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Nitrate Transformations in Nitrate-contaminated Soils and Groundwaters: Thermodynamic Aspects (Short Communication)

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Abstract. In Saudi Arabia, contamination of soils and groundwaters with nitrate and its reduction products (i.e. nitrite and ammonium) at severe levels have been observed in many locations. Consequently, nitrate transformations are considered important parameters to estimate pollution impact on agricultural ecosystem in the Kingdom. Therefore, it was found necessary to test through thermodynamic relationships the spontaneity of some reactions describing the chemical transformations of nitrate to its reduction products (NO_2^-, N_2O, N_2 and NH_4^+) at pH values between 5 and 9, and at different sets of activities comparable to those really exist in air, groundwaters and soils.

The calculated results declared that at assigned pH range, nitrate is not stable and can easily transform to nitrite NO^-_2(aq), nitrous oxide N_2O(g), dinitrogen N_2 (g) and ammonium NH_4^+(aq). These transformations can proceed easier under acidic than under alkaline conditions. On the other hand, formation of nitrogen dioxide NO_2 (g) can occur only at pH 7.52 and lower. However, at higher pH values, nitrate is stable and no formation of NO_2 (g) takes place.

The study suggested that the formation of NO_2 as an intermediate product of biological and chemical denitrification is very probable and should be considered in future practical research.

Keywords: Greenhouse gases, Air pollution, Groundwater pollution, Denitrification, Ammonification, Nitrous oxide.

Introduction

In Saudi Arabia, due to increasing agricultural activities and excess use of nitrogen fertilizers besides possible draining of sewage effluents to groundwaters, some wells in Riyadh became contaminated with nitrate and ammonia. In this concern, Aljubair [1] found that 14.4% out of 118 wells contained NO_3^- concentration more than the permissible level by WHO [2] for drinking water (i.e. 45 mgl^{-1} NO_3^-), and reached above 90 mgl^{-1} NO_3^- in some cases. Also, 24.7% of these wells were polluted with ammonia. In addition, nitrite was also found in some of these wells. The different pH

values of their studied water (between 6.2 and 8.8) may play a role in determining the type of predominant N-species. This may be useful in avoiding the toxicity hazards that arises when using such wells as a source for drinking.

Most studies on NO_3^- transformations showed, however, conflicting results due to different conditions, especially those of pH and aeration. El-Sebaay [3] confirmed that a small change in pH can cause marked effect on nitrate reduction. The most common products of nitrate transformations are known to be NO_2^-, N_2O, N_2, NO_2 and NH_4^+. In these compounds, the oxidation state of N ranges from +4 to -3, indicating that nitrate transformation to any of them requires different activation energies depending on the conditions of the reaction. Among these conditions is the pH. Therefore, it was thought necessary to use thermodynamic relationships to study theoretically what can happen to nitrate upon changing the pH conditions as the only variable factor governing the reactions, and what is the type of predominant N-product at certain pH value.

Procedure of Calculation

From the list of nitrogen reactions published by Lindsay *et al.* [4], five reactions were picked out (as shown in Table 1) including NO_3^- and H^+ as reactants and NO_2^-, N_2O, N_2, NO_2 and NH_4^+ as products. Afterwards, the Gibbs free reaction energy change (ΔG_r) was calculated according to the following formula, related to the general reaction:

$$aA + bB \ldots\ldots \;===\; cC + dD \ldots..$$

since,

$$\Delta G_r = \Delta G^o_r + RT \ln \frac{(C)^c (D)^d \ldots}{(A)^a (B)^b \ldots}$$

in which, $\Delta G^o_r = \sum \Delta G^o_f$ (products) - $\sum \Delta G^o_f$ (reactants) and ΔG^o_r , ΔG^o_f

Table 1. The considered nitrate transformations and their ΔG^o_r values

Reaction number	Nitrate transformations	ΔG^o_r (kJ mol^{-1}) at 298^o k
1	$NO_3^- + 2H^+ \;===\; NO_2^- + H_2O$	-163.19
2	$NO_3^- + 5H^+ \;===\; ½N_2O + {}^5/_2\, H_2O$	-428.72
3	$NO_3^- + 2H^+ \;===\; NO_2 + H_2O$	-74.25
4	$NO_3^- + 6H^+ \;===\; ½N_2 + 3H_2O$	-599.15
5	$NO_3^- + 10H^+ \;===\; NH^+_4 + 3H_2O$	-678.46

referring to the Gibbs standard free reaction energy and to the Gibbs standard free formation energy (Table 2), respectively.
R = 8.314 x 10^{-3} kJ mol^{-1} k^{-1} and T = 298^o k

A negative ΔG_r value indicates that the reaction equilibrium is situated at the right, so spontaneous change occurs. A positive ΔG_r value shows that the reactants remain stable (not transformed).

Table 2. Gibbs standard free formation energy of the used compounds[a]

Name	Symbol	Physical state	ΔG^o_f (kJ mol^{-1}) at 298^o k
Nitrate ion	NO_3^-	aqueous	- 110.46[b]
Nitrite ion	NO_2^-	aqueous	- 34.52[c]
Nitrous oxide	N_2O	gaseous	+103.60[c]
Nitrogen dioxide	NO_2	gaseous	+ 52.48[c]
Nitrogen	N_2	gaseous	0.00[b]
Ammonium ion	NH^+_4	aqueous	- 79.50[c]
Hydrogen ion	H^+	aqueous	0.00[b]
Water	H_2O	aqueous	- 237.19[b]

[a:] converted from kcal mol^{-1} (given in the reference) to KJ mol^{-1} (SI unit), where 1 cal = 4.18J.
[b:] krauskopf [5].
[c:] karapet' yants and karapet' yants [6].

In order to make the study more useful, the activities of the compounds involved in the reactions were chosen to be like those realy exist in soil solution and groundwater. For instance, an activity of 10^{-3} molar NO^-_3 was used. This value represents about 14 mgl^{-1} NO^-_3-N which is a realistic level in a soil solution or in contaminated groundwater. Activities behind this value were also assumed. Therefore, the following activities (for aqueous) and fugacities (for gases) were chosen:

NO^-_3 (aq), NO^-_2 (aq) and NH^+_4 (aq) between 10^{-3} and 10^{-6} molar,
H^+(aq) between 10^{-5} and 10^{-9} molar (to represent pH values between 5 and 9),

N_2O (g) and NO_2 (g) between 10^{-1} and 10^{-5} Pascal (1Pascal =10^{-5} atmosphere),
N_2 (g) between 0.78x 10^{-5} (level in atmosphere) and 10^{-5} Pascal.

Results and Discussion

Nitrate transformation to any of the given reaction products (Table 1) was investigated through the use of ΔG_r values calculated from data given in Tables 1 and 2 for ΔG^o_f and ΔG^o_r.

The ΔG_r values obtained for the different sets of activities and fugasities of the involved reactions were negative for reactions 1, 2, 4 and 5, even at the most extreme values of activities and fugasities. This indicated that nitrate was not stable at pH values between 5 and 9 . It can transform to NO^-_2, N_2O, N_2 or NH_4^+. This is true when considering the pH of the media as the only factor governing the reaction. However, it is worth mentioning that not all thermodynamically favored reactions are kinetically favored. Moreover, in order to reach equilibrium (reaction 2) between NO^-_3 and an

activity of the greenhouse gas N_2O equals to its background in the air (310 nl l^{-1} or 310 Pascal as given by Bowman, [7]), activities of 10^{-51} and 10^{-31} molar NO^-_3 must exist at pH 5 (acidic) and 9 (alkaline), respectively. These are very little NO^-_3 activities which are expected to exist in soil solution and groundwater. Similar trends were also found for the other products. Thus, higher NO^-_3 activities can lead to higher N_2O production and consequently more impact on the environment. These results coincided with the experimental results obtained by El-Sebaay and Khaled [8]; Burns *et al*. [9]; Debreczeni and Berecz [10]; Abbasi and Adams [11]; El-Sebaay [12] and Rochester [13]. Also, equilibrium between N_2 at fugacity equals to that in air (0.78 x 10^5 Pascal) and NO^-_3 (reaction 4) at pH 5 and 9 can occur in the presence of 10^{-73} and 10^{-49} molar, respectively. As such, equilibrium can be reached easily at the onset of extremely small activity of NO^-_3. In addition, at certain NO^-_3 activity and by increasing the pH value, the activity of the products of reactions 1, 2, 4 and 5 decreased. This means that nitrate transformation goes easier under acidic than under alkaline conditions. These calculated results were in conflict with the experimental data obtained by Stevens *et al*. [14]. It should be borne in mind that the used activity values were values at the point of reaction, while in soil experiments at different pH, overall values must be used.

The calculated ΔG_r of reaction 3 is presented as stability diagram in Fig. 1. The lower part of the diagram represents the area where NO^-_3 was stable or the conditions at which ΔG_r values were positive. Whereas, the upper part shows the area in which NO^-_3 is not stable (ΔG_r being negative) and NO_2 can be formed. The dotted plane is the place of equilibrium conditions (ΔG_r equals zero). Out of this figure, it can be seen that the area of NO^-_3 stability was increased by increasing of pH. The NO_2 occupied a large area at pH 5. While, at higher pH conditions, very small amount of NO_2 existed. At pH 7.52 and higher, no more NO_2 can be formed. This means that at certain NO^-_3 activity, the transformation possibility of nitrate to nitrogen dioxide was inhibited by increasing of pH. Such study gives, however, some light to consider NO_2 as an intermediate product in the nitrate reduction chain, which received almost no attention in the literatures.

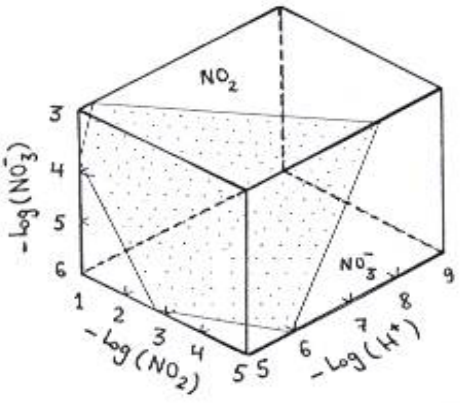

Fig. 1. Nitrate transformation to nitrogen dioxide at different pH values.

When all considered reactions had the opportunity to occur simultaneously, the reaction with the lowest negative ΔG_r would have been the one continuing to equilibrium (dominantly proceeds to the right). Hence, when considering unit activity of the participating compounds of each reaction, the lowest ΔG_r values were found for reactions 5 and 4. And less negative for reaction 2, much less negative for reactions 1 and 3. This means that NH_4^+ will be the most stable product at equilibrium followed by N_2 , N_2O , NO^-_2 and NO_2.

It can be concluded that the obtained theoretical data conform in part, with the experimental results of some authors. In addition, the transformation of NO^-_3 would increase at low pH values. Also, due to important variation in pH of different Riyadh groundwater (from 6.2 to 8.8, Aljubair [1]) one may expect different N-species with predominance of one over others. Moreover, formation of nitrogen dioxide as an intermediate product of denitrification is very probable and future research should focus on that.

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تحولات النترات في الترب الزراعية والمياه الملوثة ا: بعض اعتبارات الديناميكا الحرارية (بحث مختصر)

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ملخص البحث. نظراً لأهمية النترات في الترب الزراعية ومياه الآبار الملوثة بها خاصة بعد الثورة الهائلة في الأنشطة الزراعية بالمملكة العربية السعودية من حيث التأثير السلبي لنواتج تحولاتها على البيئة ، لذا اهتم البحث بالاستعانة ببعض أسس الديناميكا الحرارية (Thermodynamics) واستخدام القيم المتاحة بالمراجع لحرارة تكوين بعض المركبات لحساب التلقائية والتغيرات في طاقة " جيبس " الحرة لخمسة تفاعلات تصف اختزال النترات إلى نيتريت ، أكسيد نيتروز ، نيتروجين ، أمونيوم وثاني أكسيد نيتروجين. تم حساب ذلك تحت ظروف مختلفة من نشاط المواد المشاركة في كل تفاعل اشتملت على قيم متدرجة من رقم الحموضة تراوحت من ٥ حتى٩ وكذلك مدى من نشاط النترات ونواتج تحولاتها تحاكي تلك التي تتواجد بالترب الزراعية وبالمياه الملوثة بالنترات.

أشارت النتائج أن النترات تحت جميع الظروف موضع الدراسة تكون غير ثابتة وتتحول إلى نيتريت ، أكسيد نيتروز ، نيتروجين وأمونيوم ولكن بدرجات تتوقف على طاقة التفاعل (أي الظروف المحيطة بالنترات) ، أما تحول النترات إلى ثاني أكسيد النيتروجين (NO_2) فقد أظهرت النتائج أمكانية حدوث ذلك عند أرقام حموضة ٧,٥٢ أقل – أما في درجات الحموضة الأعلى تكون النترات ثابتة ولا يتكون NO_2 مطلقاً.

ألمحت الدراسة إلى إمكانية اعتبار غاز NO_2 مركباً وسطياً في عملية اختزال النترات (denitrification) سواء بيولوجياً أو كيميائياً – وأوصت بضرورة الاهتمام بدراسته مستقبلاً واعتباره أحد

مكونات سلسلة تحول النترات إلى مركبات ضارة بالبيئة مثلما يحدث تحت ظروف الترب سيئة التهوية وفي أعماق الآبار.