or bypass flow.

e. **Effect of drainage volume on nitrate measurement with the resin capsule method**

Cumulative drainage during the RC installation period was significantly and positively correlated with the RC NO_3^-. The correlation between RC NO_3^- at 15cm and cumulative drainage during the RC installation period yielded an r value of 0.835 ($p < 0.01$, $n = 11$) when >40mm of drainage was excluded and an r value of 0.914 ($p < 0.01$, $n = 9$) when only <20mm of drainage were included in the analysis (Fig. 12a). At 50cm, the concentration of RC NO_3^- was also positively correlated with the cumulative drainage (Fig. 12b) but two groups could be differentiated (similar to groups described in the previous section), Group A (May –Jul) and Group B (Aug–Nov). The separation into two groups (A and B) at 50cm reflected the relationship with available NO_3^- at this depth during these periods as well as the source of NO_3^- that passed through the vicinity of the resin capsule at this depth. Nitrate concentration was lower in subsoil than in topsoil during the active crop growth stage (May-July) while the trend was reversed from crop maturity onward (Aug-Nov, Fig. 10). During the active crop growth stage (Group A), nitrate adsorbed on the capsule at 50cm may have been derived mostly from the topsoil (applied fertilizer), but after substantial drainage or leaching (Group B), it may have been derived from both currently and previously
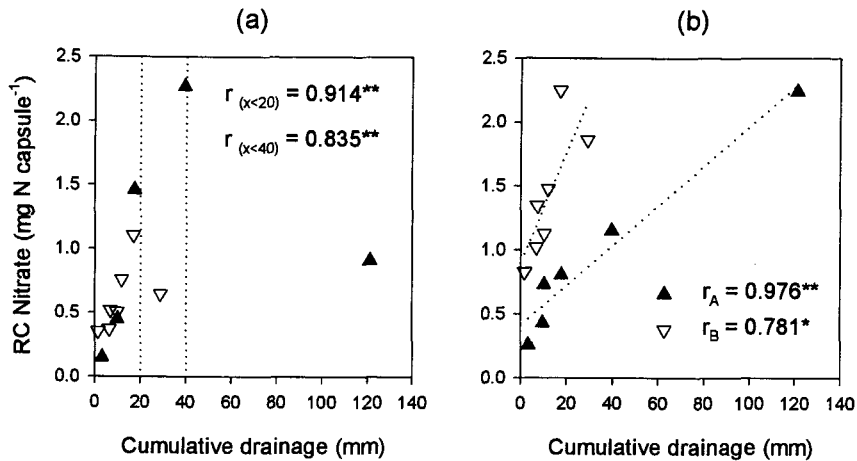
(a)   **(b)**

Fig. 12. Effect of drainage on the amount of nitrate adsorbed on the resin capsules
(RC) at (a) 15 and (b) 50 cm. Cumulative drainage refers to the total drainage
during the RC installation period (about two weeks). The subscripts A and B
of the correlation coefficient, r, refer to Groups A (▲, crop growing period,
May-July) and B (▽, crop maturity to post harvest period, Aug-Nov).
*, **   Significant at 5% and 1% level, respectively

transported nitrate.   Nitrate from the topsoil during the later period may have
originated from N mineralization of crop residues.   These results corroborate
those obtained from the correlation analysis between the RC NO_3^- and DR or PL
NO_3^-, indicating that NO_3^- was transported mostly via macropore or even bypass
flow.   In addition, these results outline the mechanisms of solute transport (water
flow) as well as the availability of solute in different soil layers during the
leaching events.

D. Conclusions

Nitrate was leached or transported to the subsurface drainage or ground-
water of a clayey soil primarily through macropore or bypass flow as reflected
by the fluxes of nitrate measured in the subsurface drainage and pan lysimeter
samples collected at the groundwater level (80-cm depth).   Installation of 10 resin
capsules at 15 or 50cm in a 135m² (9m × 15m) plot allowed the interception or
adsorption of a representative amount of nitrate transported via macropore or
even bypass flow.   Soil solutions obtained by suction cups, however, did not
reflect the concentrations of nitrate transported to groundwater level through
bypass flow.

V. EXPERIMENT 3: MONITORING TRANSPORT OF CATIONS AND PHOSPHORUS IN A CLAYEY SOIL USING PAN LYSIMETER, SUCTION CUP, AND RESIN CAPSULE

A. Introduction

Understanding the transport of cations and phosphorus in soil is important for efficient nutrient management, both for agronomic and environmental concerns. Similar to nitrate, cations and phosphorus when leached may contaminate groundwater. However, the amount of these solutes transported or leached to groundwater may vary depending on their availability or retention in the soil matrix. To gain an insight on the processes affecting transport of cations and *phosphorus in a clayey soil, I compared the use of pan lysimeter, suction cup, resin* capsule, and subsurface drainage for determining concentrations of cations and phosphorus at different soil depths.

B. Materials and Methods
a. Analysis of cations and phosphorus in water samples and resin capsule extracts

From the same setup/experiment conducted to detect nitrate leaching (Chapter IV), the concentrations of basic cations (Ca, Mg, K, Na) and phosphorus in water samples and the resin capsule (2M HCl extracts) were also determined.

The concentrations of cations and phosphorus in the water samples were analyzed using ion chromatography while those of cations in the resin capsule extracts were measured using atomic absorption spectrometry for Ca and Mg and flame emission spectrometry for K and Na. Determination of phosphorus (HPO_4^{2-}) in the resin capsule extracts was the same as in Chapter III.

b. Analysis of plant samples

Total uptake of nutrients was analyzed from digested (wet digestion method: mixture of HNO_3, H_2SO_4, and $HClO_4$) plant samples. Cations were determined using the same methods employed for RC extracts. Total content of phosphorus was determined using the ammonium vanadate method (colorimetric).

c. Fertilizer application

P and K applied as fertilizer before the study began (end of April 1999) were 166, and 208 kg/ha, respectively. Mg (27 kg/ha) was a component of the chemical fertilizer (S555) applied during that year. About a ton of quick lime (per hectare) was applied to the onion field immediately after harvest the previous year.

d. Presentation and statistical analysis of results

For the presentation and statistical analysis of results, the same procedures as those for nitrate (Chapter IV) were applied. Correlation analysis between RC cations and SC cations was not performed due to insufficiency of SC data (the requirement of at least two consecutive data during the RC installation period

was not fulfilled).   Henceforth ion (X) concentration (mg/L) in samples obtained
by SC, PL, DR, and RC will be referred to as SC X, PL X, DR X, and RC X.

C. Results and Discussion
a. Soil exchangeable cations and available phosphorus

Amounts of exchangeable cations (1M NH_4OAc, pH 7) and the cation
exchange capacity of the soil at the experimental site are shown in Table 3.
Available P (Bray II) of the soil at 0-15, 30-50, and 60-80 cm depths taken at the
onset of the experiment was 710, 293, and 31 mg P kg soil^{-1}, respectively.

Table 3. Cation exchange capacity and exchangeable cations (1M NH_4OAc,
pH 7) of the soil in Mikasa. *Source*: Yamada 1999

Soil depth (cm)	CEC	K	Na	Ca	Mg	Sum
			(cmol kg^{-1})			
0- 10	25.5	1.06	0.10	15.83	1.64	18.6
10- 33	24.6	0.51	0.10	11.23	1.37	13.2
33- 64	27.1	0.36	0.11	6.85	1.07	8.4
64-100+	33.1	0.38	0.24	5.86	3.58	10.1

b. Cations and phosphorus in suction cup, pan lysimeter, and subsurface drainage samples

Concentrations of Ca and K decreased with depth both for SC and PL while
Mg and Na did not show any trend with depth for either method (Figs. 13 and 14).
At 80cm (Fig. 15), SC K (< 4 mg K L^{-1}) was always lower than PL K and DR K
(≥ 4 mg K L^{-1}).   DR K was also higher than PL K most of the time.   PL Ca and
DR Ca registered higher than SC Ca at 80cm except from mid-June to mid-July
when concentrations of Ca in samples collected by the three methods were almost
the same.   Concentrations in PL and DR fluctuated more than SC for both Ca and
K.   Temporal and spatial (according to soil depth) variations of Ca and K
showed similarity to those of NO_3^-.   In contrast to Ca, K, and NO_3^-, the concen-
tration of Mg in SC was always higher than in DR and PL at 80cm while Na
showed almost similar concentrations in samples collected using the three
methods.   The higher concentration of K and Ca in the DR and PL than in SC
samples at 80cm reflected transport of these ions via macropore or bypass flow.
During a fast flow, it can be highly preferential and the surface applied solutes
may appear very rapidly in the effluent or drainage, irrespective of whether they
were cations or anions[17].   Note that Ca and K were applied in greater amounts
(as fertilizer and lime) compared to Mg and sodium (see earlier section on
Fertilizer Application).   Concentration of P was nil (less than 1mg P L^{-1}) in all
water samples throughout the observation period despite the addition of fertilizer
P (166 kg/ha), which showed a strong sorption of P on the soil.

Lower concentrations (compared to Ca) of K, Mg, and Na in the DR and PL
samples may indicate a high adsorption of these cations on the soil or a low

Fig. 13. Temporal variation of calcium and magnesium at different soil depths measured in samples collected using suction cups (SC) and pan lysimeters (PL). Values shown are means of 3-8 replicates for SC and 1-4 replicates for PL.
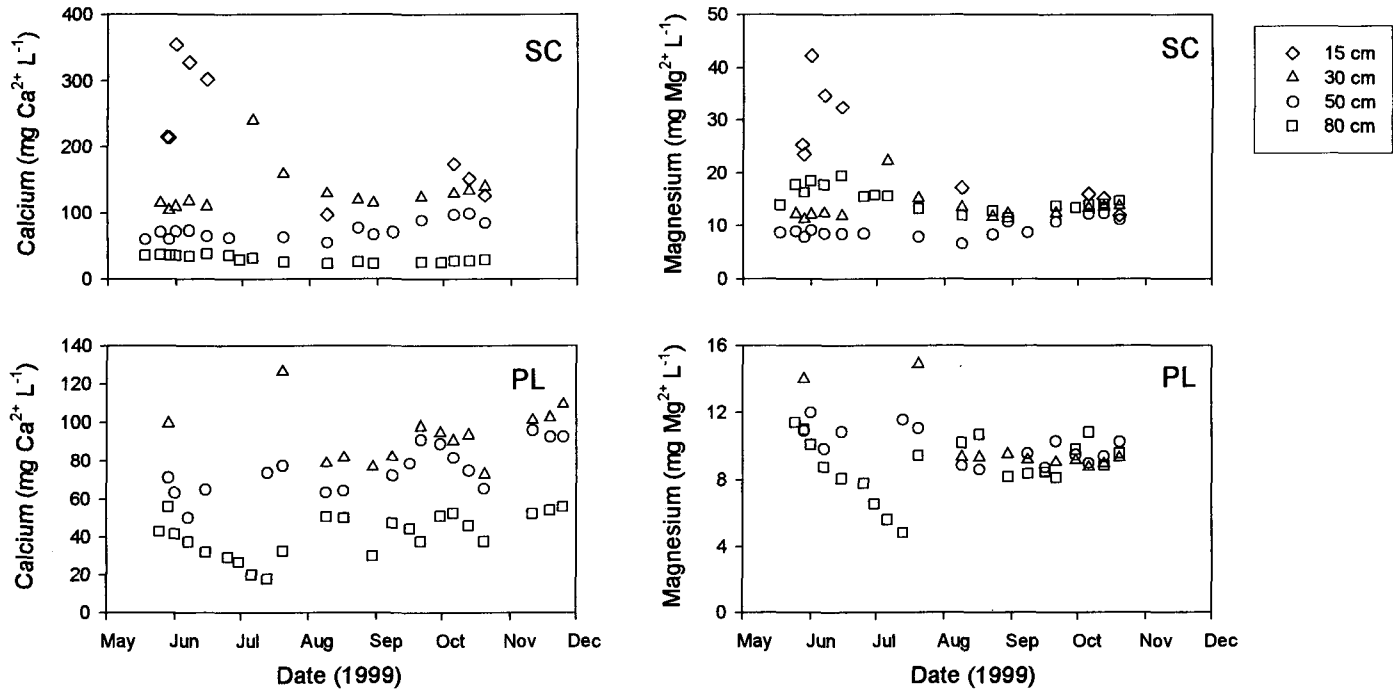
Fig. 14. Temporal variation of potassium and sodium at different soil depths measured in samples collected using suction cups (SC) and pan lysimeters (PL). Values shown are means of 3-8 replicates for SC and 1-4 replicates for PL.
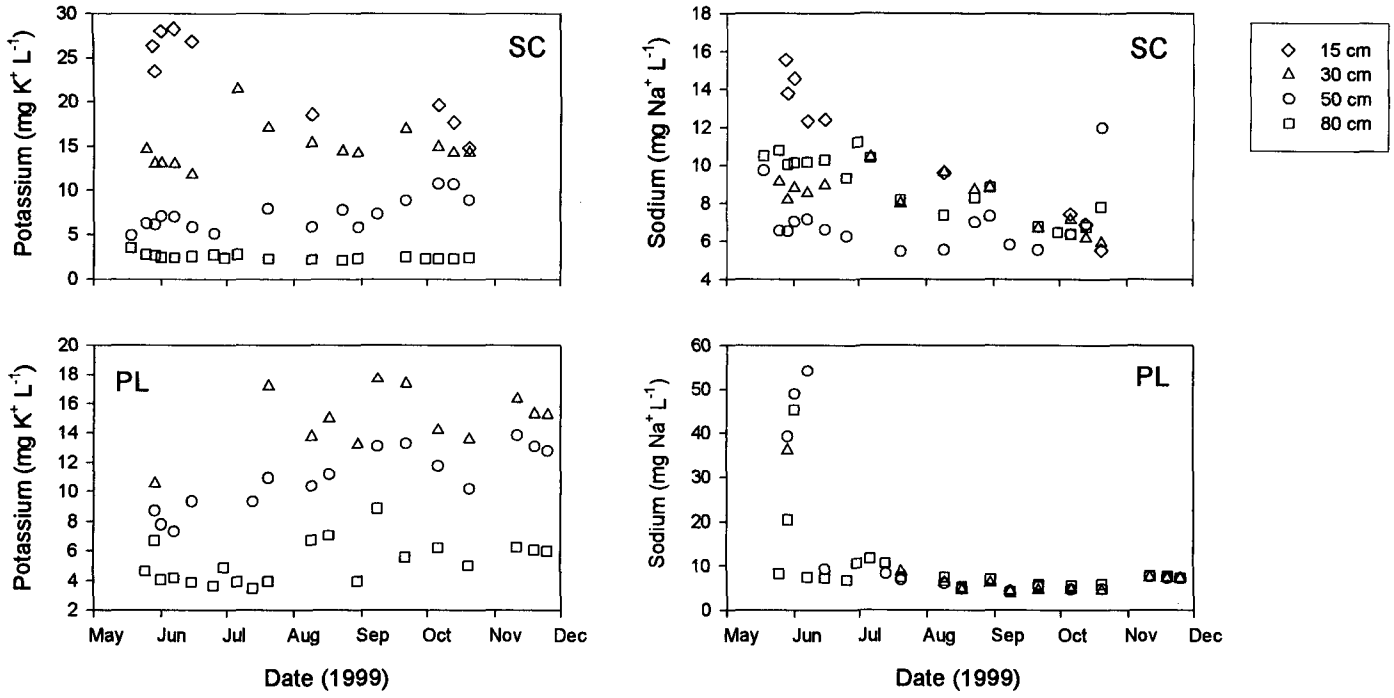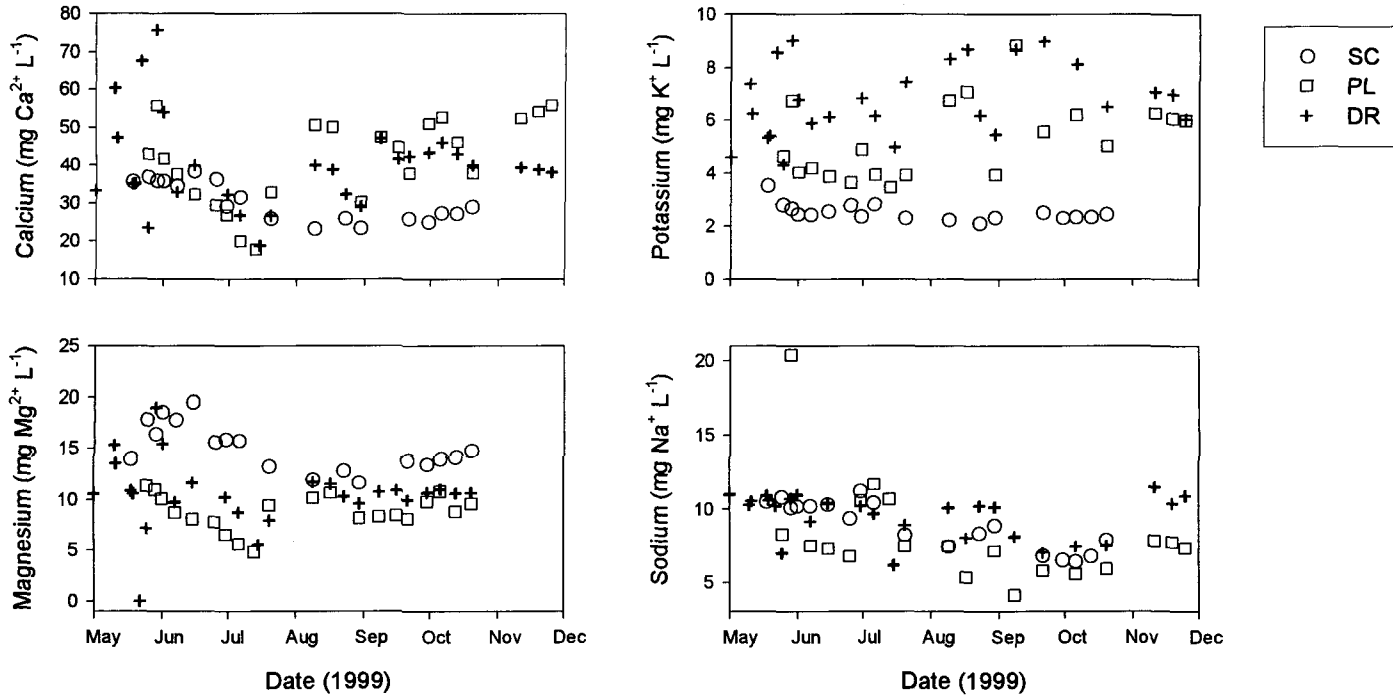
Fig. 15. Concentration of cations measured in samples collected at 80-cm depth using suction cup (SC), pan lysimeter (PL), and subsurface drainage (DR).
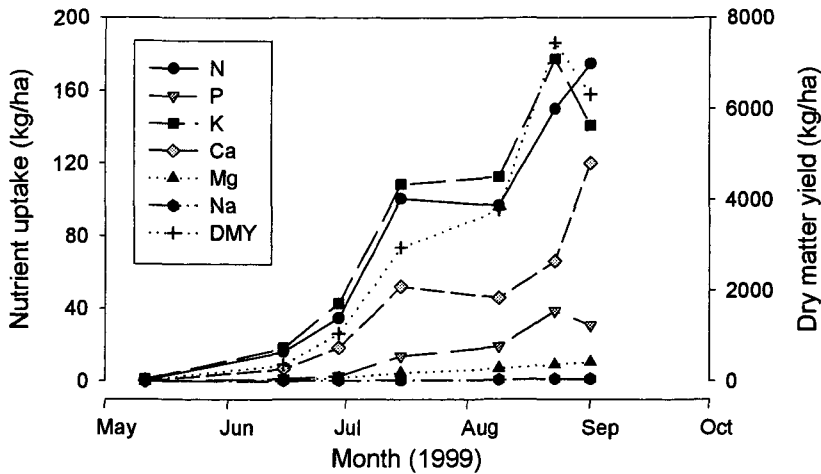
Fig. 16. Dry matter yield (DMY) and nutrient uptake of onion at the experimental
area, Mikasa, Hokkaido, Japan.

availability (Table 3).   Unlike nitrate, cations are more easily adsorbed or fixed
on the surface of soil colloids or inside soil lattices, making cations less suscep-
tible to leaching.   Added K may also have replaced Ca on the exchange sites[32],
decreasing the leaching of K but increasing that of Ca.   At a slow flow rate,
added K may replace Ca on the exchange sites but the extent of cation exchange
may be greatly reduced at a fast flow rate[17].   The higher plant uptake of K over
Ca (Fig. 16) may also explain the much lower concentration of K in drainage
water.

c. Cations and phosphorus adsorbed on the resin capsule

Amounts of Ca, Mg, and K adsorbed on the resin capsule were higher at 15
-cm depth initially (within the first month) but greater amounts were observed at
the subsoil level (50cm) starting in August (Fig. 17), after extensive leaching
(235mm drainage) and plant uptake (Fig. 16).   Such trends were similar to that of
NO_3^- (Fig. 18).   Na showed a different trend, however, since it was consistently
higher in the subsoil (Fig. 17).   The amounts of exchangeable Na (1M NH_4OAc)
at 15- and 50-cm depths also show a slightly higher reading at the subsoil level
than at the topsoil (Table 3).   In contrast to Na, P was always higher in topsoil,
except during the peak of crop growth (late June to early August) when P at 15cm
was lower than P at 50cm (Fig. 18).   Soil available P (Bray II, measured at onset
of the experiment) at 0-15 cm was also much higher than those at lower soil
depths (data recorded in earlier section).   After harvest, P in the topsoil in-
creased, probably from mineralization of crop residues.   Topsoil P content is
usually greater than that in subsoil due to the sorption of added P, greater
biological activity, and accumulation of organic material[33].

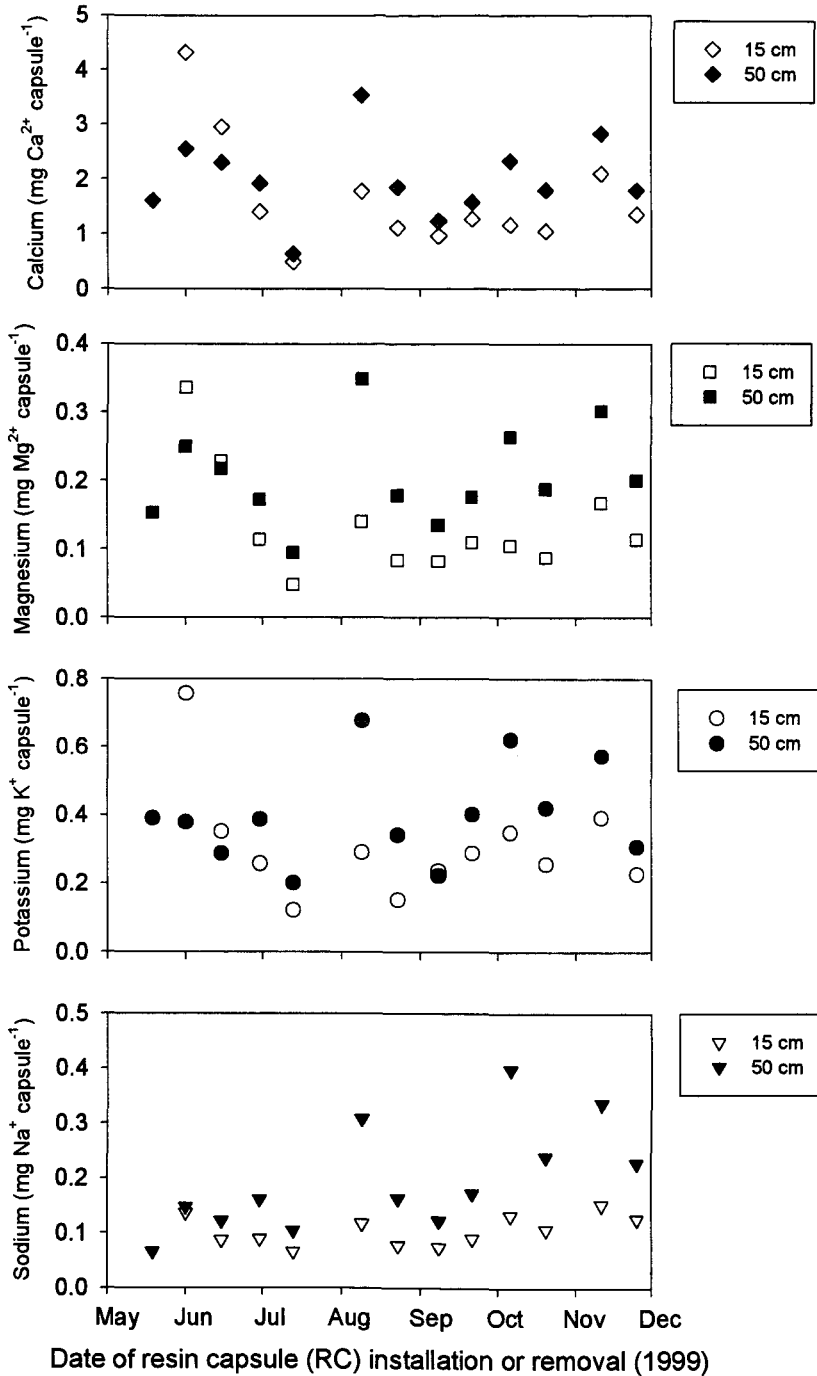In RC extracts, the highest concentration was found in Ca^{2+} ($\leq$ 4.3 mg/

Fig. 17. Temporal variation of the amounts of calcium, magnesium, potassium, and sodium adsorbed on the resin capsule installed at 15- and 50-cm depths. Values shown are means of 10 replicates.
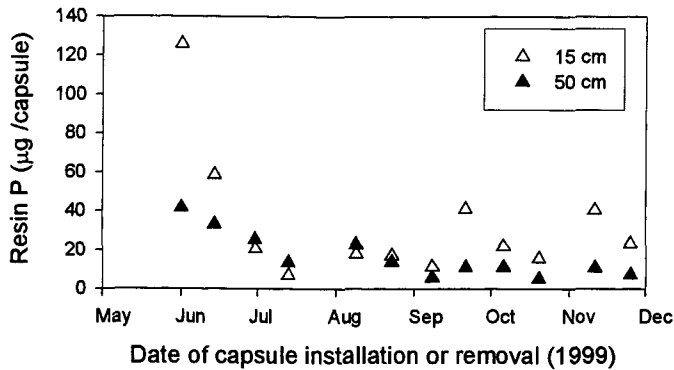
Fig. 18. Temporal variation of the amounts of phosphorus adsorbed on the
resin capsule at 15- and 50-cm depths. Values shown are means of 10
replicates.

capsule), followed by NO_3^- ($\leq$ 2.3 mg N/capsule, Fig. 10).   Highest values of K,
Mg, Na, and P were all below 1 mg/capsule, with P ($\leq$ 0.1 mg/capsule) being the
lowest.   These results agreed with concentrations of the solutes in water sam-
ples.   Among the soil exchangeable cations (1M NH_4OAc, pH 7), Ca was also
highest and Na lowest (Table 3).   Soil exchangeable K was lower than exchange-
able Mg but fertilizer K (208 kg/ha) was higher than fertilizer Mg (27 kg/ha);
hence the higher concentration of K over Mg in both the water samples and RC
extracts.

**d. Effect of drainage volume and soil moisture on the adsorption of cations
and phosphorus on the resin capsule**

Similar to nitrate, the amounts of cations and phosphorus adsorbed on RC
fluctuated with rainfall and drainage, where an increase in adsorption was
observed after peaks of rainfall (compare Figs. 17 and 18 to Fig. 7).   Adsorption
of P and cations on the RC are strongly affected by moisture content[30] (Fig. 1) due
to its effect on diffusion.   Table 4 shows positive and significant correlation
between the soil matric potential (cm H_2O) and the amounts of K, Mg, and Na

Table 4. Correlation coefficients (r) between soil moisture and the
amount of elements adsorbed on the resin capsule

Element in RC	Soil matric potential (cm H_2O)		
	15 cm (n = 10)	50 cm (n = 10)	15 and 50 cm (n = 20)
Ca	0.318 ns	0.739 *	0.371 ns
Mg	0.330 ns	0.802 **	0.490 *
K	0.424 ns	0.534 ns	0.454 *
Na	0.699 *	0.527 ns	0.498 *
P	0.336 ns	0.015 ns	0.113 ns

adsorbed on RC when data from both soil depths (15 and 50cm) were included in the analysis. A high correlation between RC Ca and soil matric potential was obtained but only at a depth of 50cm. The amount of RC P did not show a significant correlation with the soil matric potential but RC P at 15cm was highly correlated ($r = 0.813$, p$<$0.01, $n = 12$) with cumulative drainage ($>$ 40mm data excluded) during the RC installation period (Table 5). Amounts of the cations adsorbed on RC both at 15- and 50-cm depths were also highly and positively correlated to cumulative drainage during the RC installation period. These results indicate that the amount of drainage improves ion diffusion by increasing the soil moisture content as well as transporting ions through the soil.

e. Comparison between the resin capsule method, subsurface drainage, and pan lysimeter methods

The amounts of RC Ca at 15- and 50-cm depths were significantly correlated to DR Ca but not to PL Ca at 80cm (Table 5). Positive and significant correlations were also obtained between RC Mg at 50cm and PL Mg at 80cm and between RC K at 50cm and DR K. A negative correlation was obtained between RC Na at 50cm and DR Na.

Positive correlation of the RC cations (Ca, K, Mg) to their DR or PL (at 80cm) counterparts indicates that the amounts of resin-adsorbed cations were mostly contributed by macropore or bypass flow. Yet, the correlation of RC cations to cumulative drainage or soil moisture suggests an improved diffusion of cations from the soil matrix as a result of increased soil moisture.

f. Correlation between nitrate and each cation or phosphorus

Table 5. Correlation coefficients (r) between the amount of elements adsorbed on the resin capsule (RC) and the mean concentration of elements in the subsurface drainage (DR) and pan lysimeter at 80-cm depth (PL 80) samples and the amount of cumulative drainage (mm) during the RC installation period.

Element in RC	Soil depth (cm)	Drainage (mm)		Element in DR and PL	
				DR	PL 80
		(n = 13[a])		(n = 11[b])	(n = 10)
Ca	15	0.791 **		0.740 *	0.197 ns
	50	0.786 **		0.766 **	0.576 ns
Mg	15	0.811 **		0.363 ns	0.448 ns
	50	0.775 **		0.226 ns	0.789 *
K	15	0.892 **		−0.023 ns	−0.082 ns
	50	0.679 *		0.605 *	0.425 ns
Na	15	0.714 *		−0.164 ns	0.455 ns
	50	0.437 ns		−0.646 *	0.229 ns
P	15	0.813 **			
	50	0.173 ns			

*, ** Significant at 5 and 1% level, respectively; [a] >40 mm drainage was excluded in the correlation of 15-cm depth data (n = 12); [b] n = 10 for 15-cm depth data

Generally, the concentrations of NO_3^- were positively and significantly correlated to those of Ca, Mg, and K for RC, SC, and PL methods at all sampling depths (Table 6). For DR samples, the concentration of NO_3^- was significantly correlated to those of Ca and Mg but not to those of K and Na. Low or no correlation was common between NO_3^- and Na except for RC at 50cm, SC at 80cm, and PL at 30cm. Phosphate adsorbed on RC was also highly correlated (r = 0.930) to RC NO_3^- at 15cm, but there was no correlation between the two ions at 50cm.

Table 6. Correlation coefficients (r) between nitrate and each of the cations (Ca, Mg, K, Na) and phosphorus in samples collected with the resin capsules (RC), suction cup (SC), pan lysimeter (PL), and subsurface drainage (DR). Data used for SC, PL, and DR were ion concentrations (mg/L), while for RC, amount (mg) of ion adsorbed per capsule.

Method	Depth (cm)	n	Ca	Mg	K	Na	P
RC	15	12	.985 **	.988 **	.921 **	.585 *	.930 **
	50	13	.796 **	.895 **	.836 **	.914 **	-.358 ns
	All	25	.879 **	.937 **	.887 **	.778 **	.309 ns
SC	15	7	.973 **	.952 **	.884 **	.707 ns	–
	30	13	.561 *	.511 ns	.605 *	-.284 ns	–
	50	15	.953 **	.918 **	.883 **	.130 ns	–
	80	17	.924 **	.795 **	.579 *	.802 **	–
	All	52	.967 **	.620 **	.957 **	.311 *	–
PL	30	10–13	.588 *	.909 **	.259 ns	.814 **	–
	50	14–17	.412 ns	.370 ns	.536 *	-.545 *	–
	80	19–22	.946 **	.854 **	.649 **	-.073 ns	–
	All	43–52	.826 **	.690 **	.816 **	-.166 ns	–
DR	80	26–29	.869 **	.563 **	.364 ns	.295 ns	–

*, ** Significant at 5% and 1% level, respectively; ns: not significant

D. Conclusions

Substantial amounts of cations (when added or available in high amount) were transported through fast macropore flow but bypassed the suction cups. Installation of resin capsules at depths of 15 and 50cm (10 capsules per 135m² plot) allowed the adsorption of representative amounts of cations transported through macropore flow. Increased drainage and soil moisture content improved the adsorption of cations and phosphorus on the resin capsules.

VI. GENERAL DISCUSSION

A. Measurement of Nutrient Availability

Nutrient availability has been defined in a variety of ways[4]. The term includes forms of nutrients that are close or can move to plant roots for absorption[8,2,45,40], which is the theoretical basis for the use of resin capsules in assessing soil nutrient availability. The resin capsule acts as a sink for nutrients simulat-

ing a plant root[38,49]. The quantity of adsorbed nutrient will relate to both 1) the soil solution concentration at initiation of the extraction or adsorption (this factor relates closely to mass-flow delivery of nutrients to plant roots as well as to the diffusion gradient which will be developed) and 2) the diffusion rate of nutrient through the soil (the process which is most rate-limiting for many nutrients). The resin capsule method provides a universal extraction of ions allowing simultaneous determination over a broad range of nutrients or solutes.

Results of the laboratory incubation study showed that adsorption of P and K on resin capsules are much lower under unsaturated (UNSAT) than saturated (SAT) soil conditions due to the effect of soil moisture on diffusion. Soils with the same P concentrations according to the Bray II method but of different texture (proportion of sand, silt, and clay particles) had different contents of resin P due to the effect of texture on diffusion.

Under UNSAT conditions, and with the amount of soil used for incubation (50 g) as a basis for comparison, the amount of resin N (predominantly NO_3^-) after 28d was comparable to that of KCl-extractable N in SiL after 7d of soil incubation. In the case of SL, however, the content of resin N was only 50-60% that of KCl-extractable N, suggesting a faster diffusion or transport of N to plant roots in the finer-textured soil. Under SAT, the transport of N, primarily as NH_4^+, to the resin was faster and more efficient in SL than in SiL.

The power function, $RAQ_i = a_i t^{b_i}$, described well the release kinetics of N, P, and K from soil to resin in two soils of different texture and origin under SAT conditions and N and K under UNSAT conditions. The release kinetics of P under UNSAT also fit the power function in SiL soil but not in SL soil. The adsorption of P at UNSAT was very low in SL soil even after 28 days. High estimates of b_P under SAT corresponded with the high Bray II P values of both SiL and SL soils (Fig. 4, Table 1). But, a_P was higher in SiL than in SL, indicating a greater supply of readily available P in SiL despite the similarity of Bray II P values of both soils. The coefficient a_K (indicator of the readily available K) conformed to the amounts of NH_4OAc-extractable K, where it was higher in the SiL soil than in the SL. The b_K values of the two soils were both high, probably due to the same content of organic C and clay in both.

The cumulative RAQ_N ($NH_4^+ + NO_3^-$) after 28d in both soils were identical, which agreed with the similar amounts of total N as well as organic C. However, the shapes (determined by the coefficients a_N, b_N) of the kinetic curves differed somewhat, probably due to the different patterns of mineralization between a volcanic ash soil (SL) and an alluvial soil (SiL).

B. Detection of Solute Transport

Methods employed for measuring solute transport in soils may vary or yield different results depending on the characteristics of the soil (e.g., texture and structure), which determine the nature of water flow, and the kind of target

solute.

a. Nitrate leaching

In a clayey Gray Lowland soil grown to onion that received 322 kg N/ha, applied only at the start of the growing season, topsoil solutions collected with SC had higher concentrations of NO_3^- than the PL-collected samples (Fig. 8).   At a depth of 80cm, however, concentrations of NO_3^- were higher in the DR and PL samples than in the SC samples, and nitrate concentrations in DR and PL fluctuated with drainage, while those in SC samples showed a decreasing trend with time. Such results suggest that bypass or macropore flow was the primary means of NO_3^- transport to subsurface drainage or groundwater (Fig. 19), while solutions collected by SC for the most part were representative of those inside soil aggregates (Fig. 20).   The suction cups may have been bypassed by water flowing
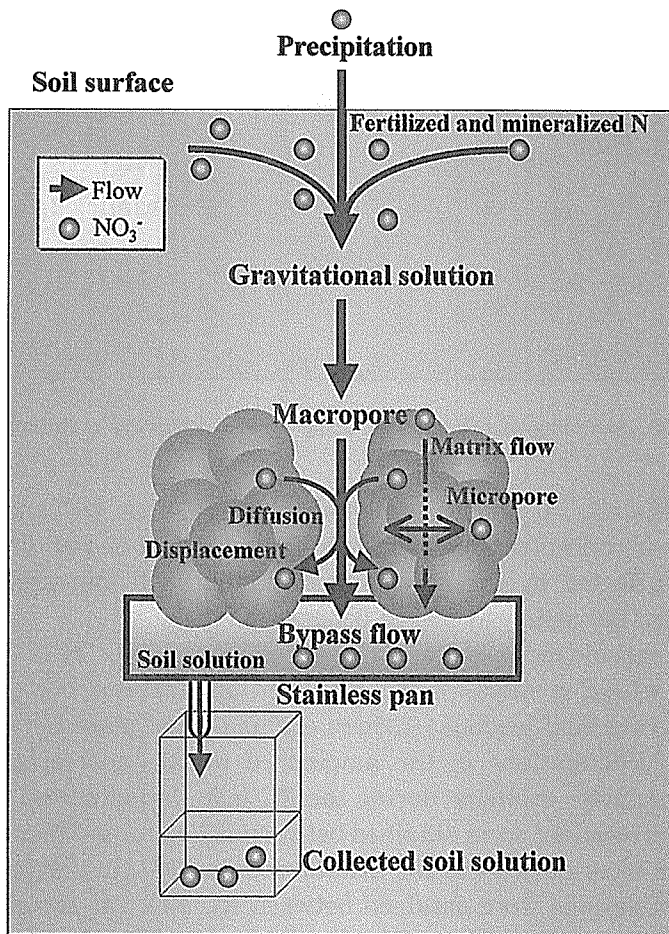

Fig. 19. Mechanism of water flow and sample collection using a pan lysimeter.
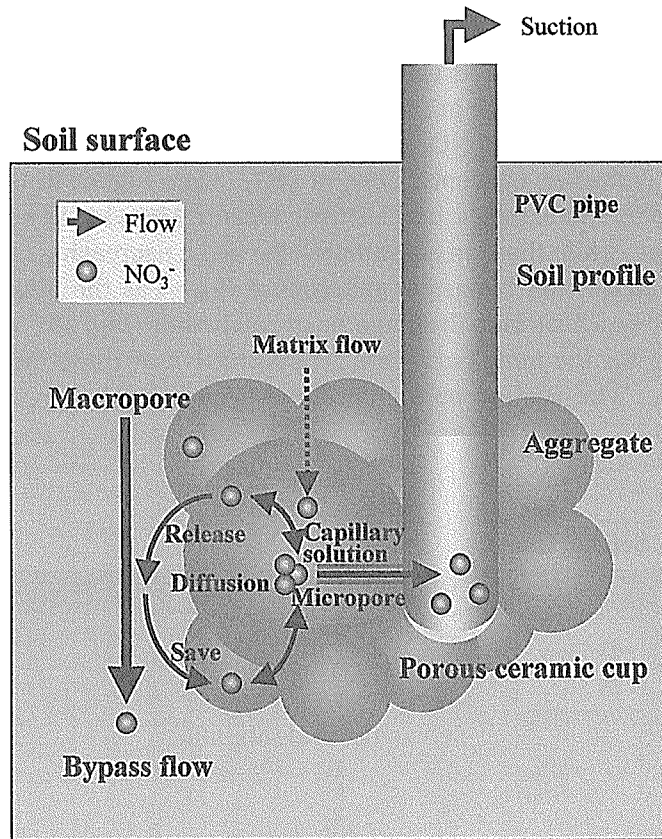
Fig. 20. Sampling of soil solution using a suction (porous ceramic) cup.

through macropores. It should be noted, however, that DR and PL at 80cm yielded different concentrations of nitrate probably due to the difference in the area covered/affected by the two methods. The total pan area for PL was 0.24m² while the DR area was 0.95ha (Chapter IV-B).

The resin capsule method showed higher values of NO_3^- at 15- than at 50-cm initially (i.e., within a month after fertilizer application) but the trend was reversed after sufficient leaching (235mm drainage) and plant uptake (100 kg N/ ha) (Fig. 10). Fluctuations in the amount of nitrate corresponded with the amount of cumulative drainage during the RC installation period.

Positive correlations were obtained between RC NO_3^- and the mean DR NO_3^- or PL NO_3^- at 80cm during the RC installation period. In particular, high and significant correlations were obtained between RC NO_3^- at 15cm and the mean DR NO_3^- and between RC NO_3^- at 50cm and the mean PL NO_3^- at 80cm (Fig. 11). These relationships indicate that the resin capsules were able to intercept continuously a representative amount of the nitrate moving through macropore flow
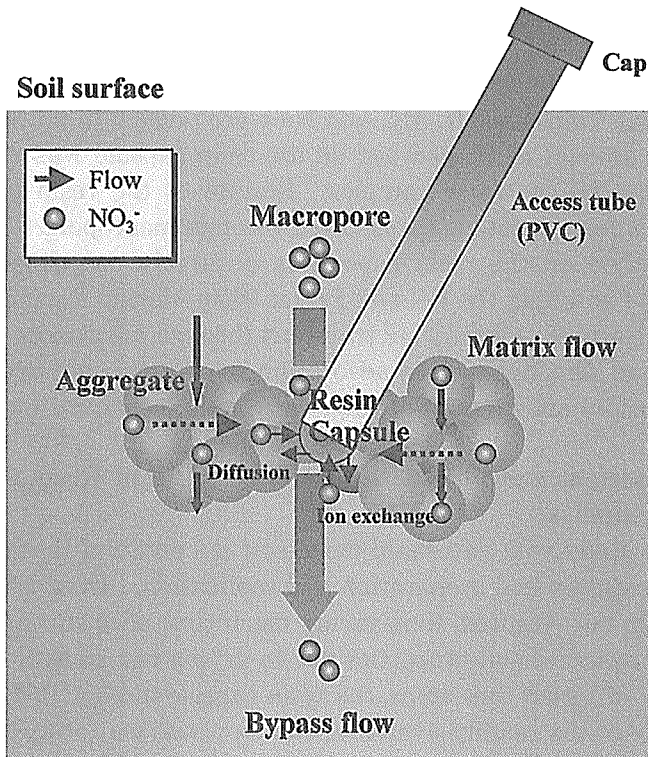
Fig. 21. The use of resin capsule for detecting solute transport under field
conditions.

(Fig. 21).   Adsorption of ions or solutes on the resin capsule is determined both
by diffusion and mass flow (solute that comes in contact with the capsule through
water flow).   Results of this study indicate that where the target solute was a
mobile ion (nitrate) and macropore flow predominant, macropore flow rather
than matrix flow (or diffusion) primarily affected the amount of nitrate adsorbed
on the resin capsule.

b. Leaching of cations and phosphorus

Ca and K in the soil solution (Figs. 13 and 14) exhibited similar trends with
NO_3 where concentrations of the solutes decreased with soil depth, both for SC
and PL, although the concentration of K was much lower than NO_3 and Ca.   The
higher concentrations of K and Ca in the DR and PL from 80cm samples over the
SC samples at the same depth (Fig. 15) indicated transport of these solutes
through macropore flow.   Mg and Na showed different patterns from those of K
and Ca, and differences between the methods of water sampling were not clear.

The resin capsule method showed a temporal variation of Ca, K, and Mg (Fig.
17) similar to that of NO_3, where initial values were higher at 15- than at 50cm
until sufficient leaching (235mm drainage) and plant uptake (i.e., end of July, Fig.

16). However, Na showed a consistently higher value in subsoil while P was always higher in topsoil (Fig. 17). The amount of solutes adsorbed on the resin capsule corresponded to concentrations of solutes in water samples, where Ca and NO_3 showed high values but K, Mg, and Na were present in much lower concentrations. The amount of P adsorbed on the resin capsule was very low ($\leq$ 0.1 mg/capsule) and nil in water samples. Results of the resin capsule method indicated that when a solute is transported through macropore flow, the amount of solute adsorbed on the resin capsule is positively correlated to the mean concentration of solute in the DR and PL (at 80cm) during the capsule's installation period. However, when solute transport through macropore flow is limited, the main factors affecting solute adsorption on the capsule are soil moisture (effect on diffusion) and content of the solute in the soil itself (nutrient pools).

C. Recommendations and Considerations on the Use of Resin Capsules
a. Laboratory studies

Incubation study with saturated paste soil (a condition that allows uniform ion diffusion) requires less preparation and replication. Drying and grinding of soil samples are not required, thus saving much time spent for soil preparation. Moreover, alteration of soil properties due to drying can be avoided. If the test is conducted at different time steps, the resin capsule method is dynamic, providing an estimate of the readily available and slow-release forms of nutrients[13,36]. The resin capsule is very easy to use and variability of results is low when used with homogenized saturated soils[14].

The effect of moisture is very important when measurement is conducted under unsaturated conditions, and texture is an important consideration when comparing different soils. Soil sampling strategy (time of sampling, depths, subsampling, and bulking) must be defined according to the objectives of the study.

b. Field studies

For field studies, the RC method has exhibited the following advantages:
1) Monitoring of solutes at the same point in the field is possible (by means of access tubes).
2) Fluxes of ions are detected (in contrast to destructive soil sampling or using suction cups where sampling is not continuous).
3) Water flows through the capsule as it flows through the soil (without distorting the flow field) because of the macropores between resin beads.

Important considerations and precautions are to be taken, however, such as the following:
1) Large numbers of replication are required due to high variability under field conditions. However, this problem is not unique to the resin capsule but is also true of suction cups. Even pan lysimeters need to be replicated and a large pan area is desirable for allowing collection of a representative amount

of solute.

2) The resin capsule is very sensitive to moisture content. Depending on the objective of the study, a more frequent monitoring of soil moisture and drainage (e.g. use of a data logger) may be necessary for the interpretation of results.

3) Immediate washing (within a few hours) of the capsules is necessary after removing from the soil. When conducting experiments in fields very far from the laboratory, deionized water (for washing capsules) should be brought to the experimental site.

4) Access tubes should be installed or fixed while the soil is soft (moist, soon after crop is established) in order to avoid the formation of cracks in the soil or channeling of water flow around the tube. The access tube should be installed at about a 30° angle from the vertical line to avoid interference with vertical flow at the point of sampling[21].

5) Resin capsule to soil contact must be ensured (feel method) during installation.

6) The resin capsule may be very expensive if only one element is to be considered. Since a range of multiple elements can be simultaneously extracted, the cost may turn out to be reasonable, however.

VII. SUMMARY AND CONCLUSIONS

Assessment of nutrient availability in soils is important for enhancing crop growth and providing efficient management of agricultural resources. Likewise, detection of transport or leaching of agricultural chemicals is necessary for improving crop production, but its impact on the quality of surface water or groundwater (i.e., possible pollution) is of utmost consideration.

The resin capsule (RC) has a spherical shape (2-cm diameter) and consists of equal amounts of cation (H^+) and anion (OH^-) exchange resins with a 2.2mmol$_c$ of cation + anion exchange capacity. The use of RC for measuring nutrient availability and solute transport is unconventional, but previous studies have shown its usefulness for such measurements. In addition, problems associated with conventional methods are common. Thus, I compared the use of RC with the conventional methods of measuring soil P, K, and N, considering the effect of soil moisture and texture. I also compared the use of RC with the conventional methods of monitoring solute (nitrate, basic cations, and phosphorus) transport under field conditions in a clayey soil cultivated with onion.

A. Measurement of Nutrient Availability
a. Effect of soil moisture and texture on P, K, and N measurements

A laboratory incubation study was conducted using sieved (<2mm) sandy loam (SL) and silt loam (SiL) soils collected from the plow layer of two upland fields in Hokkaido, Japan. The contents of P, K, and N in saturated (SAT,

gravimetric water content = 0.65 kg kg^{-1}) and unsaturated (UNSAT, 0.32 kg kg^{-1}) soils were measured using conventional soil tests and resin capsules. Soils with RC were incubated at four time steps (1, 7, 14, and 28d), while soils without RC (for conventional tests) were incubated for only 7d, both at 25°C. N was added at 0, 10, 20, 40, and 60 mg kg soil^{-1}. P and K were determined using conventional methods from 7d incubated soils only.

The amounts of RC-adsorbed P (RC P) and K (RC K) were significantly less under UNSAT than under SAT conditions. The two soils had the same P content according to the Bray II method but RC P was much lower in SL than in SiL. The difference in RC P indicated a negative effect of the coarse texture on P diffusion, while the difference between the two methods reflected a difference in the chemical characteristics of the reagents used. Under UNSAT conditions, the amount of RC-adsorbed N (RC N, predominantly NO$_3^-$) was greater in SiL than in SL, suggesting a faster diffusion or transport of N to plant roots in the finer-textured soil. Under SAT conditions, however, the transport of N (mostly NH$_4^+$) to the resin was faster in SL than in SiL. Correlations between RC N and KCl-extractable N were high, especially after 14 and 28 d of RC incubation.

b. Release kinetics of P, K, and N

Using the RC data of the +0N treatment only (of the above incubation study) at different time steps, I analyzed the release kinetics of P, K, and N from the two soils. The power function, $RAQ_i = a_i t^{b_i}$, described well the release kinetics of P, K, and N in the two soils under SAT conditions and N and K under UNSAT conditions. Resin adsorption quantity (RAQ) is the amount of nutrient i adsorbed per unit surface area of RC at time t, and a and b are the rate coefficients used to describe the adsorption kinetics of the ion on RC. For P, high estimates of b_P were obtained under SAT conditions in both soils, suggesting that their P-supplying capacity was high. However, a low value of a_P was obtained in SL, indicating the presence of a small amount of readily available P in this soil. Kinetics of RC K showed the presence of a high amount of readily available K in SiL but a low amount in SL, in conformity with the amounts of NH$_4$OAc -extractable K in the two soils. RC N (NH$_4^+$ + NO$_3^-$) kinetics showed comparatively high RAQ$_N$ and b_N values between SiL under UNSAT conditions and SL under SAT conditions, indicating a similarity in the N-supplying capacity of the two soils, although transport and loss of N were determined by moisture and texture.

B. Monitoring Solute Transport

The fluxes of NO$_3^-$ measured in the subsurface drainage and pan lysimeter samples collected at groundwater level (80-cm depth) reflected that NO$_3^-$ was leached or transported to the subsurface drainage or groundwater of a clayey soil primarily through macropore or bypass flow. Similarly, results of the pan lysimeter and subsurface drainage methods showed that a substantial amount of

cations (Ca^{2+}, Mg^{2+}, K^+, Na^+), when added or available in high amounts, were transported through macropore flow.   Fluxes of solutes indicating macropore or bypass flow, however, were not reflected in the samples collected with suction cups.   On the other hand, the amount of solutes (NO_3^- and cations) adsorbed on RC (10 capsules/135 m²) installed at 15- and 50-cm depths reflected concentrations of solutes transported through macropore or bypass flow to the groundwater level.

C. Conclusions

The resin capsule is sensitive to factors (e.g., soil moisture, texture) affecting diffusion or transport of nutrients to plant roots, suggesting its usefulness for estimating plant-available nutrients.   Further research is necessary, however, for the purpose of standardizing its use in upland conditions.   The resin capsule can be used for detecting or monitoring solute transport via macropore or bypass flow.

Acknowledgments

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