

# Role of Anion in Controlling Mineral Ion Concentration of the Soil Solution

HIDEO OKAJIMA and HIROKI IMAI

Faculty of Agriculture, Hokkaido University

Soil solution is the main source supplying nutrients required for the growth of crops. It has been considered that the nutrient concentration of the soil solution has an important role as a so-called intensity factor in the nutrient supply system of the soil.

As a rule, the chemical composition or nutrient concentration of the soil solution changes with nutrient uptake of crops, fertilizer application, precipitation etc.. The authors have stressed, however, that the changes of nutrient concentration due to various factors described above must be induced directly through the changes of anion concentration in the soil solution<sup>1),2),3)</sup>.

Cation and anion exist in an equal amount in a soil solution as electroneutrality prevails in it. Most of the anions are in the soil solution while the cations are mainly held as the exchangeable ones on particles in solid phase keeping an equilibrium with cations in the soil solution. Therefore, when the balance of cation and anion in the soil solution is disturbed by nutrient uptake of crops or fertilizer application, the anion concentration determines the cation concentration in order to keep the electroneutrality of the soil solution.

For example, when the nitrate anion in a soil solution decreases with the nitrate absorption of crop, cations such as calcium also decrease equivalently through transference of cation to solid phase to keep electroneutrality, resulting in a reduced nutrient concentration of the soil solution. On the contrary, when the nitrate anion in-

creases with the nitrification by microbial activities, cation increases equivalently in the soil solution by the release of cation from the solid phase.

Accordingly, it may be said that the nutrient concentration of soil solution in most cases in fields is mainly dependent on the behavior of anions. Several experiments supporting this assumption will be described briefly in the paper.

## Effect of nitrogen salts on the concentration of soil solution

$(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  were added to a soil (Brown Lowland Soil). Amounts of the nitrogen salts added were 0.5, 1, 1.75, 2.5, 5 m.e. per 100 g of dry soil. The soil samples mixed with the salts were adjusted to 30% in moisture, and a 4 day period was allowed to attain an equilibrium in the low temperature room (4°C). Thereafter, the soil solutions were separated from the samples by the centrifugal method<sup>4)</sup> for 30 min at 13,000 rpm, equilibrated with pF value 4.2 in moisture intensity.

The electrical conductivity (EC) of the soil solution increased with an increasing amount of nitrogen salts added as given in Fig. 1.A. An increasing effect of salt addition on EC was in the order of  $\text{NH}_4\text{Cl} = \text{NH}_4\text{NO}_3 > (\text{NH}_4)_2\text{SO}_4 > (\text{NH}_4)_2\text{HPO}_4$ . In the case of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$ , EC increased linearly with the increase of salts added upto EC 15–16 mmho/cm. On the other

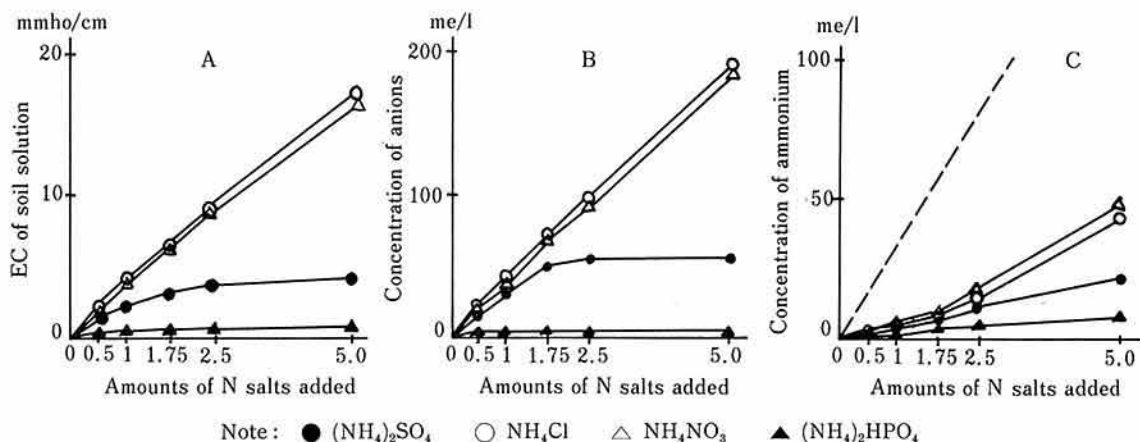


Fig. 1 Changes of electrical conductivity, concentration of anions and ammonium in soil solution with the amounts of nitrogen salts added. (Okajima, H., Imai, H. and Araki, S., 1974 unpublished)

hand, with  $(\text{NH}_4)_2\text{SO}_4$  added, it reached 5–7 mmho/cm and thereafter no increase was observed with further increase of salts added. With  $(\text{NH}_4)_2\text{HPO}_4$ , the increase of EC was only within a range of 0.5–1.0 mmho/cm.

Tendency of the increase of EC by the addition of different kinds of nitrogen salts is coincident with the increase of anions as shown in Fig. 1.B. Concentration of ammonium ion in the soil solution was also increased with the increase of salts added, but it was low compared with the concentration calculated on an assumption that all the ammonium ions added were solved completely in the soil solution (dotted line in Fig. 1.C). As the difference between measured concentration and calculated concentration is considered to be due to the adsorption of ammonium by solid phase, the extent of ammonium adsorption can be regarded in the order of  $(\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{NO}_3 = \text{NH}_4\text{Cl}$ .

These findings suggest that the different concentrations of ammonium ion in soil solution are determined by the concentration of anions originated from the salts added, even though the same amounts of nitrogen are added. The same conclusion was given by Yamazaki et al.<sup>4)</sup> using potassium salts.

### Successive changes of nutrient concentration and chemical composition of soil solution by the addition of nitrogen fertilizers with the incubation

Three kinds of nitrogen fertilizer were added to the same soils used in the previous experiment and the moistened samples were incubated at 30°C constant temperature. The soil solutions obtained successively with time intervals by the centrifugal method were

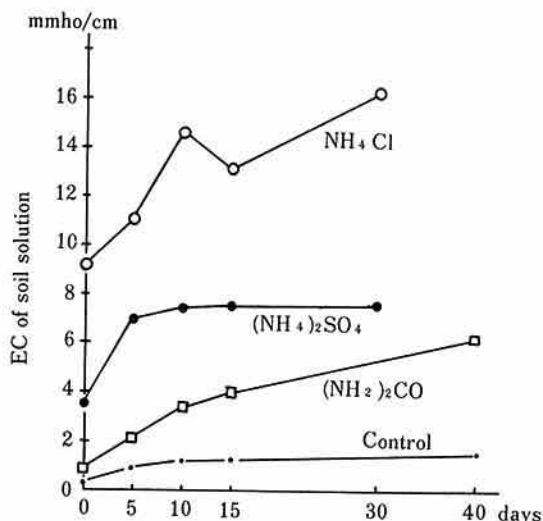


Fig. 2 Changes of electrical conductivity of soil solution with the incubation

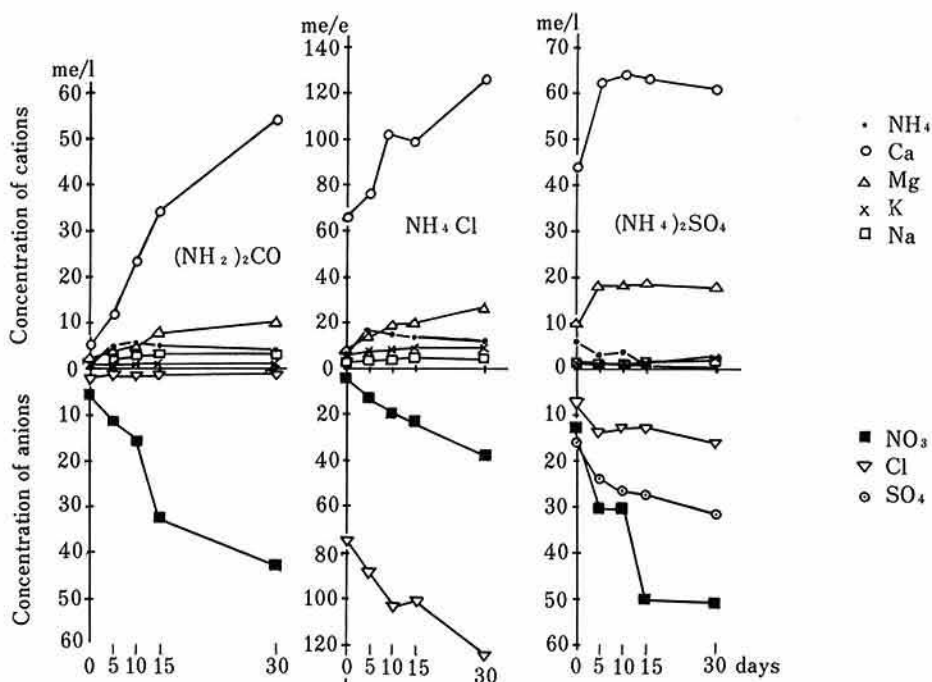


Fig. 3 Changes of anion and cation concentrations of the soil solutions with the incubation

analyzed for cations and anions as shown in Figs. 2 and 3<sup>3)</sup>. EC increased with the incubation and the rate of increase was highest with  $\text{NH}_4\text{Cl}$ , followed by  $(\text{NH}_4)_2\text{SO}_4$  and lowest with  $(\text{NH}_2)_2\text{CO}_3$ . Though EC of the urea-added plot was low at the beginning because of non-dissociated character of urea, it increased with an accumulation of nitrate anion caused by the gradual change of urea

to nitrate which occurred during the incubation. The nitrate anion thus formed must have induced the release of cation adsorbed on the solid phase, according to the above-mentioned theory.

In the case of  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$ , the concentration of the dissociated  $\text{Cl}$  and  $\text{SO}_4$  anions was high, resulting in high EC of the soil solution. Especially  $\text{NH}_4\text{Cl}$  gave the

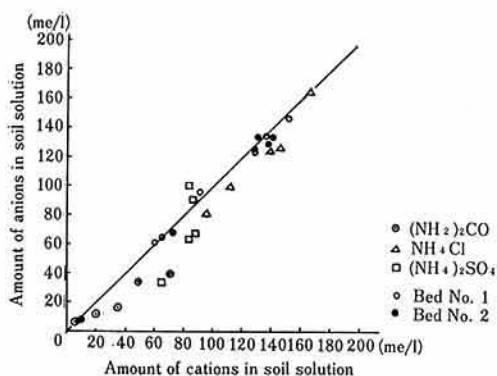


Fig. 4 Interrelation between contents of anion and cation in soil solution

Table 1. Trends of activity ratio

$\left[ \text{pk} - \frac{1}{2} \text{p}(\text{Ca} + \text{Mg}) \right]$  in the soil solution treated with different nitrogen sources, during the incubation

Dates	Nitrogen source		
	$(\text{NH}_2)_2\text{CO}$	$\text{NH}_4\text{Cl}$	$(\text{NH}_4)_2\text{SO}_4$
0	2.43	1.86	2.28
5	2.28	1.82	2.23
10	2.28	1.85	2.23
15	2.29	1.85	2.20
30	2.37	2.02	2.20

highest EC values because of a large solubility of chloride. With the incubation,  $\text{NO}_3$  anion was also increased by the nitrification of  $\text{NH}_4$  added in the form of  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$ , and which in turn induced an increased cation concentration through the release of cation from the solid phase. The release of cation is achieved based on a principle of keeping electroneutrality because the ratio of cation and anion in the soil solutions is nearly 1:1 in all the cases as shown in Fig. 4 and also on a principle of activity ratio. Activity ratio, the latter principle, is that changes of cation concentration is achieved within certain limits to keep constant value of activity ratio such as  $\text{pK} - \frac{1}{2} \text{p} (\text{Ca} + \text{Mg})$  in an equilibrated system of soil solution and exchange site of soil<sup>5)</sup>. Table 1 shows that  $\text{pK} - \frac{1}{2} \text{p} (\text{Ca} + \text{Mg})$  of the soil solution remains relatively constant with the incubation with all the nitrogen sources.

These phenomena may suggest that the amount of anion in the soil solution is the main causal factor to determine the mineral nutrient concentration of the soil solution. An exceptional case, however, was found in the case of  $(\text{NH}_4)_2\text{SO}_4$  as shown in Fig. 3. That is, release of cations such as calcium reached its maximum before the maximum in nitrate accumulation occurs. This fact will be understood by the formation of gypsum in the soil solution as shown in the following experiment.

### Mineral ion concentration in the soil solution of upland nursery beds for rice seedlings

Fig. 5 indicates the trends of cation and anion concentrations in the soil solution obtained from the soil of nursery beds during the seedling growth in a green house<sup>6)</sup>. The moisture content of soils was adjusted to 40% before separating the soil solution from the soil samples by the centrifugal method. Soils used in nursery bed No. 1 was the

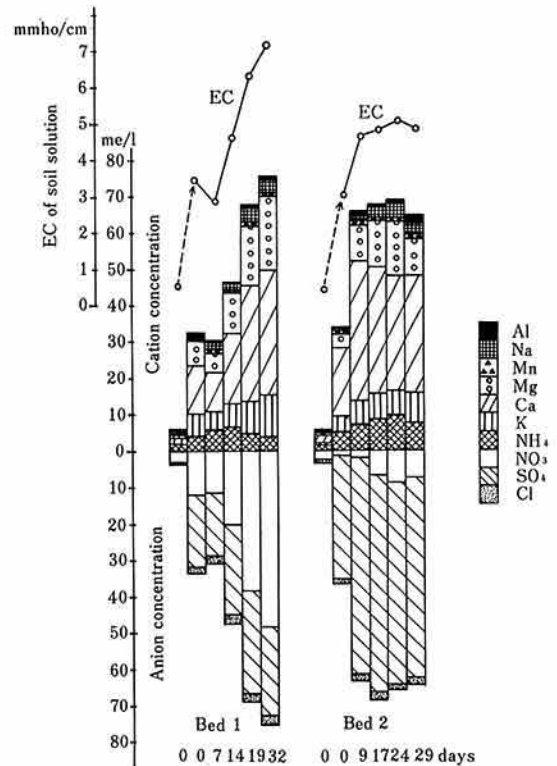


Fig. 5 Trends of EC and cation anion concentration in soil solution obtained from the soils of two nursery beds (Arrows dotted show increase of EC by fertilizer application)

same one used in the previous experiment while the soil used in bed No. 2 was andosol. The bed No. 2 was treated with elemental sulfur at a rate of 120 g per  $\text{m}^2$  to lower pH of the soil in order to protect seedlings from *Fusarium* attack.

EC of the soil solution obtained from the bed No. 1, to which urea was used as nitrogen fertilizer, increased with the seedling growth as given in Fig. 5, due to the nitrification as described in the foregoing experiment. EC of the soil solution in the bed No. 2, on the contrary, reached the maximum at the early stage and its maximum value was relatively low. There, sulfate anion was accumulated with the oxidation of sulfur by microbial activity besides the accumulation of nitrate. The growth of the rice seedlings was superior in bed No. 2

compared with bed No. 1. Namely, dry weights of seedlings of bed No. 2 and bed No. 1 were 4.23 g and 3.60 g per  $m^2$  respectively.

### Electrical conductivity and activity products of calcium sulfate in the soil solution of the nursery beds under different moisture levels

Moisture contents of soil of nursery bed fluctuate with the evapotranspiration and water supply. The moisture contents of the two nursery beds fluctuated from 40% to 28% during the seedling growth. Needless to say, changes of nutrient concentration of soil solution caused by the fluctuation of soil moisture is an important environmental factor affecting nutrient uptake and crop growth.

Therefore, soils obtained from the two beds were adjusted experimentally from 40% to 28% of soil moisture in order to estimate the change of nutrient concentration due to the variations of moisture in the upland nursery beds.

A moisture level at the ratio of soil to water of 1:10 was also included. The soil solution and water extraction obtained from these materials were analyzed for EC and mineral ion concentration, as shown in Fig. 6 on EC.

Decrease in EC due to the increase in soil moisture occurred throughout the entire range of moisture levels, the rate of the decrease being higher in the low moisture range. In other words, EC increased markedly by the decrease of soil moisture, especially in the bed No. 1, within upland field moisture ranges. EC increment of bed No. 2, however, was very limited. This difference between two soils may be attributable to whether a sparing soluble gypsum was formed or not.

In the bed No. 2, calcium increased in the soil solution with the increase of  $SO_4$  by the oxidation of elemental sulfur, result-

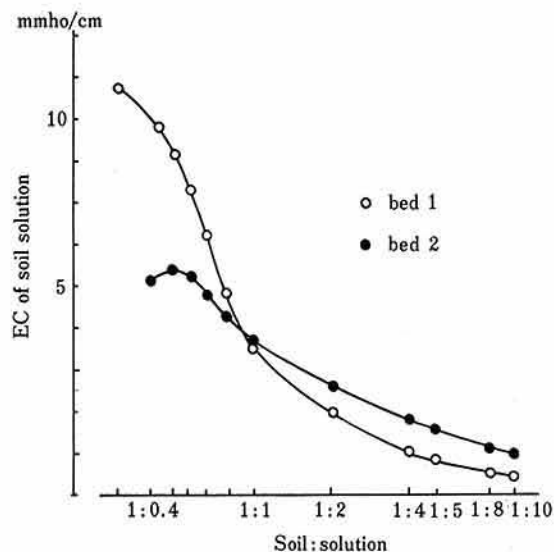


Fig. 6 Changes in electrical conductivity values in relation to soil solution ratio

ing in enough amounts of both the elements to produce sparing soluble gypsums. That is, the soil solution of the bed No. 2 became saturated with calcium sulphate, and therefore the content of sulfate anion which determines electrical conductivity of the soil solution was kept constant even when the soil moisture fluctuated. In other word, the concentration of mineral ion of the soil solution of the bed No. 2 is kept relatively constant against the variation of soil moisture content caused by the evapotranspiration or irrigation, while those of bed No. 1 is unstable.

These findings suggest that in some cases a sparing soluble gypsum will be the regulator of the concentration of the soil solution, through controlling the concentration of sulfate anion. In order to give the evidence for supporting this assumption, calculation on the activity products of calcium sulfate was carried out by the method of thermodynamics.

Generally speaking, a soil-solution ion may be present in several different forms. For example, soil solution calcium is present as ionpairs, such as  $CaSO_4^\circ$ ,  $CaHPO_4^\circ$ ,  $CaH_2PO_4^+$  and  $CaHCO_3^+$  besides  $Ca^{2+}$ . Since

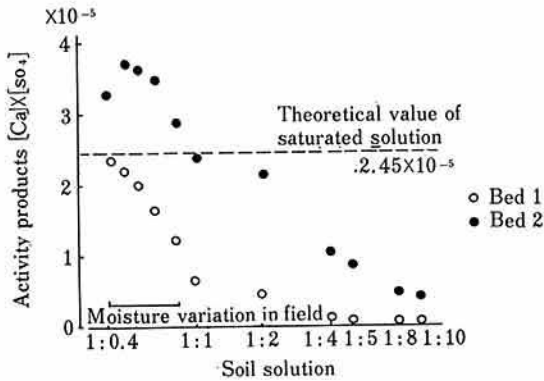


Fig. 7 Activity products of calcium sulfate in soil solution of two nursery beds at different ratio of soil to solution.

chemical analysis of calcium of the soil solution measures the sum of  $\text{Ca}^{2+} + \text{CaSO}_4^{\circ} + \text{CaHPO}_4^{\circ} + \text{CaH}_2\text{PO}_4^{\circ} + \text{CaHCO}_3^{+}$ , the actual concentration of them should be obtained separately. Otherwise, no accurate values of activity product of  $\text{CaSO}_4$  will be obtained. One of the way to obtain the actual  $\text{Ca}^{++}$  concentration from the calcium content measured by chemical analysis is the successive approximation method with the computer<sup>(7),8)</sup>. The successive approximation method was carried out for this purpose in this paper.

Fig. 7 shows activity products of calcium sulfate calculated from the actual concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  obtained. The activity product of calcium sulfate of soil solution in bed No. 2 was over the activity product of calcium sulfate,  $2.5 \times 10^{-5}$ <sup>9),10)</sup> at the field moisture condition but those of the bed No. 1 was below. Namely, the soil solution of the bed No. 2 was saturated with gypsum while those of bed No. 1 was not.

## Conclusion

The key point of fertilization techniques is the efficient use of fertilizers for crop production. As an important item for this purpose, placement of fertilizer, time of application and rate of fertilization have been considered in relation to soil characteristics, crop characteristics or fertilizer charac-

teristics.

The fundamental principle of all these fertilization practices, however, is how to keep the suitable nutrient concentration of soil solution under a given condition. Too low or too high concentrations are unfavorable to crop growth. In addition, high concentration may accelerate nutrient loss in wet areas or salt injury in dry areas. It implies that one of the criteria for choosing fertilizers is to check the kinds of anion originating from fertilizer, because of their role of controlling the nutrient concentration of soil solution.

## References

- 1) Okajima, H. & Imai, H.: Nutrient supplying power of soils (preliminary report). Plant growth and release of nutrients in soil. *J. Sci. Soil Manure, Japan*, 43, 199-203 (1972) [In Japanese].
- 2) Okajima, H. & Imai, H.: Nutrient supplying power of soils. I. Effect of nutrient and water absorption by the rice plants on the nutrient release in soils. *J. Sci. Soil Manure, Japan*, 44, 23-31 (1973) [In Japanese].
- 3) Okajima, H., Imai, H. & Makita, N.: Nutrient supplying power of soils. III. Effect of nitrification on the chemical composition of the soil solution. *J. Sci. Soil Manure, Japan*, 45, 389-394 (1974) [In Japanese].
- 4) Yamazaki, S. & Kishita, A.: Studies on soil solution with reference to nutrient availability. I. Effect of various potassium fertilizer on its behavior in the soil solution. *Soil Sci. and Plant Nutr.*, 18, 1-6 (1972).
- 5) Moss, P.: Some aspects of the cation status of soil moisture. I. The ratio law and soil moisture content. *Plant and Soil*, 18, 99-113 (1963).
- 6) Okajima, H. & Imai, H.: Nutrient supplying power of soils. IV. Mineral ion concentration and its constitution in the soil solution of upland nursery beds for rice seedlings. *J. Sci. Soil Manure, Japan*, 46 [In Japanese] (In press).
- 7) Paul, J. L., Tanji, K. K. & Anderson, W. P.: Estimating soil and saturation extract composition by a computer method. *Soil Sci. Soc. Am. Proc.*, 30, 15-17 (1966).
- 8) Adams, F.: Ionic concentrations and activities in soil solutions. *Soil Sci. Soc. Am. Proc.*, 35, 420-426 (1971).

- 9) Moreno, E. C. & Osborn, G.: Solubility of gypsum and dicalcium phosphate dihydrate in the system  $\text{CaO-P}_2\text{O}_5\text{-SO}_3\text{-H}_2\text{O}$  and in soils. *Soil Sci. Soc. Am. Proc.*, **27**, 614-619 (1963).
- 10) Rance, J. M. & Davey, B. G.: Determination of the solubility product of soil constituents such as gypsum. *Soil Sci. Soc. Am. Proc.*, **32**, 670-672 (1968).