LETTERS TO THE EDITOR

Comments on “Modeling Soil Response to Acidic Deposition in Nonsulfate Adsorbing Soils”

The recently proposed model of soil acidification by Bloom and Grigal (1985) in the Journal of Environmental Quality contains an approach that incorrectly describes soil buffering relationships. They assume the formula for a weak acid (the Henderson-Hasselbach equation) can be applied to soils. This formula predicts very strong buffering around a soil’s “pK” and very poor buffering at low and high base saturations. However, soils do not behave as particular weak acids. They behave as if they contain a vast number of weak acid groups, each with its own pK. Thus, the relationship between pH and base saturation is linear for most soils within the pHs range of 4 to 6.5 (Magdoff and Bartlett, 1985). The use of the “weak acid” model, \( \text{pH} = a + b \log \left[ \text{BS}/(1 - \text{BS}) \right] \), is the real reason that the authors obtained such a poor relationship between the predicted and actual titration curve for the lowest BS soil (see Fig. 1d in their article). The weak acid formula will vastly underestimate the buffering abilities of a soil at low BS (far from its supposed pK) compared with buffering at a BS corresponding to a pH near the soil’s pK.

One of the problems that has mislead soil chemists is that since soils exhibit weak acid characteristics, it was thought they should behave like specific weak acids. In addition, it is possible to obtain a fairly good correlation for the equation \( \text{pH} = a + b \log \left[ \text{BS}/(1 - \text{BS}) \right] \). However, this good correlation occurs because:

1. There is a very good linear correlation between pH and BS.
2. By calculating BS/(1 – BS) you are really just transforming BS to another parameter which has a curvilinear relationship with BS.
3. When pH is correlated with \( \log \left[ \text{BS}/(1 - \text{BS}) \right] \) it is actually being correlated with a parameter which is highly correlated with BS. Therefore, the fact that pH and \( \log \text{BS}/(1 - \text{BS}) \) are correlated in no way implies that when soils are acidified, they actually behave as a particular weak acid.

Thus, the myth is continued that soils are well buffered around a particular pK. When data from Magdoff and Bartlett (1985) are recalculated to conform to a “Henderson-Hasselbach” curve, the pK is 5.7. This indicates that a soil around pH 5.7 is four to five times as well buffered as soil at about pH 4 to 4.5. We have found that this has nothing to do with the real situation when individual soils are actually titrated. Most soils are equally well buffered within the whole range between pH 4 and 6.5. Thus, a very strongly buffered below 4 and

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REFERENCES


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We welcome the questions of Magdoff and Bartlett concerning our paper. We are certainly not guilty of saying soils are most well buffered around a pH value defined by the extended Henderson-Hasselbach equation. The buffering mechanism at low pH is aluminum described by Eq. [2] (Bloom and Grigal, 1985). This dominates over the buffering described by the Henderson-Hasselbach equation. This is shown in Fig. 1D and Fig. 2 (Bloom and Grigal, 1985). We included a component for the precipitation of CaCO3 that would show the buffering above pH 6.8 that Magdoff and Bartlett (1985), but our model was for nonacid soils. This carbonate buffering is described by the extended Henderson-Hasselbach equation. The importance of aluminum buffering in low pH carbonate buffering in nonacid soils is well known (Ulrich, 1983).

We are also not guilty of using the extended Henderson-Hasselbach equation without empirical or theoretical foundation. We agree with Magdoff and Bartlett (1985) that the buffering in acid soils is due to soil organic matter mentioned in our paper (Bloom and Grigal, 1985). Data for humic acids and peats fit the extended Henderson-Hasselbach equation. The empirical foundation for this was reviewed by Bloom (1981). Most are more complex than a fraction of extracted organic matter, and we found that the apparent pK, values and n values lower in mineral soils than in peats. The basic approach, however, is well justified.