Mobility of Nitrate and Phosphate through Small Lysimeter with Three Physico-chemically Different Soils

Kyung-Hwa Han,* Hee-Myong Ro¹, Hyun-Jun Cho, Lee-Yul Kim, Seon-Woong Hwang, Hee-Rae Cho, and Kwan-Cheol Song

Small lysimeter experiment under rain shelter plastic film house was conducted to investigate the effect of soil characteristics on the leaching and soil solution concentration of nitrate and phosphate. Three soils were obtained from different agricultural sites of Korea: Soil A (mesic family of Typic Dystrudepts), Soil B (mixed, mesic family of Typic Udifluvents), and Soil C (artificially disturbed soils under greenhouse). Organic-C contents were in the order of Soil C (32.4 g kg⁻¹) > Soil B (15.0 g kg⁻¹) > Soil A (8.1 g kg⁻¹). Inorganic-N concentration also differed significantly among soils, decreasing in the order of Soil B > Soil C > Soil A. Degree of P saturation (DPS) of Soil C was 178%, about three and fifteen times of Soil B (38%) and Soil A (6%). Prior to treatment, soils in lysimeters (dia. 300 mm, soil length 450 mm) were stabilized by repeated drying and wetting procedures for two weeks. After urea at 150 kg N ha⁻¹ and KH₂PO₄ at 100 kg P₂O₅ ha⁻¹ were applied on the surface of each soil, total volume of irrigation was 213 mm at seven occasions for 65 days. At 13, 25, 35, 37, and 65 days after treatment, soil solution was sampled using rhizosampler at 10, 20, and 30 cm depth and leachate was sampled by free drain out of lysimeter. The volume of leachate was the highest in Soil C, and followed by the order of Soils A and B, whereas the amount of leached nitrate had a reverse trend, i.e. Soil B > Soil A > Soil C. Soil A and B had a significant increase of the nitrate concentration of soil solution at depth of 10 cm after urea-N treatment, but Soil C did not. High nitrate mobility of Soil B, compared to other soils, is presumably due to relatively high clay content, which could induce high extraction of nitrate of soil matrix by anion exclusion effect and slow rate of water flow. Contrary to Soil B, high organic matter content of Soil C could be responsible for its low mobility of nitrate, inducing preferential flow by water-repellency and rapid immobilization of nitrate by a microbial community. Leached phosphate was detected in Soil C only, and continuously increased with increasing amount of leachate. The phosphate concentration of soil solution in Soil B was much lower than in Soil C, and Soil A was below detection limit (0.01mg L⁻¹), overall similar to the order of degree of P saturation of soils. Phosphate mobility, therefore, could be largely influenced by degree of P saturation of soils but connected with apparent leaching loss only more than any threshold of P accumulation.

Key words: Lysimeter, Nitrate, Phosphate

Introduction

The impact of horticultural and agricultural uses of nutrients on water quality generally starts as they leave the original point of application, i.e., through leaching or runoff, rather than the presence in soil (Pierzynski et al., 1994). Transport of non-point source pollutant such as nitrate in soils mostly accompanies water flow, and thereby solute forms have high migration potential to water system. Most solutes such as phosphate, however, are generally reactive in the unsaturated soil/plant root system, due to interactions with the solid phase and soil biota, and the interaction with solutes. Especially, the soil matrix, by retaining and releasing solutes, has a buffering mechanism that attenuates “short term” fluctuations in the solute concentration at the soil boundaries (van der Zee and Destouni, 1992). Besides, the occurrence of preferential flow of water and solutes, and apparent “protection” of solute inside aggregate from leaching (White et al., 1998) add more complexity in transport of non-point source (NPS) pollutants.
The dominant soluble forms of soil nitrogen and phosphorus are generally nitrate and phosphate. Excess nitrate in drinking water is a threat to human health, related to methemoglobinemia, and phosphate is responsible for eutrophication of surface water. Our question is whether the nitrate and phosphate enriched in soil may transport out of the rhizosphere or not and how much, if transports. First of all, the highest potential risk of nitrate and phosphate on water quality could be generated from a situation with no plant uptake. In this case, soil would interact with environmental factors such as precipitation and temperature. In this study, thus, lysimeter experiment without plant was conducted to investigate the effect of soil characteristics on mobility of nitrate and phosphate.

Materials and Methods

Lysimeter experiment was performed under rain shelter plastic film house. Figure 1 showed schematic view of lysimeter setup.

The characteristics of soils For lysimeter experiment, surface soil (0-20 cm) was sampled from three cultivated soil types; Soil A (mesic family of Typic Dystrudepts), Soil B (mixed, mesic family of Typic Udifluvents), and Soil C (artificially disturbed soils). Soils A and B have been cultivated for at least 50 years under upland conditions, while Soil C with intensive horticultural cultivation more than three times cropping per year for about 10 years under plastic-film house conditions. Due to steep topography, Soil A was susceptible to water erosion, which causes losses of soil particles and nutrients. Physico-chemical properties of the soils are given in Table 1. Organic-C contents were in the order of Soil C (32.4 g kg\(^{-1}\)) > Soil B (15.0 g kg\(^{-1}\)) > Soil A (8.1 g kg\(^{-1}\)). Inorganic-N concentration also differed significantly among soils, decreasing in the order of Soil B > Soil C > Soil A. Degree of P saturation (DPS) of Soil C was 178%, about three and fifteen times of Soil B (38%) and Soil A (6%).

<table>
<thead>
<tr>
<th>Soil A</th>
<th>Soil B</th>
<th>Soil C</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (1:1)</td>
<td>4.97</td>
<td>5.04</td>
</tr>
<tr>
<td>Organic C (g kg(^{-1}))</td>
<td>8.1</td>
<td>15.0</td>
</tr>
<tr>
<td>Total N (g kg(^{-1}))</td>
<td>0.58</td>
<td>1.33</td>
</tr>
<tr>
<td>C/N ratio</td>
<td>14.1</td>
<td>11.3</td>
</tr>
<tr>
<td>Total P (g kg(^{-1}))</td>
<td>0.24</td>
<td>0.51</td>
</tr>
<tr>
<td>C/P ratio</td>
<td>33.8</td>
<td>29.4</td>
</tr>
<tr>
<td>CEC (cmol kg(^{-1}))</td>
<td>7.5</td>
<td>11.2</td>
</tr>
<tr>
<td>Mineral N (mg kg(^{-1}))</td>
<td>NH_4(^+)-N</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>NO_3(^-)-N</td>
<td>5.0</td>
</tr>
<tr>
<td>Degree of P saturation (%)</td>
<td>5.7</td>
<td>37.6</td>
</tr>
</tbody>
</table>

Table 1. The physico-chemical properties of soils used.

Yielding small lysimeter experiment, six plastic lysimeters (three soils, two replicate) of internal diameter 300mm and depth 500 mm were packed with sea sand to 5 mm from the bottom, and then with air-dried and sieved soil (< 2 mm) to 450 mm from the top of sea sand. To ensure uniform packing, the lysimeters were packed in increments of 100 mm. For stabilizing soil and water flow, drain after saturation was
performed repeatedly for two weeks. Upper 50 mm soil was incorporated with urea 150 kg N ha\(^{-1}\) (2.27 g) and KH\(_2\)PO\(_4\) 100 kg P\(_{2}\)O\(_5\) ha\(^{-1}\) (1.35 g).

Time Domain Reflectometry (TRASE, Soil moisture corp., USA) was used to measure the soil’s volumetric water content. Rhizosampler, small soil solution sampler, was used to sample soil solution. Three-rod TDR probe (2 mm in diameter and 200 mm long) and rhizosampler (2 mm in diameter and 50 mm or 100 mm long) were installed horizontally into the lysimeters at the depth of 100, 200, and 300 mm from soil surface. Soil temperature sensors were installed at the depth of 100 and 300 mm from soil surface. TDR and soil temperature measurements were made daily.

0.001 N CaCl\(_2\) solution was used as water supply source and curved array of tube having very small holes was used for water supply. Soil solution was sampled using 10 mL syringe by connecting with rhizosampler and leachate using hand vacuum pump.

Hydraulic properties At the termination of the experiment, the hydraulic properties of the soil were measured. Retention curves were measured using intact soil samples, 50 mm in diameter and 30 mm height. Pore water pressures from -30 cm to -1000 cm were measured using pressure plate equipment. Mean pore diameter (dp, \(\mu\)m) at a given soil water tension was estimated from water-retention using the following equation (Danielson and Sutherland, 1986):

\[
d_p = \frac{\sigma}{\rho_w} \times 10^{5}
\]

where \(\sigma\) is surface tension of water (0.0724 J m\(^{-2}\) at 25 \(^\circ\)C), \(\rho_w\) is density of water (1 Mg m\(^{-3}\)), \(g\) is gravitational acceleration (9.8 N kg\(^{-1}\)), and \(h\) is the soil water tension expressed in cm of water.

Chemical analyses Nitrate and phosphate in sampled solution were measured by Ion chromatography (Dionex, USA). pH was measured with a pH meter (DMP 200, DMS, Korea).

Degree of P saturation was calculated using 0.02M acidified ammonium oxalate-extractable Fe, Al and P (i.e., Fe\(_{oa}\), Al\(_{oa}\), and P\(_{oa}\)), analyzed with ICP (Shimazu, Japan). The calculation equation is DPS= P\(_{oa}\)/PSC x100, where PSC is 0.5x(Al\(_{oa}\) + Fe\(_{oa}\)) (mmol kg\(^{-1}\)).

Results and Discussion

Soil water content during experiment period (Fig. 2) varied with seven times water application of which total amount was 213 mm. During initial ten days after treatment, the soil water content close to or lower than field capacity maintained, which reflected aerobic condition in three soils. In this condition, urea hydrolysis and subsequently nitrification could occur actively. Over the period, Soil C had higher soil water content than other soil, presumably due to the highest total porosity and high organic matter content. Meanwhile, pore size distribution of Soil C was similar to Soil A (Fig. 4). Macroporosity larger than 50 \(\mu\)m was the highest in Soil A, and decreased in the order of Soil C and Soil B (Fig. 4).

Soil temperature at PM 4:00 was not significantly different between three soils (Fig. 3). The differences of soil temperature between soil depth 10cm and 30 cm were 0–4 \(^\circ\)C, depending on atmosphere temperature. At morning time, the soil temperature at depth of 30 cm was 0–4 \(^\circ\)C higher than at depth of 10cm. Maximum daily differences of soil temperature were about 5 \(^\circ\)C and 2 \(^\circ\)C at
depth of 10 cm and 30 cm, respectively. Figure 5 showed soluble nitrate-N content per soil volume. During experiment period, NO$_3^-$-N content sampled with soil solution sampler was a range of 10~120 mg L$^{-1}$, 42~167 mg L$^{-1}$, and 16~86 mg L$^{-1}$ in Soils A, B and C, respectively. At 25 days after treatment, significant increase of soluble NO$_3^-$-N content at 10 cm depth was observed in Soils A and B but not in Soil C.

All three soils had large decrease of soluble NO$_3^-$-N content at 10 cm depth but it increased at 20 cm and 30 cm depth at final sampling. This means that surface-applied urea hydrolyzed and nitrified and then

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Fig. 4. Soil water retention curves and pore size distribution of three lysimeter soils. SA, SB, and SC indicate Soils A, B, and C, respectively. Bare means no plant on the soil surface.

Fig. 5. Changes in soluble nitrate-N content per soil volume during the experimental period. Values are the means of triplications. Horizontal bars indicate standard deviations of the means.

Fig. 6. Changes in soluble phosphate-P content per soil volume during the experimental period. Values are the means of triplications. Horizontal bars indicate standard deviations of the means.

Fig. 7. Cumulative leached nitrate-N and phosphate-P during the experimental period. SA, SB, and SC indicate Soils A, B, and C, respectively.
transferred vertically.

The concentrations of the soluble phosphate-P content sampled by soil solution sampler (Fig. 6) were 0.05–0.3 mg L\(^{-1}\) and 0.4–1.0 mg L\(^{-1}\) in Soils B and C, respectively, and not detected in Soil A. Contrasting to NO\(_3^-\)-N, phosphate-P content profile did not represent the transport of applied P but rather had a decreasing trend over time.

Vertical water outflow was the highest in Soil C and decreased in the order of Soils A and B, while nitrate-N leaching was the opposite (Fig. 7). Unlike nitrate, phosphate leaching was observed at Soil C only, but not detected in other soils.

Nitrate leaching mass in small lysimeter of three physico-chemically different soils, Soil B > Soil A > Soil C, was inverse to the amount of water leachate, Soil C > Soil A > Soil B. Although nitrate concentration of soil profile for Soil C was high, nitrate leaching did not occur until 35 days after treatment. This was probably due to physical protection of nitrate in Soil C with highest organic matter content. Wallis and Horne (1992) reported that organic coating of soil matrix could cause soil water repellency. In water-repellant soil, preferential flow readily occurs and the solute in immobile region rarely transports (Beven and Germann, 1992; Chen and Wagenet, 1992; White, 1985). Besides, Evans et al. (2008) suggested that wet-deposited nitrate could be rapidly immobilized by microbial communities present on the surfaces of preferential paths in upland organic soils. Contrasting to nitrate, phosphate leaching in Soil C was positively correlated with water outflow, continuously from initial experimental time. Once P saturates in soil, P leaching may occur continuously for several decades (Beauchemin et al., 1996; Heckrath et al., 1995). In fact, larger application rates of mineral P fertilizer did not necessarily result in greater leaching losses (Leinweber and Meissener, 1999) as shown in Soils A and B. The leaching losses were probably due to high DPS of Soil C.

Why did not P protection in Soil C occur, although the concentration of phosphate in soil solution was lower rather than that of nitrate? To answer this question, we could think that the biochemical reactivity of P in soil is mainly controlled by mineral pool whereas that of N by organic pool (Pierzynski et al., 1994). Macroaggregate formation and subsequently physical protection are generally related to organic matter and soil microbial activity (Denef et al., 2001). Unlike nitrate leaching, therefore, P leaching in Soil C may be rarely regressed despite of high organic matter content.

For Soil B, the amount of nitrate leaching was the highest probably due to highest concentration in soil solution and anion exclusion. Figure 8 showed the relationship between water extractable and 2M KCl extractable nitrate-N. High salt extracting agent such as 2M KCl solution makes diffuse double-layer thin, whereas distilled water is the opposite (Sposito, 1989). In other words, anion exclusion effect by the negative charge of clay surface may be negligible in 2M KCl extraction, but not negligible in distilled water extraction. For Soil B, water extractable nitrate-N was 1.27 times higher than 2M KCl extractable nitrate-N, presumably

Fig. 8. The relationship between water and 2M KCl extractable nitrate-N in three soils.
due to anion exclusion effect. For Soil A, however, the difference of nitrate concentration between the two extractions was not observed. Unlike Soil A and B, nitrate-N of the water extraction in Soil C was slightly lower than that of 2M KCl extraction. Besides, slow rate of water flow could result in an increase of residence time of water and subsequently enhance the extraction of solute by incoming water (Wagenet and Chen, 1998).

**Conclusion**

In this research, Soil B with to relatively high clay content, compared to other soils, had high nitrate mobility, because clay could induce the high extraction of nitrate of soil matrix by anion exclusion effect and slow rate of water flow. Contrary to Soil B, high organic matter content of Soil C could be responsible for its low mobility of nitrate, inducing preferential flow by water-repellency and rapid immobilization of nitrate by a microbial community. Leached phosphate was detected in Soil C with highest DPS of three soils, and the phosphate concentration of soil solution was same to the order of degree of P saturation of soils. Phosphate mobility, therefore, could be largely influenced by degree of P saturation of soils but connect with apparent leaching loss only more than any threshold of P accumulation.

**References**

소형 라이시메터시험을 통한 토양특성에 따른 질산과 인산의 이동성 비교

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질산과 인산의 수치이동성에 대한 토양특성의 영향을 규명하고자 비가림 하우스에서 소형라이시메터(저금 300 mm, 토양깊이 450 mm) 시험을 수행하였다. 대상토양은 농경지 세 지점으로부터 표토 0~20cm를 채취한 후
이 토양의 풍건체토분획을 이용하여 수행하였다: mesic family of Typic Dystrudepts (토양 A, 사양토, 유기물
함량 1.4%): mixed, mesic family of Typic Udifluvents (토양 B, 양토, 유기물함량 2.6%): 시설채배토양(토양
C, 사양토, 유기물함량 5.6%). 2주 동안 안정화시험 토양의 표면에 질소와 인을 150 kg urea-N ha⁻¹ 과 100 kg
NH₄PO₄-P₂O₅ ha⁻¹ 만큼 처리하고, 65일 동안 7번 관수(총관수량 213 mm, 약 1 pore volume)하며 주기적으로
짐이 10, 20, 30 cm의 토양용액과 용탈액을 채취하여 점검과 인산농도를 분석하였다. 총 용탈액량은 토양 C >
토양 A > 토양 B 순으로 질산 용탈량. 토양 B > 토양 A > 토양 C과 역의 관계를 가졌다. 토양 A와 B에서는
요소처리 후 집이 10 cm에서 토양용액 중 질산 농도 증가가 두렷이 나타나지 않았으나, 토양 C에서는 나타나지 않았
다. 토양 B의 높은 점산이동성은 상대적으로 높은 점토함량으로 움직인 측으로의 음이온배치와 누런 수분호
흡으로 물의 흡착물질이 깊이 토양베트릭스 점산의 추출을 촉진하기 때문으로 볼 수 있었다. 반면 토양 C는 점산의 이동성이 낮게 나타났다. 이는 유기물 함량이 높아 생기는 복수성으로 선탁류와 질산의 이동을 부동화
때문으로 주로 하였다는 점에 있었다. 인산용량은 질산과 달리 인포화도가 가장 높은 토양 C에서만 검출되었다. 토양용
액 중 인산농도는 인포화도의 순서와 동일하게 토양 C > 토양 B의 순서였고 토양 A에서는 검출되지 않았다.
따라서 인산의 이동성은 인포화도에 의해 크게 영향을 받으며, 일정 수준으로 축적될 때 까지는 용달손실은 나
타나지 않는다고 판단할 수 있었다.