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CHEMICAL STABILITY OF NITRATE IN SOILS

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ABSTRACT

The chemical stability of nitrate and its reduction into nitrous oxide or nitrogen gases as end products was theoretically studied using Nernst's equation , under different sets of Eh (0,200 and 400mv) and pH (5, 7 and 9) comparable to those of soils.

Calculations using Nernst's equation and published data on ion activities and redox potential declared that nitrate stability is very sensitive to little changes in soil reaction (pH) and/or redox (Eh) values. Nitrate transformation into N_2O and N_2 goes easier at low than at high pH and Eh values. A decrease of pH by one unit increases the activity of the produced N_2O and N_2 by 10^{10} and 10^{12} folds, respectively. Also, their activities increased by 10^{11} and 10^{16} folds due to decreasing Eh value by 100 millivolts. In addition, when increasing the nitrate activity by 10 folds, the activity of any of the two gases increases by 100 folds. Among the two gases, N_2 production was more sensitive than N_2O production towards the changes in pH and Eh values.

Similar trends were found by other workers as to the effect of pH and Eh on nitrate reductions. Therefore, it is expected that small changes in soil pH and/or Eh can cause important chemical reduction of the applied nitrate fertilizers especially under extensive cropping systems to form N_2O gas which shares in the environmental problems through its reaction with the ozone layer.

Key Words: Nitrate Reduction, Redox Potential, Nitrous oxide Gas

INTRODUCTION

In Egypt, due to intensive cropping, great amounts of nitrate fertilizers are consumed (FAO, 1979). Nitrate is considered one of the most important electron acceptors during the biochemical processes taking place in soil where it undergoes reduction to nitrous oxide (N_2O) or dinitrogen (N_2). Recently, for both economic and environmental reasons, nitrate transformations in soils has received a lot of attention (Bouwman, 1990, EL-Sebaay, 1991, Van Kessel *et al,* 1993, Weier *et al*, 1993 Hojberg *et al,* 1996 and Stevens et al, 1998). It was estimated that fertilizer–derived emission of N_2O in the year 2000 will account for 0.1 to 1.5% of the global source in the atmosphere (Eichner, 1990). Moreover, the contribution of agricultural soils to the total N_2O emission is estimated at approximately 90% (Mosier and Schinel, 1991). The proportion of N_2O and N_2 gases entering the atmosphere depends on a number of factors. The most important ones are soil redox potential (Eh) and soil reaction (pH), as mentioned by Arah and Smith (1990). Both parameters are well linked to each other as found by Ponnamperuma (1972),. EL-Sebaay (1986) and Larson et al (1991). Nernst's equation is highly reliable in describing such link.

According to Mehran and Tanji (1974) two basic approaches in modeling of transformation processes have been followed. One consists of fitting the behaviour of a system based on experimental data by use of

approximation, regression analysis, etc. The other approach uses physical laws and mathematical relations to describe and predict the performance of the system under a specified set of conditions. It is the aim of the author to apply the second approach by using Nernst's equation to calculate and hence predict to what extend nitrate is chemically stable under changing Eh and pH condition comparable to those occurring in soils.

The objective of the current study is to develop meaningful diagrams that can show the instability of nitrate and its transformation into N_2O and N_2 at different Eh and pH values comparable to real values occurring in soils.

PROCEDURE OF CALCULATIONS

The mode of calculation is based on the use of:

1- Nernst's equation

$$Eh = E° + \frac{RT}{nF} In \frac{oxidized\ forms}{reduced\ forms} \ where,$$

Eh = Redox potential as referred to hydrogen electrode
E° = Standard redox potential of the reaction.
R = Gas constant (8.314 J mol^{-1} K^{-1})
T = 298K.
F = Faraday's constant (96500 coulombs)
n = number of electrons involved in the reaction .

2- The published data of E° (Karapet' Yants and karapet' Yants, 1970).

3- Set of activities of the participating ions (H^+ and NO^-_3) together with set of values representing different redox conditions comparable to those occurring in soils as follow:

H^+ : ranging between 10^{-4} and 10^{-9} mol dm^{-3} (pH 4 to 9)

NO^-_3 : ranging between 10^0 and 10^{-10} mol dm^{-3} . For example within this range a value of 10^{-3} mol dm^{-3} NO^-_3 is equivalent to 14 ppm N which is a realistic value in soil solution.

Eh : ranging between –400 mV (most reduced conditions) to +400 mV (most oxidized conditions).

RESULTS AND DISCUSSION

By the use of Nernst's equation, the stability of nitrate and its transformation into nitrous oxide and nitrogen gas as a function of a wide range of pH and Eh values was calculated according to the following reactions:

$$NO^-_{3\ (aq)} + 5H^+_{(aq)} + 4e^- = 1/2\ N_2O_{(g)} + 5/2\ H_2O_{(L)} \qquad (E° = 1.11V.)$$

$$NO^-_{3\ (aq)} + 6H^+_{(aq)} + 5e^- = 1/2\ N_{2(g)} + 3\ H_2O_{(L)} \qquad (E° = 1.24V.)$$

The results were presented in cubes. Each cube is divided into two parts by a plane representing the equilibrium conditions. The lower part of the cube shows the area wherein nitrate is stable. The upper part represents the area in which nitrate is not stable and N_2O or N_2 can be formed.

Production of N_2O out of nitrate as an important contributor to the greenhouse effect (Bouwman, 1990) and causes partial depletion of the ozone layer (Crutzen and Ehhalt, 1976), is given in figure (1). It can be seen that, irrespective of the Eh value, the area of nitrate stability increases by increasing pH value. This means that NO^-_3 can easier be transformed to N_2O under acidic than under alkaline conditions. These theoretical results coincide with experimental data obtained by EL-Sebaay (1981), Atta and Van Cleemput (1981), El-Sebaay (1986 , 1991) and Stevens et al (1998) who found that soils having pH below 7 produced N_2O more than those of pH above 7. Moreover, calculations declared that a decrease in pH by one unit (which is expected in soil) can increase the activity of the produced N_2O by 10^{10} folds. Of course, the absolute amount of N_2O produced depends on the amount of nitrate present at this moment. Regarding the effect of Eh, as indication of aeration status on nitrate stability, data in the same figure showed that at given pH value the stability of nitrate decreases by lowering the Eh value. This can easily be recognized from the slope of the equilibrium plane. So, nitrate can easily be transformed to N_2O under anaerobic (reduced) conditions than under aerobic (oxidized) conditions. Calculations showed that at any given pH value, a decline of 100 millivolts in Eh, which is very possible to occur in soil, increases the activity of N_2O by as much as 10^{11} folds. This means that the stability of nitrate is much affected by little change in Eh value. On the other hand, increasing the activity of nitrate in the media by 10 folds (e.g from 10^{-3} to 10^{-2} mol dm^{-3}) lead to increase N_2O activity by 100 times. Also, the activity of nitrate itself in the soil solution at equilibrium can play a role in its stability. One may notice in figure (1) that the stability area of nitrate (area under the plane) increases as NO^-_3 activity decreases. This is evident from the slope of the plane of equilibrium. Thus, at certain pH and Eh values, high NO^-_3 activity enhances its transformation to N_2O. Although these results contradict with those obtained by Kroese et al (1989) who found that N_2O production is independent on the initial NO^-_3 content, they appear to fit the observations of many authors (Eichner, 1990; EL-Sebaay; 1991; Kralova et al, 1992; Van Cleemput, 1994; Van Cleemput et al, 1994; DeGroot et al, 1994 and Vermoesen et al, 1996). Hence, the stability diagrams of nitrate developed in this study support the hypothesis that agricultural soils are responsible for most of N_2O in air which attacks the ozone layer as concluded by Mosier and Schinel (1991). Therefore, one may be able to predict the instability of nitrate fertilizers and its reduction to the greenhouse gas N_2O at a site when measuring its pH and Eh values at certain moment and applying them in the diagrams depicted in figure (1) or applying the values in Nernst's equation .

Production of N_2 as the end product of nitrate reduction as affected by changes in pH and Eh values is given in figure (2). Similar to nitrous oxide, nitrogen production increases (nitrate stability decreases) as a result of decreasing both pH and Eh values. However, the absolute amounts of the

Figure(1):Nitrate reduction to nitrous oxide at different pH and Eh

values

Figure(2): Nitrate reduction to nitrogen at different pH and Eh values

two gases differ at similar conditions, since N_2 is always more than N_2O. This can easily be recognized from the values written in the vertical scale in figures 1 and 2. In addition, calculated data showed that a decrease of pH by one unit increases the activity of N_2 by 10^{12} times. While, decreasing Eh value by 100 millivolts increases N_2 activity by 10^{16} times. Similar to N_2O , the activity of N_2 increases by 100 times as NO^-_3 activity in the media increases by 10 times. Experimental results on the reduction of NO^-_3 to N_2 obtained by EL-Sabaay (1986), Kralova et al (1992) and Stevens et al (1998) coincided with the obtained calculation. This may also be helpful in predicting the instability of NO^-_3 and its transformation to N_2 gas. It should be born in mind that the presented data resulting from the calculations do not give any answer to questions on the velocity of reaching equilibrium. It is also important to note that the used values of pH, Eh or NO^-_3 activity represent values in pure system, while in soil system overall values are encountered. Hence, experimental testing on the stability of nitrate at different pH and Eh values is still required to verify the obtained calculated results.

From the above-mentioned results one may conclude that (a) A very small decrease in soil pH and /or Eh can cause important decrease in the stability of nitrate and enhance its transformation to N_2O and N_2 gases. Under similar conditions, nitrate produces more N_2 than N_2O, (b) Increasing NO^-_3 activity in soil solution by for instance 10 folds causes increase in the activity of both gases (i.e. N_2O and N_2) by 100 folds, (c) Nernst's equation can be used to predict the transformation of nitrate (and other compounds) under a set of conditions comparable to those of soils.

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الثبات الكيميائي للنترات فى الأراضي

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باستخدام معادلة نرنست تم حساب مدى ثبات النترات واختزالها كيميائياً إلى غاز أكسيد النيتروز (N_2O) أو النيتروجين (N_2) تحت ظروف مختلفة من رقم الحموضة (pH) تراوحت من 5 حتى 9 ومن جهد الأكسدة والاختزال (Eh) تراوحت بين صفر ، 400 ملليفولت لتماثل تلك الموجودة بالتربة .

أوضحت الحسابات أن ثبات النترات يتأثر بدرجة كبيرة نتيجة لأي تغيرات فى قيم pH أو Eh . حيث كان تحولها أسهل تحت الظروف الحامضية وجهد الأكسدة والاختزال المنخفض (تهوية سيئة) عنها تحت الظروف القلوية وجيدة التهوية . أوضحت القيم المحسوبة أن انخفاضا فى pH يعادل وحدة واحدة يسبب زيادة فى نشاط كل من N_2O ، N_2 مقداره 10^{10} ، 10^{12} مرة على الترتيب . أيضاً زاد نشاطهما بمقدار 10^{11} ، 10^{16} مرة نتيجة خفض قيمة جهد الأكسدة والاختزال بمقدار 100 ملليفولت. أظهرت النتائج أيضاً أنه بمضاعفة نشاط النترات فى وسط التفاعل عشر مرات فإن نشاط أي من N_2O أو N_2 يزداد مائة مرة . وبصفة عامة فإن إنتاج N_2 كان أكثر تأثراً من إنتاج N_2O نتيجة تغير قيم pH أو Eh بالتربة .

أوضحت النتائج المتحصل عليها توافقاً كبيراً مع نتائج التجارب المعملية التى قام بها آخرون ولهذا فمن المتوقع أن اختزال الأسمدة النيتراتية التى تضاف للأراضي الزراعية بكميات كبيرة تحت نظم الزراعة المكثفة إلى غاز أكسيد النيتروز يساهم فى زيادة المشاكل البيئية من خلال تفاعل ذلك الغاز مع طبقة الأوزون .