Acid Ionization Constant of Ammonia in Silage

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Introduction

Nitrogen losses during ensiling are approximately half the dry matter (DM) losses. Under typical U.S. conditions, there are two mechanisms of loss: nitrate reduction to nitrogen and nitrogen oxide gases and ammonia volatilization. The former mechanism may be important in heavily fertilized or drought-stressed corn and grasses where the crop may have elevated levels of nitrate. However, ammonia volatilization is likely to be the most common mechanism in silages.

The rate of ammonia volatilization in a silo will be determined by the level of air exchange and the pH of the silage. The pH is a factor because volatilization is related to the concentration of unionized ammonia in silage, which is a function of the acid ionization constant (pK) and pH. The pK is simply the pH at which the ionized and unionized concentrations of ammonia are equal.

The objective of the study was to determine the pK of alfalfa and corn silages as a function of temperature.

Methods

Samples of six alfalfa silages and three corn silages were collected from a variety of bunker, tower and bag silos. The DM contents ranged from 22 to 55%. Silage (4 g) was diluted with distilled water to 200 g in a blender jar and macerated for 30 sec. The diluted silage was tranferred to a beaker and placed on a magnetic stir plate. The pH was reduced with HCl to pH 3 or less to remove carbonate. Then the silage was titrated with 0.1 N NaOH to pH 11.5 over approximately 20 min using a peristaltic pump and temperature-compensated pH meter. Temperature and pH were recorded by computer at 15 sec intervals. The pK was determined graphically from the titration curve. Titrations for each silage were performed with and without the addition of NH_4Cl at room temperature, in a hot room (39°C) and in a cold room (5°C). The NH_4Cl improved the accuracy of the pK determination, particularly of the corn silages which had low ammonia contents.

Results

The pKs for ammonia could not be determined in unamended corn silage and some of the alfalfa silages because the buffering of other constituents masked the buffering range of ammonia. However, NH_4Cl addition made it possible to consistently determine the pK for ammonia. The pKs from the titrations of the NH_4Cl-amended alfalfa and corn silages are shown in Fig. 1. There were no significant differences in the results between corn and alfalfa. There was greater variability in the alfalfa results due to difficulties in rapidly mixing the titrant with the more fibrous alfalfa slurries. At lower temperatures, the pKs were similar to those for ammonia in water. At higher temperatures, pKs in the silages were higher than those for water.

Conclusions

Based on work in animal manures, we would anticipate that the pKs in undiluted silages would be raised slightly relative to the values that we obtained here. Nevertheless, these results will be useful in helping to estimate both the loss of nitrogen from silage as well as air exchange that occurs in silos under field conditions.

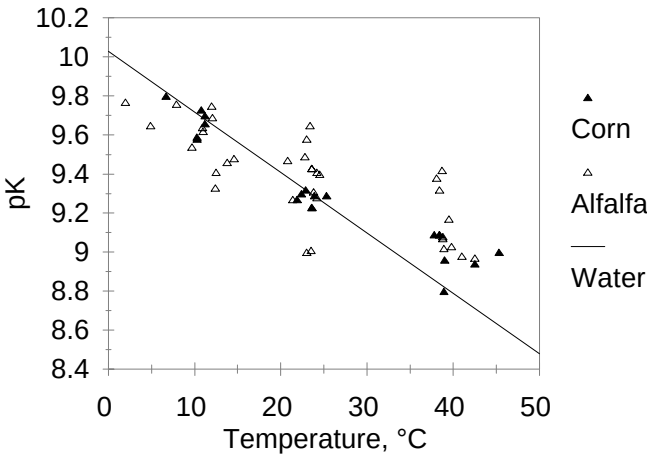

Figure 1. The pK of ammonia in diluted alfalfa and corn silages as compared with that of ammonia in water.