

## Release Pattern of Urea from Metal-urea-clay Hybrid with Montmorillonite and Its Impact on Soil Property

Kwang Seop Kim, Choong Lyeal Choi, Dong Hoon Lee, Young Jin Seo<sup>†</sup>, and Man Park\*

Soil Science Laboratory, College of Agriculture and Life Sciences, Kyungpook National University, Daegu 702-701, Korea, <sup>†</sup>Gyeongsangbukdo Agricultural Research and Extension Services, Daegu 702-708, Korea

Urea intercalated into montmorillonite (MT) exhibits remarkably enhanced N use efficiency, maintaining its fast effectiveness. This study dealt with the release property of urea from metal-urea-clay hybrid with MT (MUCH) under continuous-flow conditions and the cumulative impacts of its successive application on physicochemical properties of soils. Releases of urea were completed within 4 hrs under continuous-flow condition regardless of the types and the leaching solutions. However, urea release property was significantly affected by both the form of fertilizer and the presence of electrolytes in solution. The fast release property of urea from MUCH in continuous-flow condition was not significantly affected by soil properties such as soil pH and soil texture. In addition, its successive application did not lead to any noticeable change in soil physicochemical properties, water stable aggregate rate, water holding capacity and cation exchange capacity in both sandy loam and clay loam soils. Therefore, this study strongly supported that urea intercalated into MT could be applied as fast-effective N fertilizer, in particular for additional N supply.

**Key words:** N use efficiency, Urea intercalation, Montmorillonite, Release pattern, Soil property

### Introduction

Urea as the N nutrient source for crop is one of the most preferred fertilizer in agriculture worldwide because it has attractive merits such as peerless fast effectiveness, high N concentration, cheapness and easy handling (Purakayastha and Katyal, 1998). However its use efficiency is very low to be estimated less than 30-40% (Dobermann and Cassman, 2002). Such low efficiency has led to economic losses and environmental detriments such as water eutrophication, soil acidification and greenhouse gas emission (Lea et al., 2006; Sanz-Cobena et al., 2008; Cissé and Vlek, 2003). To increase its use efficiency, many researchers have focused on the development of modified ureas like condensed urea, urea-aldehyde and coated- or encapsulated urea (Liang and Liu, 2006; Tong et al., 2009). Although they showed the noticeable improvement in urea use efficiency, it is still difficult to meet with N nutrient demand of crops throughout growth stages (Gruber and Galloway 2008; Kim and Dale 2008). Furthermore, they have the high

manufacture cost and ambiguousness about soil compatibility (Park et al., 2004; Tong et al., 2009). Therefore, it has been strongly demanded to develop the alternative fertilizers that exhibit both fast effectiveness and urea use efficiency.

We suggested that urea could be intercalated into layered clay minerals in the form of metal-urea ligand complex (Park et al., 2004). Recently, we showed that 'metal-urea-clay hybrid with MT (hereafter referred to as MUCH)' could be massively prepared by simply mixing Ca and/or Mg-urea complexes in molten state with the dehydrated MT (Park et al., 2004; Kim, 2010). It is also confirmed that MUCH broadcasted over soils led not only to remarkable enhancement of N uptake by crop plant but also to remarkable suppression of both NH<sub>3</sub> and NO<sub>x</sub> emissions (Kim, 2010). Distinct characteristics of MUCH are its fast effectiveness and protection of urea by the natural layered minerals against rapid loss of urea molecules, suggesting high possibility of MUCH application as a fast effective additional N fertilizer.

Soil structure may be affected by continuous application of MUCH mainly due to MT. MT significantly affects physicochemical qualities of soils such as soil aggregate distribution, water holding capacity (WHC) and cation

exchange capacity (CEC) (Bronick and Lal, 2005). Unfortunately, swelling clay minerals such as MT may disrupt aggregates during shrink-swell cycles due to its high dispersivity and expandability. MT moved into soil pores along with water flow can inhibit the vertical flow of water (Bronick and Lal, 2005; Lado and Ben-Hur, 2004). Thus input of a large amount of MT on soil may lead to deterioration of soil structure. Hence, impact on soil structure by successive input of MT must be evaluated as MT may be an important factor for aggregate stability. Therefore, we dealt with the release property of urea from MUCH under continuous-flow conditions and the cumulative effects of its succession application on physicochemical properties of soils.

## Materials and Methods

**Preparation of MUCH** Intercalation of metal-urea complex into MT was carried out in this study at a weight ratio of  $\text{Ca}_{0.7}/\text{Mg}_{0.3}$ -urea complex/MT of 1.0 (MUCH).  $\text{Ca}_{0.7}/\text{Mg}_{0.3}$ -urea complex was prepared by thermal treatment (at  $100 \pm 5^\circ\text{C}$ ) of a mixture of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  at molar ratio of 7 to 3. Particularly, this molar Ca/Mg ratio of 7/3 was used because many crops generally require similar ratio for healthy growth. As-synthesized MUCH lump was used for further experiment after a mild grinding (see photograph of the Fig 1). The basal spacing of MUCH

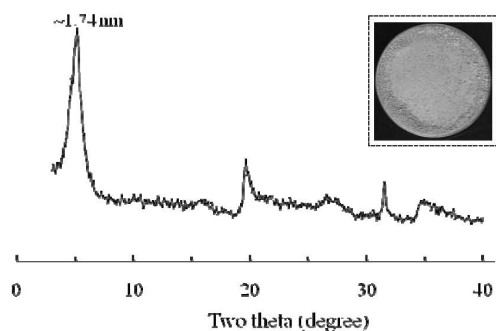


Fig. 1. XRD pattern and photo (dot-lined box) of MUCH used in this study.

estimated from  $001$  peak had a value of  $\sim 1.74$  nm as shown Fig. 1, showing that  $\text{Ca}_{0.7}/\text{Mg}_{0.3}$ -urea complex was successfully intercalated into the interlayer space of MT. As-synthesized MUCH was found to have a chemical composition of 54.0%  $\text{SiO}_2$ , 16.7%  $\text{Al}_2\text{O}_3$ , 3.4%  $\text{Fe}_2\text{O}_3$ , 5.8%  $\text{MgO}$ , 10.0%  $\text{CaO}$ , 0.3%  $\text{K}_2\text{O}$  and 9.8%  $\text{Cl}$  (dry weight basis). Its N content and CEC were evaluated to be about 19% and  $84.5 \text{ cmol}_c \text{ kg}^{-1}$ , respectively. All other chemicals used in this experiment were of analytical grade.

**Soil** The three soils with different textures were chosen for this study. Soil samples were air-dried and crushed to pass through a 2 mm sieve. The physicochemical properties are shown in Table 1.

**Flow system** The release properties of urea and  $\text{Ca}^{2+}$  without (A experiment) and with soil (B experiment), and the effects of MUCH on physicochemical property (C experiment) were investigated in a continuous flow system. Columns with one glass-filter end, 350 mm long with a diameter of 27 mm were used for A and B experiments and the ones with an open bottom, 120 mm long with a diameter of 40 mm for C experiment, respectively. The sample was deposited on filter papers (No. 5B) placed on certain level of cottons. In A experiment, 250 mg of MUCH and the mixture (103.9 mg urea + 15.5 mg  $\text{CaCl}_2$  + 5.6 mg  $\text{MgCl}_2$  + 125 mg MT) were loaded. While MUCH and the mixture were deposited on the filter paper at the rate of 87 mg urea per 20 g of soil in B experiment. C experiment involved a relatively higher application rate, 525 mg of MUCH per 40 g of soil, to evaluate a cumulative effect of its continuous application for 30 years by an usual recommendation rate. Two different solutions, deionized water (DW) and simulated soil solution (SS) were used as the leaching solutions to examine the release property of urea and  $\text{Ca}^{2+}$ . The SS consisted of 6 mM  $\text{MgCl}_2$  and 0.25 mM  $\text{KCl}$ , which was modified from the previous study (Park et al., 2005). The leaching solution was continuously

Table 1. Primary physicochemical properties of soil used in this study.

Soil	pH	Organic matter	Clay	Silt	Sand	CEC
	(1:5)	----- % -----	----- % -----	----- % -----	----- % -----	$\text{cmol}_c \text{ kg}^{-1}$
<sup>†</sup> SC-1	5.0	0.3	7.0	10.1	82.9	11.2
CL-1	5.5	0.9	23.0	43.5	33.5	12.4
CL-2	7.8	0.7	25.2	39.8	35.0	13.0

<sup>†</sup>Abbreviation: SL (Sandy loam), CL (Clay loam).

eluted through the column at a flow rate of  $\sim 2.2 \text{ mL min}^{-1}$  for A experiment,  $\sim 2.0 \text{ mL min}^{-1}$  for B and C experiments, respectively. The leachates were fractionated by every 20 mL aliquots. A and B experiments were conducted for 2 days, while C experiment prolonged for one month.

Urea and  $\text{Ca}^{2+}$  concentrations in the effluents were analyzed by a colorimetric method (U-2001, Hitachi Japan) and an inductively coupled plasma spectrophotometer (Perkin Elmer, Optima 3200RL, USA) respectively. The soil sample in the C experiment was air-dried and used to examine soil properties such as water-stable aggregates (WSA), CEC, and WHC. Aggregate size distribution was determined by a wet sieving method as described by Yoder (1936). CEC was determined with  $1 \text{ N NH}_4\text{NO}_3$  at pH 7.0, and WHC was measured by gravimetric method (Allen, 1989). X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Rigaku JP/D/MAX-2200H) using Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 30 mA at a scanning speed of  $5^\circ \text{ min}^{-1}$ . Chemical composition was obtained from an X-ray fluorescence spectrometer (XRF, Phillips PW2400).

## Results and Discussion

**Release property of urea and  $\text{Ca}^{2+}$  from MUCH** MUCH synthesized in this study involve two different forms of urea; The one is urea-metal complex and the other is free urea ( $\sim 13 \text{ wt}\%$ ) because urea-metal complex in this study was formed in excess presence of urea at a molar urea/metal cations ratio of 9.0 (Kim, 2010). A theoretical molar ratio between the metal cations and urea for complexation is calculated to be a value, 6.0 (Park et al., 2004). In MUCH, urea could be existed in different forms; Intercalated urea and metal-urea complex, external urea and urea-metal complex. XRD pattern of MUCH in Fig. 1 showed the presence of free urea at  $2\theta 31.6^\circ$  along with increased  $d_{001}$  space. This result indicated that urea-metal complexes were fully intercalated. The absence of XRD peaks assignable to the complex clearly shows that urea-metal complexes were fully intercalated in MT as cationic and neutral urea-metal complexes. Therefore, release of urea from MUCH could be affected by their types in the interlayer space. Release patterns of urea from MUCH and mixture by DW and SS were shown in Fig. 2. Releases of urea were completed within 4 hrs under continuous-flow condition regardless of the types and the leaching solutions. Release patterns are quite different

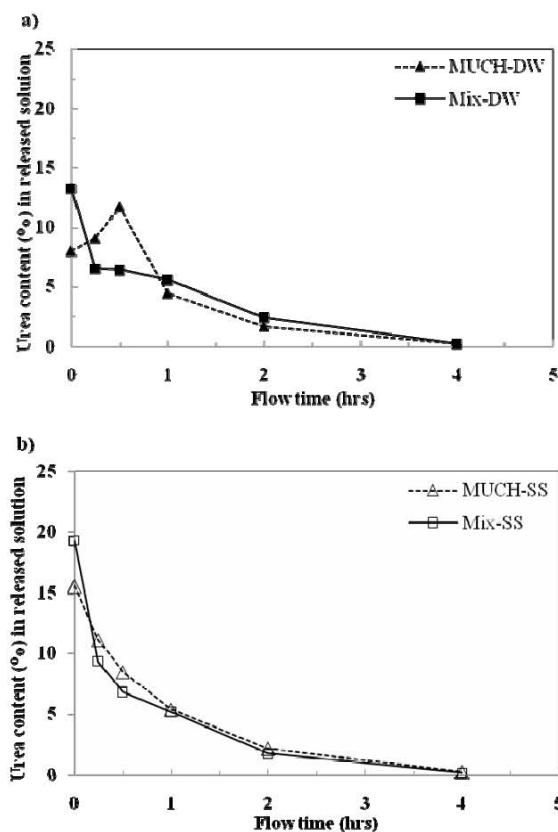


Fig. 2. Released urea content (%) from MUCH and urea-mixture by a) deionized water (DW) and b) simulated soil solution (SS) in continuous-flow system.

between MUCH and the mixture during 30 min. The highest urea release (11.6 wt%) from MUCH was observed at 30 min, whereas the mixture showed it at the initial time (Fig. 2a). These results clearly showed that release of intercalated urea was a little delayed mainly because of the time for the intercalated urea to be hydrated and diffused out of the interlayer space of MT. On the other hand, similar release pattern between MUCH and the mixture resulted from SS because the presence of electrolytes facilitated hydration and diffusion. However it is worth to note that a slight difference was found between MUCH and the mixture in the release amount at the initial time (Fig. 2b). Meanwhile, MUCH showed the different urea release pattern between DW and SS because SS facilitates the two release mechanisms, dissolution and cation exchange of which are not available in DW (Park et al. 2005).

Dissolution mechanism of metal-urea complex intercalated into MT could be deduced from  $\text{Ca}^{2+}$  release pattern from MUCH and the mixture in both DW and SS (Fig. 3). Release patterns of  $\text{Ca}^{2+}$  in all treatments were very similar to those of urea within 4 hrs. This results strongly supported metal-urea complexes in MUCH were fully intercalated

into MT for reasons mentioned above. However, released  $\text{Ca}^{2+}$  in SS was detected until 32 hrs unlike release of urea molecule (Fig. 2b). This result could be explained that urea of urea-metal complexes intercalated into MT was quickly removed by water molecules then a certain amount of hydrated  $\text{Ca}^{2+}$  were combined at exchangeable sites of MT and the rest was easily released with urea molecules from MT interlayer. In succession,  $\text{Ca}^{2+}$  bound in exchangeable site of MT was only removed in SS due to the presence of counter ions such as  $\text{Mg}^{2+}$  and  $\text{K}^{+}$  (Park et al. 2005). Actually, previous study (Kim, 2010) showed that the amount of exchangeable cation as much as CEC of MT was remained in MT after fully washing of MUCH with DW. Although the mixture showed similar  $\text{Ca}^{2+}$  release pattern in SS, the release mechanism of the mixture is quite different from that of MUCH, i.e.  $\text{Ca}^{2+}$  of MUCH had been already intercalated before release experiment, on the other hand,  $\text{Ca}^{2+}$  in the mixture had the process of dissolution of metal-urea complex in DW or SS prior to intercalation into MT as much as CEC during the flow experiment. After that, release mechanism of intercalated  $\text{Ca}^{2+}$  in the mixture is the same of MUCH.

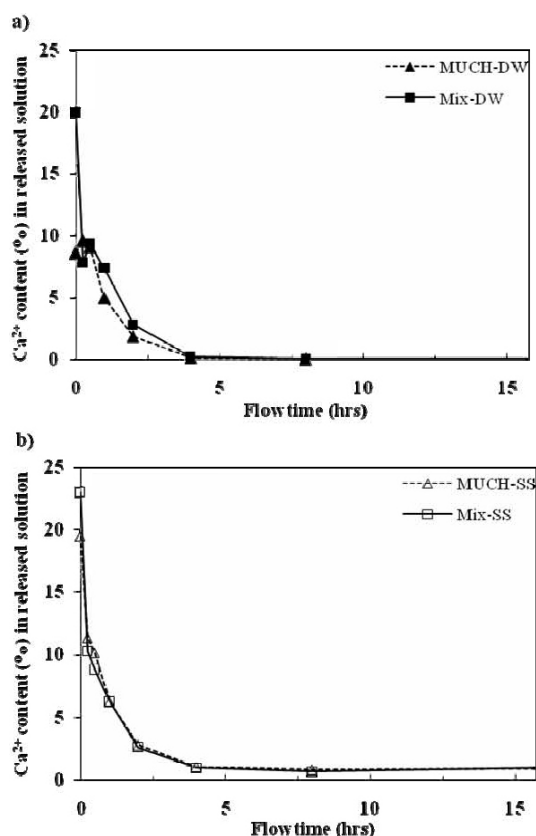


Fig. 3. Released  $\text{Ca}^{2+}$  content (%) from MUCH and urea-mixture by a) deionized water (DW) and b) simulated soil solution (SS) in continuous-flow system.

The release of urea from MUCH and the mixture treated with soil (B experiment) was quickly ended within 1 hr regardless of soil properties such as soil pH and soil texture (data not shown). Only slightly difference of urea content in released solution was observed at 30 min by different soil pH and soil texture; Urea contents in treatment of the higher soil pH and more clay content were higher than in lower and less. These results can be explained by both the higher protonation of  $\text{NH}_2$  of urea at low soil pH and the slower release rate in more clay content of soil. Nevertheless, we did not observe, in this study, the notable difference of urea release properties between MUCH and the mixture by soil property. This result might occur as treated urea in soil was too low in order to investigate the release property of urea in continuous-flow condition because of its high dissolution in water. Therefore, MUCH could be expected more effect in dry-field because they are easily released from MT when they are in contact with soil water and adsorbed water of soil particles. All results, mentioned above, suggest that metal-urea complexes in MUCH could be utilized as a fast-effective source of N with high urea use efficiency.

**Movement of MT in soil and impact on soil physical property by MUCH treatment** When MUCH is applied the farm land, behavior of MT in soil is very important because of its inhibition on the vertical flow of water by dispersion in pore and forming a 'clay pan' in soil. Distributions of MT in column after 30 days under continuous-flow condition were shown in Fig. 4. Although small particles of MT were placed sporadically in soil, they did not form the horizontal clay band. Vertical movement of MT may seem to take place with water along the macropore space, which seems to be promoted by loose packing of

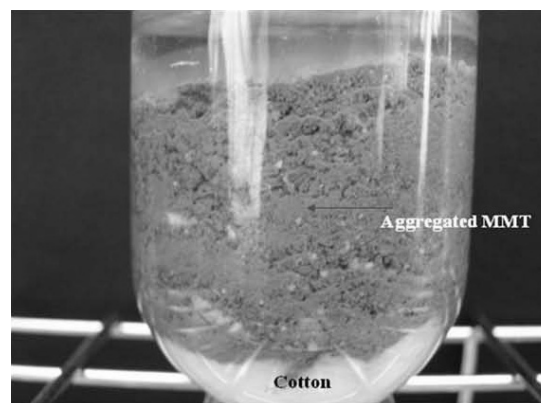


Fig. 4. Photograph of soil treated with MUCH at 30 days. Soil was kept in continuous-flow condition during 30 days.

**Table 2. Impacts on soil properties by MUCH treatment. The experimental condition was the same as Fig. 4.**

Treatment	Water-stable aggregate rate (%)					WHC <sup>†</sup>	CEC
	> 2.00	1.00-2.00	0.25-1.00	0.01-0.25	< 0.01		
	----- mm -----					%	cmol <sub>c</sub> kg <sup>-1</sup>
SC <sup>‡</sup>	0.5	7.2	45.2	21.4	25.7	20.0	11.2
SC-MUCH	0.2	8.8	49.1	15.7	26.1	23.3	11.7
CL <sup>§</sup>	0.0	5.5	39.0	19.8	35.6	42.6	12.4
CL-MUCH	0.0	4.7	37.3	22.5	35.5	42.2	13.0

<sup>†</sup>Abbreviation: WHC (Water Holding Capacity), <sup>‡</sup>SL (Sandy loam), <sup>§</sup>CL (Clay loam).

soil in glass column. Nevertheless, the flow rate of water in MUCH treatment during the experiment periods was not observed the significant difference compared that of without MUCH. Of course, water flow rate in all treatment was slower and slower as time passes until certain periods of time because of the promotion of soil compaction by continuous water flow. This result indicated that use of MUCH as N fertilizer had little influence on vertical flow of water, even if its successive application would be practiced on the same soil for 30 years (NIAST, 2006). Actually, amount of MT which will be applied to soil is estimated to be only 0.4 wt%.

Soil aggregate distribution, WHC and CEC were used as indicators of soil physical quality, in this study, because these parameters could be sufficiently explained the soil structure (Bronick and Lal, 2005). Table 2 showed physical properties of soil through continuous-flow condition during 30 days after MUCH treatment. Although, slight increase (10%) in macroaggregates (> 0.25 mm, Tisdall and Oades, 1982) by MUCH treatment in sandy loam soil was observed, soil physicochemical properties such as water stable aggregate rate, WHC and CEC were not significantly affected by MUCH in both sandy loam and clay loam soils. Actually, soil physicochemical property related to soil structure is mainly affected by livestock treading, cropping, tillage and input of organic materials (Topp et al. 1997; Rasool et al. 2008). In addition, the soil physicochemical quality in crop land has mostly evaluated through long-term land management (Rasool et al., 2008; Schjøning et al. 2006; Reynolds et al. 2008). Thus, further study has to carry out through long term field experiment for a more detailed evaluation of impact on soil structure by MUCH treatment. Nevertheless, these results confirmed that continuous application of MUCH on soil did not lead to any noticeable change in affected in soil properties and soil structure.

## Conclusion

Releases of urea were completed within 4 hrs under continuous-flow condition regardless of the types and the leaching solutions. The fast release of urea from MUCH in continuous-flow condition was observed regardless of soil properties such as soil pH and soil texture. Use of MUCH as N fertilizer had little influence on vertical flow of water, even if the successive application of MUCH would be practiced on soil during 30 years. Soil physicochemical properties such as water stable aggregate rate, WHC and CEC were not significantly affected by MUCH treatment in both sandy loam and clay loam soils. Therefore, this study strongly supported that massive urea intercalated into MT maintained its fast effectiveness along with remarkably increased N use efficiency.

## Acknowledgements

This study was supported by Technology Development Program for Agriculture and Forestry (No. 106135-3), Ministry for Agriculture, Forestry and Fisheries, Republic of Korea.

## Reference

- Abramova, E., I. Lapidés, and S. Yariv. 2007. Thermo-XRD investigation of monoionic montmorillonites mechanochemically treated with urea. *J. Therm. Anal. Calorim.*, 90:99-106.
- Allen, S.E. 1989. *Chemical Analysis of Ecological Materials*. Blackwell, Oxford, UK.
- Bronick, C.J. and R. Lal. 2005. Soil structure and management: a review. *Geoderma*. 124:3-22.
- Cissé, M. and P.L.G. Vlek. 2003. Conservation of urea-N by immobilization-remobilization in a rice-Azolla inter crop. *Plant Soil* 250:95-104.

- Dobermann, A. and K.G. Cassman. 2002. Plant nutrient management for enhanced productivity in intensive grain production systems of the United State and Asia. *Plant Soil*. 247:153-175.
- Gruber, N. and J.N. Galloway. 2008. An Earth-system perspective of the global nitrogen cycle. *Nature* 451:293-296.
- Kim, S.D. and B.E. Dale. 2008. Effects of nitrogen fertilizer application on greenhouse gas emissions and economics of corn production. *Environ. Sci. Technol.* 42:6028-6033.
- Kim, K.S. 2010. Suppression of fertilizer N loss through massive urea intercalation into montmorillonite. Ph.D. Thesis, Kyungpook National University, Daegu, Korea.
- Lado, M. and M. Ben-Hur. 2004. Soil mineralogy effects on seal formation, runoff and soil loss. *Appl. Clay Sci.* 24:209-224.
- Lea, P.J. and R.A. Azevedo. 2006. Nitrogen use efficiency. 1. Uptake of nitrogen from the soil. *Ann. Appl. Biol.* 149:243-247.
- Liang, R. and M. Liu. 2006. Preparation and properties of a double-coated slow-release and water-retention urea fertilizer. *J. Agric. Fod Chem.* 54:1392-1398.
- NIAS (National Institute of Agricultural Science and Technology). 2006. Fertilizer recommendation for crops. RDA. Suwon, Korea.
- Park, M., C.Y. Kim, D.H. Lee, C.L. Choi, J. Choi, S.R. Lee, and J.H. Choi. 2004. Intercalation of magnesium-urea complex into swelling clay. *J. Phys. Chem. Soilds.* 65:409-412.
- Park, M., J.S. Kim, C.L. Choi, J.E. Kim, N.H. Heo, S. Kormarneni, and J. Choi. 2005. Characteristics of nitrogen release from synthetic zeolite Na-P1 occluding  $\text{NH}_4\text{NO}_3$ . *J. Conrol. Release.* 106:44-50.
- Purakayastha, T.J. and J.C. Katyal. 1998. Evaluation of compacted urea fertilizers prepared with acid and non-acid producing chemical additives in three soils varying in pH and cation exchange capacity. *Nutr. cycl. in Agroecosy.* 51:107-115.
- Rasool, R., S.S. Kukal, and G.S. Hira. 2008. Soil organic carbon and physical properties as affected by long-term application of FYM and inorganic fertilizers in maize-wheat system. *Soil Till. Res.* 101:31-36.
- Reynolds, W.D., C.F. Drury, X.M. Yang, and C.S. Tan. 2008. Optimal soil physical quality inferred through structural regression and parameter interactions. *Geoderma* 146:466-474.
- Sanz-Cobena, A., T.H. Misselbrook, A. Arce, J.I. Mingot, J.A. Diez, and A. Vallejo. 2008. An inhibitor of urease activity effectively reduces ammonia emissions from soil treated with urea under Mediterranean conditions. *Agr. Ecosyst. Environ.* 126:243-249.
- Schjønning, P., B.T. Christensen, and B. Carstensen. 2006. Physical and chemical properties of a sandy loam receiving animal manure, mineral fertilizer or no fertilizer for 90 years. *Eur. J. Soil Sci.* 45:257-268.
- Tisdall, J.M. and J.M. Oades. 1982. Organic matter and water-stable aggregates in soil. *J. Soil Sci.* 33:141-163.
- Tong, Z., L. Yuhai, Y. Shihuo, and H. Zhongyi. 2009. Superabsorbent hydrogels as carriers for the controlled-release of urea: Experiments and a mathematical model describing the release rate. *Biosyst. Eng.* 102:44-50.
- Topp, G.G., W.D. Reynolds, F.J. Cook, J.M. Kirby, and M.R. Carter. 1997. Physical attributes of soil quality. In: Gregorich, E.G., Carter, M.R. (Eds.), *Soil quality for crop production and ecosystem health. Developments in soil science*, vol. 25. Elsevier, New York, NY, pp. 21-58.
- Yoder, R.E. 1936. A direct method of aggregate analysis of soils and study of the physical nature of soil erosion losses. *Am. Soc. Agron. J.* 28, 337-351.