

COMPARING GIBBS ENERGY RELATIONSHIPS FOR AMMONIA VOLATILIZATIONS FROM AGRICULTURAL SOILS FOR POTATO PRODUCTION

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ABSTRACT

Soil drought, that can be enhanced by global warming increases ammonia (NH₃) volatilization. This laboratory study was conducted with two soils: Krome Gravelly Loam (KGL) from Florida and Warden Silt Loam (WSL) from Washington State and two fertilizers: Ammonium sulfate [(NH₄)₂SO₄] or ammonium nitrate (NH₄NO₃). Two water regimes including 20 and 80% Field Capacity (FC) were used at 20°C which is the average temperature in the potato growing season in Washington State. The data demonstrated that variation in NH₃ volatilization subject to different soil water regimes can be explained by changes in Gibbs free energy of Nitrogen (N) fertilization in soils with varying water contents. The absolute values of Gibbs free energy of (NH₄)₂SO₄ or NH₄NO₃ applied to soil at 20% FC soil water regime were 5-fold greater than at 80% FC. Accordingly, the equilibrium constant (K) of deprotonation of ammonium ions in soil solutions at 20% FC was 3,000- or 50-fold greater than that at 80% FC for (NH₄)₂SO₄ or NH₄NO₃, respectively. Nitrogen loss via NH₃ volatilization was 4-to 7-fold greater at 20% FC than that at 80% FC. This study suggests potential acceleration of NH₃ volatilization from soils under drought. Therefore, optimal water management is critical to mitigate NH₃ volatilization from agricultural soils.

Keywords: Ammonia Emission, Soil Moisture, Gibbs Free Energy, Water Management

1. INTRODUCTION

The global ammonia (NH₃) volatilization from Nitrogen (N) fertilizers routinely used for crop production is estimated to be 11 million t N per year (Tg N/yr), which is about one seventh of the nitrogen (N) fertilizers used (FAO/IFA, 2001). While NH₃ is not regarded as a greenhouse gas, it can affect global warming considerably by being oxidized to nitrous oxide (N₂O) or reacting with nitric and sulfuric acids in the atmosphere to form secondary aerosols (Barthelmie and Pryor, 1998; Turner *et al.*, 2010). Dentener and Crutzen (1994) estimated 3 Mg N/yr of

the globally emitted NH₃ can be oxidized by OH radicals and NO₂ (Finlayson-Pitts and Pitts, 2000). A fraction of the oxidized NH₃ is transformed to Nitrous Oxide (N₂O), a very powerful greenhouse gas and this process accounts for up to 5% of the global N₂O emission (Ferm, 1998). After deposition on land surface and water bodies, NH₃ acts as a secondary source of N₂O which contributes to ozone depletion (Martikainen, 1985; Mosier *et al.*, 1998). As a potent greenhouse gas, N₂O is approximately 310-fold powerful than CO₂ in trapping heat in the atmosphere (Finlayson-Pitts and Pitts, 2000; IPCC, 1996). Thus, NH₃ emitted from agricultural soils contributes to global warming.

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Global warming causes not only climate change but also soil drought. Temperature increase of 1% (0.32°C) can increase evapotranspiration by 15 mm (Goyal, 2004). Evapotranspiration, in turn, can worsen soil drought if the irrigation rate is not adjusted to compensate for the increased loss of moisture. There is evidence that the progression of anthropogenic global warming is accompanied by increased risk of drought, since rising temperature increases the rate of drying (Dai *et al.*, 2004). An increase in either temperature or decrease in soil moisture content significantly accelerates NH₃ volatilization from fertilized soils. Soil drought from 80 to 20% Field Capacity (FC) of soil moisture enhances NH₃ volatilization rate by 113 fold (Liu *et al.*, 2007a); while high temperature from 20 to 29°C increases the NH₃ volatilization rate by 10 fold (Liu *et al.*, 2007b). These increases suggest that NH₃ volatilization induced by soil drought impacts global warming and *vice versa*.

Ammonia volatilization entails a series of steps including a chemical reaction. The spontaneity of each of these steps is determined by the Gibbs free energy according to the second law of thermodynamics. However, no published literature is available for describing the effects of changes in Gibbs free energy on either NH₃ volatilization or on the acceleration of NH₃ volatilization by soil drought. Therefore, understanding of the relationship between Gibbs free energy and NH₃ volatilization is too limited to enable effective control of NH₃ volatilization from crop production. Our experimental evidence presented on a mechanism whereby soil drought enhances NH₃ volatilization controlled by Gibbs free energy. This mechanism provides clues to alleviate NH₃ volatilization from fertilized by improved water management, which minimizes the negative Gibbs free energy of the deprotonation of NH₄⁺ ions and in turn minimize NH₃ volatilization.

The objectives of this study were to: (1) quantify Gibbs free energy for NH₃ volatilization in two different soils and (2) assess Gibbs free energy in each step of NH₃ volatilization from the fertilized soils.

2. MATERIALS AND METHODS

2.1. Measurement of NH₃ Volatilization

Three hundred g dry soil of either Krome Gravelly Loam (KGL) collected from Florida or Warden Silt Loam (WSL) from Washington State was placed in an incubation bottle (500 mL in size). The surface area of the soil in the bottle was ~ 60 cm². The soil water content was adjusted to either 20 or 80% of Field Capacity (FC). The percentage of water in the KGL and WSL soils (v/m

based on oven dry soils) was 8.4 and 6.7% for 20% FC and 33.4 and 26.0% for 80% FC, respectively. One ml of N solution consisting of an aqueous solution of either (NH₄)₂SO₄ or NH₄NO₃ was uniformly applied on the soil surface with a micropipette. The amount of N applied was 45 mg N per bottle, equivalent to 75 kg ha⁻¹ based on the surface area. A treatment with only deionized water (no N) was included as a control to measure the NH₃ volatilization from the soils. Thus, this experiment consisted of two soils × three N sources (two N fertilizers plus blank control) × two water regimes × three replications which required 36 incubation bottles. Each incubation bottle was placed in a sealed plastic storage bag (23×30 cm) and maintained at 20°C in an incubator (Precision Incubator, 6DM, THELCO® High Performance Incubators, Precision, Ottawa, Canada). Ammonia volatilization was measured on 1, 3, 7, 14 and 28 days after incubation. A sponge with trapping solution was sampled at each sampling period and a new sponge (with trapping solution) was placed to trap emitted NH₃ for the subsequent sampling period (Liu *et al.*, 2007a; 2007b).

2.2. Calculation of Gibbs Free Energy

Because NH₃ volatilization involves three steps: Step 1, dissolution of the applied ammonium fertilizer compound; step 2, deprotonation of NH₄⁺ ions; and step 3, transformation of aqueous NH₃ into gaseous NH₃. In the soil solution, the relative stability of the chemical system, i.e., the tendency of the system to react or change is determined by the Gibbs free energy or simply free energy, quantity derived from the relationships between heat and work in thermodynamics of NH₃ volatilization. Systems change toward minimum free energy. Equation (1) is one form of Gibbs fundamental equation:

$$G = H - TS \quad (1)$$

where, G = the Gibbs free energy (kJ); H = the enthalpy (kJ); T = the absolute temperature (°K); and S = the entropy (kJ °K⁻¹). For each of the above three chemical steps in soil solution, Equation (1) can be rewritten in Equation (2):

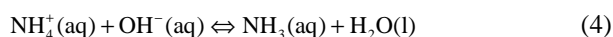
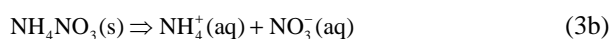
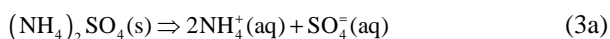
$$\Delta G = G_{\text{products}} - G_{\text{reactants}} = \Delta H - T\Delta S \quad (2)$$

where, ΔG = the difference in the Gibbs free energy between products (G_{products}) and reactants (G_{reactants}) in the chemical system. ΔH and ΔS = the differences in enthalpy and entropy between the products and reactants,

respectively. Equation (2) predicts the spontaneity of the steps involved in NH_3 volatilization:

- $\Delta G < 0$ natural tendency for process to occur (spontaneous)
- $\Delta G = 0$ neither the forward nor the reverse process prevails (equilibrium)
- $\Delta G > 0$ no natural tendency for process to occur (non-spontaneous)

The changes in Gibbs free energy of formation for Equation (3a or 3b, 4 and 5) were calculated based on Equation (1). The parameters of enthalpy (H) and entropy (S) for each of the products and reactants in Equation (3a or 3b, 4 and 5) can be found from Haynes (2013):



2.3. Calculation of Equilibrium Constant of Deprotonation of Ammonium Ions IN Soil Solutions

The spontaneous equilibrium constant of the deprotonation after fertilization was calculated according to Equation (6) (Majer *et al.*, 2004):

$$K = e^{\frac{-\Delta G}{RT}} \quad (6)$$

where, ΔG = the reaction's Gibbs free energy which is the difference between the sum of the standard Gibbs energies of the products (i.e., NH_3 and H_2O) and reactants (i.e., NH_4^+ and OH^-) in the reaction of deprotonation Equation (4). R is the gas constant (8.314 J K^{-1}) and T the absolute temperature ($^\circ\text{K}$).

2.4. Data Analysis

The Statistical Analysis System (SAS) version 9.1 was used for the statistical analysis. The data were analyzed by one-way ANOVA. Results were considered significant at $p < 0.05$. After running the SAS program, the critical ranges ($\text{LSD}_{2,0.05}$) of Duncan's Multiple Range Test were used to identify significantly different means (Hubbard, 2012).

3. RESULTS AND DISCUSSION

3.1. Results

Ammonia volatilization entails the above three steps, which occur after the application of N fertilizer and culminate in gaseous N loss via NH_3 emission from agricultural soils. These three steps are as follows: (1) dissolution of the applied fertilizer in soil solution (Equation 3a or 3b); (2) deprotonation of ammonium (NH_4^+) ions from the dissolved fertilizer (Equation 4) and (3) transformation of aqueous NH_3 into gaseous NH_3 (Equation 5). Each of the three steps influences the rate and extent of NH_3 volatilization from agricultural soils.

Figure 1 presents the differences in Gibbs Free Energy for each of the three steps of NH_3 emission from the two tested soils fertilized with ammonium sulfate and ammonium nitrate at two soil moisture regimes. **Table 1** compared the equilibrium constants of deprotonation of ammonium sulfate and ammonium nitrate applied to the two tested soils with 20% or 80% FC. **Figure 2** shows the cumulative loss of N via NH_3 volatilization.

3.2. Discussion

3.2.1. Change in Gibbs Free Energy of the Three Steps

The change in Gibbs free energy (ΔG) of step 1 (dissolution of the applied NH_4^+ -N fertilizer) was negative and small for both ammonium sources, step 2 (deprotonation of NH_4^+ ions) was negative and large, but step 3 (transformation of aqueous NH_3 into gaseous NH_3) was positive and small. Therefore, steps 1 and 2 are exergonic (proceed spontaneously); but step 3 is endergonic (does not proceed spontaneously). Accordingly, steps 1 and 2 favor NH_3 volatilization, but reduce N use efficiency and worsen air quality. Step 2 is always the dominant driver of NH_3 volatilization. Therefore, any agricultural practice intended to reduce NH_3 volatilization should focus on step 2. Thus, either the avoidance of deprotonation of NH_4^+ ions or the improvement of protonation of NH_3 in the soil solution may greatly decrease the rate of step 3 and reduce net NH_3 volatilization. For example, based on Equation 2 and 5, the value of $-\Delta G$ becomes 90% less if the pH value of the soil solution is changed from 7 to 6. Therefore, a combinational application of N fertilizers and physiologically acidic fertilizers, such as potassium sulfate, may greatly reduce NH_3 volatilization and enhance N use efficiency (Dalling and Green, 1943; Hershey, 1991).

Table 1. Equilibrium constant of deprotonation (K) of NH_4^+ leading to NH_3 volatilization from either $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 from two soils^a at either 80 or 20% Field Capacity (FC) water content

Soil	FC (%)	Equilibrium constant, K	
		$(\text{NH}_4)_2\text{SO}_4$	NH_4NO_3
KGL	80	43	6
	20	131649	310
WSL	80	67	8
	20	243688	489

^aKGL = Krome Gravelly Loam soil; WSL = Warden Silt Loam soil

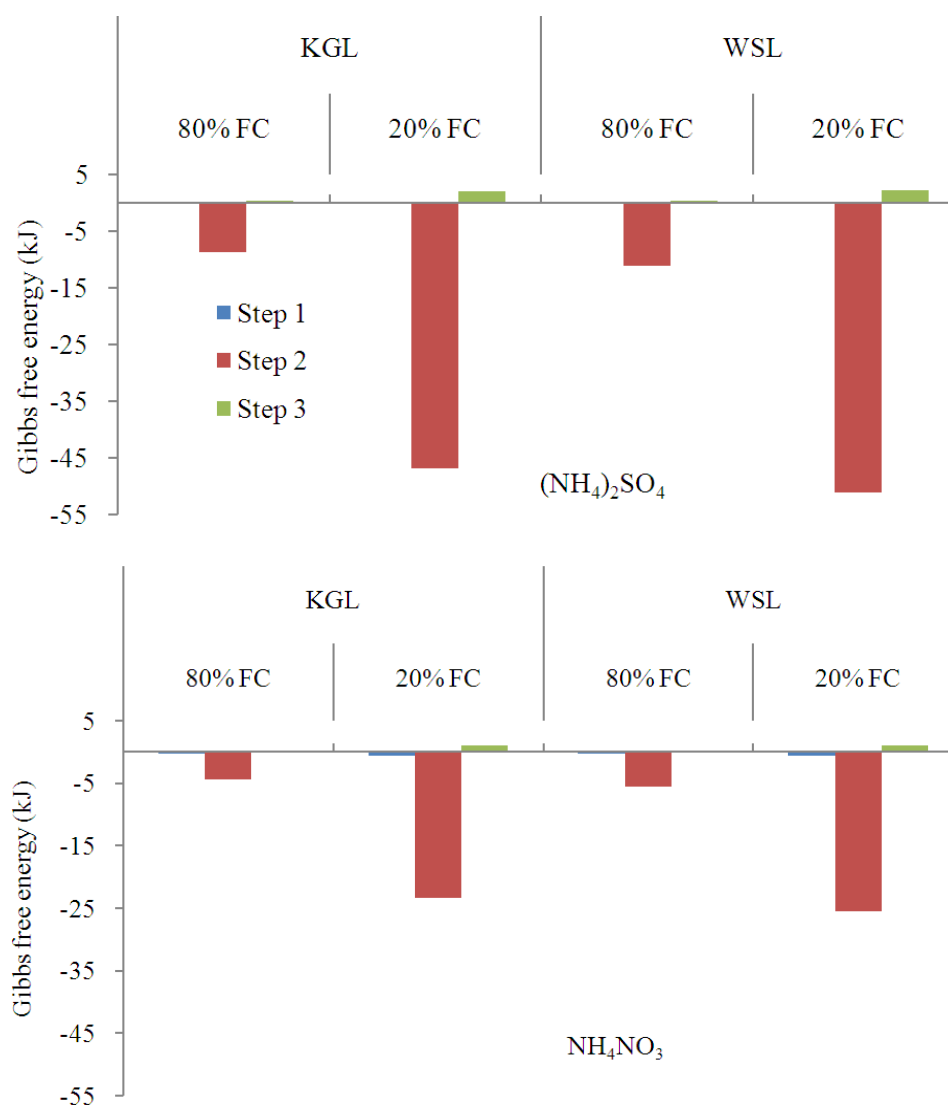


Fig. 1. Differences in Gibbs free energy (ΔG , kilojoules per mole) of the 3 steps involved in ammonia volatilization from ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$] and ammonium nitrate (NH_4NO_3) applied to two agricultural soils at 20% and 80% Field Capacity (FC) at 20°C. Krome Gravelly Loam (KGL) soil from Florida and Walden Silt Loam (WSL) soil from Washington State were used

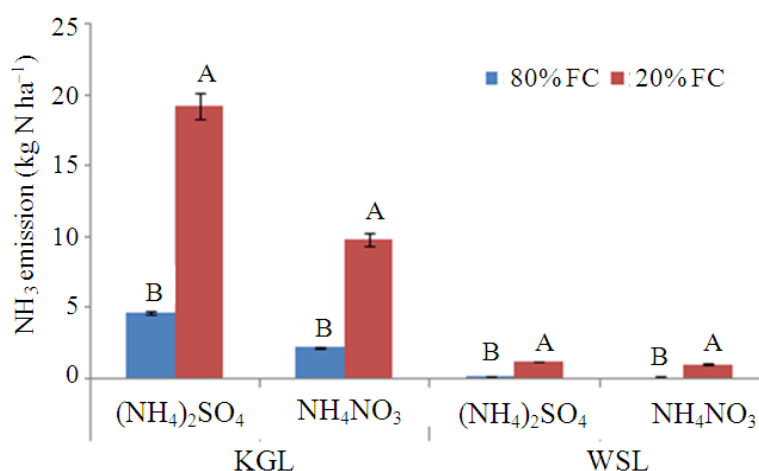


Fig. 2. Cumulative N loss (kg N ha⁻¹) via NH₃ volatilization (28 d at 20°C) from ammonium sulfate [(NH₄)₂SO₄] and ammonium nitrate (NH₄NO₃) applied to Krome Gravelly Loam (KGL) and Warden Silt Loam (WSL) soils at 80 and 20% Field Capacity (FC) soil water regimes

At 20% FC (soil drought), $-\Delta G$ was always 4-to 5-fold greater than that at 80% FC. This suggests that soil drought accelerated the deprotonation of NH₄⁺ ions and enhanced NH₃ emission from both N sources. Deprotonation of NH₄⁺ ions is closely associated with the soil water content. In potato production systems in Florida, intermittent soil droughts occur during the growing season. Global warming may increase the frequency of occurrence of soil droughts (Sheffield and Wood, 2008). Thus, optimal water management is critical for mitigation of NH₃ volatilization (Liu *et al.*, 2007a).

Both (NH₄)₂SO₄ and NH₄NO₃ were applied at the same N rate (75 kg ha⁻¹). However, (NH₄)₂SO₄ dissociates into two fold greater NH₄⁺ ions than that from NH₄NO₃ (Fig. 1). Accordingly, the absolute value of $-\Delta G$ for (NH₄)₂SO₄ was twice that for NH₄NO₃. The magnitude of $-\Delta G$ was dependent on NH₄⁺ concentration.

3.2.2. Equilibrium Constant (K) of Deprotonation of Ammonium Ions in Soil Solutions

The equilibrium constant (K) of deprotonation of NH₄⁺ ions were much greater than 1 across both N sources, soils, as well as soil water regimes (Table 1). This indicates that the deprotonation of NH₄⁺ ions has a high potential across all variables in this study. The K values of (NH₄)₂SO₄ at 20% FC were 3,060- and 3637-fold greater than those at 80% FC, in the KGL and WSL soils, respectively. The corresponding values for NH₄NO₃ were 52-and 61-fold greater.

These data indicate that the concentration of NH₄⁺ ions in the soil solution is a major factor in determining the extent of NH₃ volatilization. Thus, the magnitude of $-\Delta G$ increased with increasing concentrations of NH₄⁺ ions. Both N fertilizers were applied to attain a similar N rate (75 kg ha⁻¹) but the concentration of NH₄⁺ ions in the soil solution of the soil which received (NH₄)₂SO₄ was twofold greater than that for NH₄NO₃. Thus at 20% FC, the K values of (NH₄)₂SO₄ was 425- and 498-fold greater than those of NH₄NO₃ in the KGL and WSL soils, respectively. The corresponding values for 80% FC were 7-and 8-fold. These results imply that dilution of NH₄⁺ ions in the soil solution decreases the absolute value of $-\Delta G$ and can, therefore, reduce NH₃ volatilization.

3.2.3. Nitrogen Loss Via Ammonia Volatilization

Cumulative NH₃ volatilization (28 d) at 20% FC was 4- to 5-fold greater than that at 80% FC in both soils across both N sources (Fig. 2). Soil droughts, which occur frequently during the growing season, in some production regions, increase the concentrations of NH₄⁺ ions in soil solutions.

At the USDA Experiment Site in Paterson, WA in the Columbia River Basin, the alfalfa reference evapotranspiration reached 14 mm d⁻¹ particularly in July and August, 2010 (Fig. 3). Under such evapotranspiration rates, soil drought develops rapidly if water management is inadequate or inappropriate.

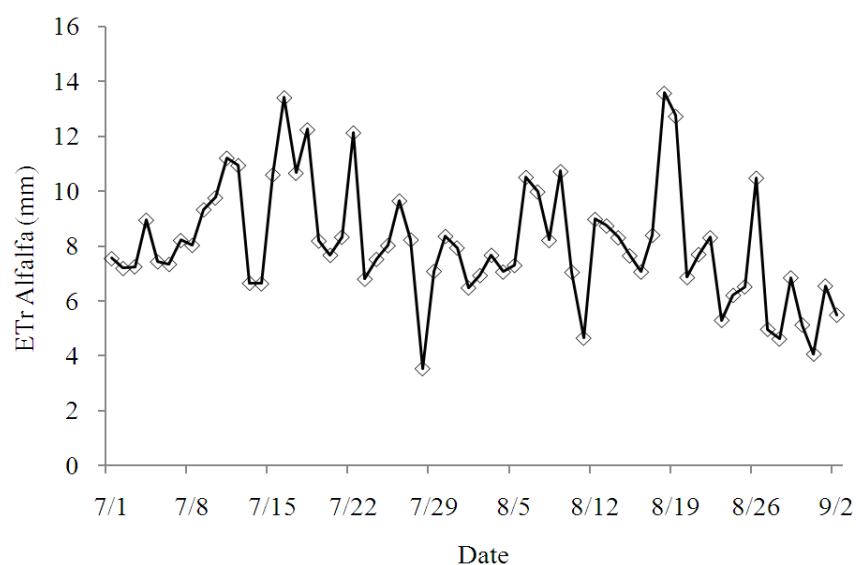


Fig. 3. Alfalfa reference evapotranspiration (mm d^{-1}) at the USDA Experiment Site in Paterson, Washington State during July and September 2010 (<http://weather.wsu.edu/awn.php>)

Global warming is expected to increase evapotranspiration, reduce soil moisture (Zavaleta *et al.*, 2003) and exacerbate the incidence of elevated soil droughts. Soil properties can also significantly affect the NH_3 emissions. For example, soil acidity ($\text{pH} < 6.3$) can reverse the deprotonation of NH_4^+ ions, i.e., protonate NH_3 molecules to form NH_4^+ ions. This mechanism can be exploited by applying physiological acidic fertilizers with NH_4^+ -N fertilizer together to reduce NH_3 volatilization from fertilized soils. Furthermore, soil particles can bind considerable amounts of NH_4^+ ions by chemical, physicochemical, or physical adsorption. In particular, a high cation exchange capacity that favors increasing NH_4^+ adsorption can prevent NH_3 volatilization (Freney *et al.*, 1981). For example, even though the $-\Delta G$ for ammonium fertilizers were greater in the WSL soil than in the KGL soil, net NH_3 volatilization from the former soil was less than that from the latter soil (Fig. 2). The pH and electrical conductivity were both lower for the WSL soil than those for the KGL soil (Liu *et al.*, 2007b).

4. CONCLUSION

Ammonia volatilization from agricultural soils following the application of N fertilizers involves three steps: Fertilizer dissolution; deprotonation of NH_4^+ ions;

and phase transformation of NH_3 . Among the three steps, the first two are spontaneous, i.e., $-\Delta G$, while the third step is not spontaneous, i.e., $+\Delta G$. Step 2, deprotonation of NH_4^+ ions dominates the overall process of fertilizer dissolution leading to NH_3 emission. Step 2 contributes over 95% of $-\Delta G$ of the overall process which culminates in NH_3 emission. The management strategies aimed to reduce NH_3 volatilization should focus on delay or restriction of deprotonation of NH_4^+ ions. Soil drought greatly accelerates deprotonation and, hence, increased N loss via NH_3 emission. The value of $-\Delta G$ in the soil at 20% FC was 5-fold greater than that at 80% FC. Soil drought greatly accelerates NH_3 volatilization from fertilized soils. Potential increases in temperature, a possible outcome of continued global warming, increases evapotranspiration and in turn enhances soil drought that can lead to increased NH_3 volatilization from fertilized soils. Therefore, optimal soil water management is an important strategy to reduce N loss via NH_3 volatilization from cropping systems.

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