

Base saturation and cation exchange in forest soils: a history of concepts and problems

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INTRODUCTION

Cation exchange was one of the first areas of research in soil science, dating from the mid-1800s. A number of our current concepts of cation exchange and 'base' cation saturation have not changed in well over a century. In those times, neither exchangeable Al nor variable charge was generally recognized.

The early concepts, and the methods developed to measure them, are not readily transferrable to acid, high-carbon forest soils. The primary source of charge in these soils is derived from organic carbon (Kalisz and Stone 1908, Johnson 2002) and the retention of cations, especially Al, cannot be easily modeled by simple exchange phenomena.

Early work on cation exchange

- ▶ 'As early as 1819, the Italian chemist Gazzeri showed that clay decolourates liquid manure and keeps back its soluble substances which gradually are delivered to the plants.' [from Wiklander's 1946 review]
- ▶ Way (1850, 1852) showed rapid 1:1 exchange of NH_4^+ for Ca^{2+} in a variety of materials, including chalky soil.
- ▶ Ramann (1911) may have been the first to observe that acid soils are unsaturated with respect to bases.

Exchangeable Hydrogen

- ▶ The missing cation in acid soils was thought to be exchangeable hydrogen (not Al).
- ▶ Researchers noticed that even with continued leaching, many soils would still release H^+ (i.e. continue to acidify the leachate).
- ▶ This was interpreted as difficult-to-remove exchangeable H^+ .
- ▶ Today we would ascribe this to slow hydrolysis of functional groups (e.g. on OM) and metals (e.g. aluminum).

Acidified leachate (oversimplified schematic)

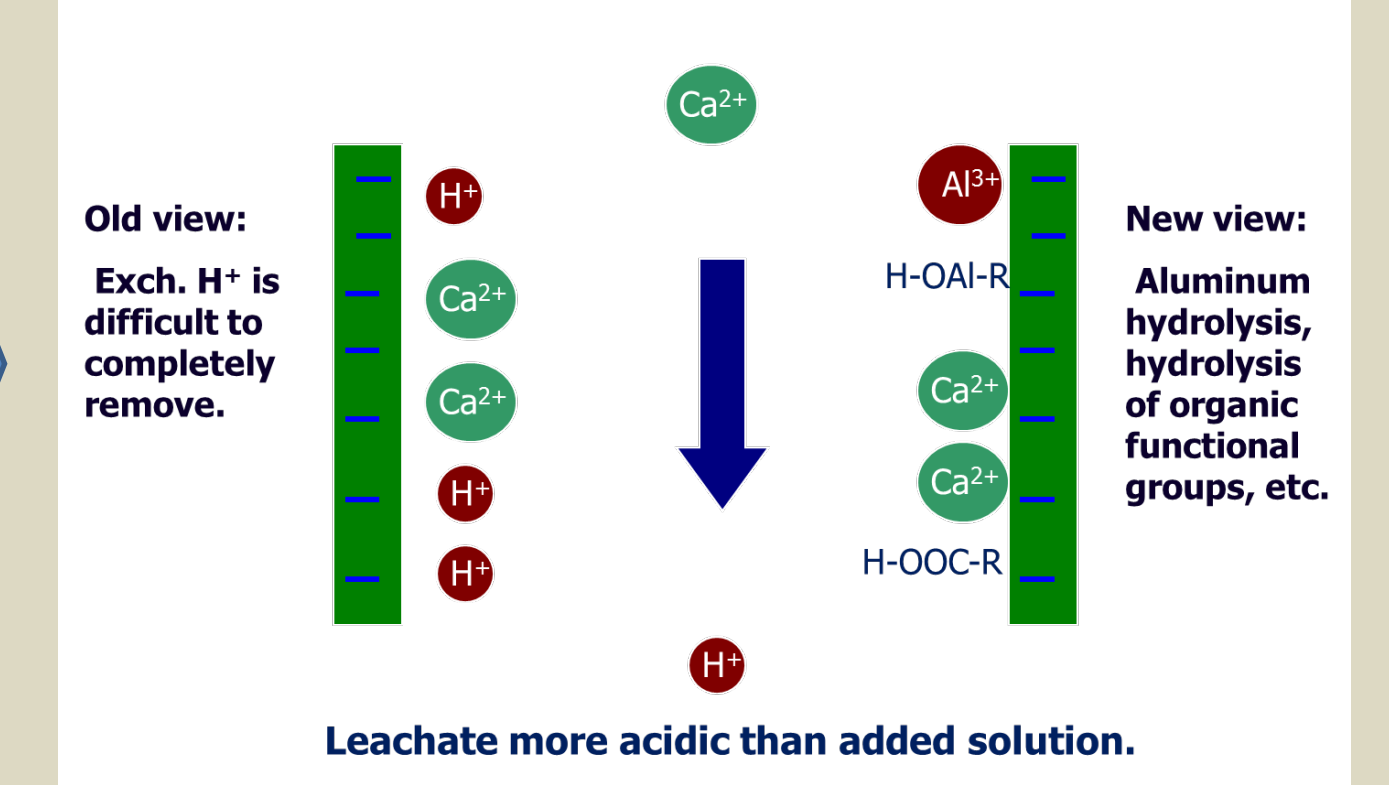


Figure 1. Is acidification of leachate due to exchangeable H^+ or hydrolysis?

Buffered CEC extractants

- ▶ Because of the perceived difficulties with removing exch. H^+ , buffered reagents were proposed.
- ▶ pH 7 NH_4 -acetate: Schollenberger (1927) in **Science!**
- ▶ pH 8.2 BaCl_2 -triethanolamine: Mehlich (1939).
- ▶ We now know that these buffered CEC methods will give erroneously high values in acidic forest soils where charge is dominated by OM.

Effective CEC vs. buffered CEC (oversimplified schematic)

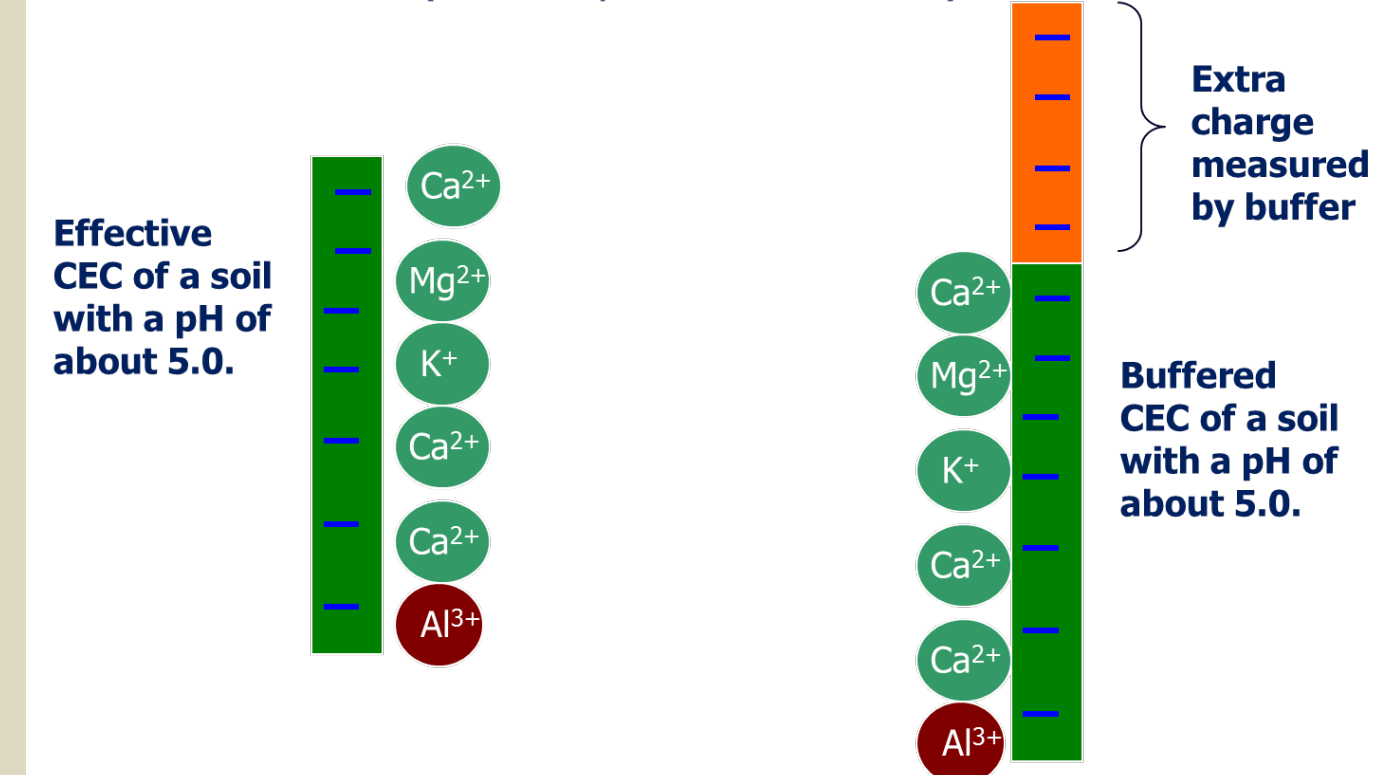


Figure 2. CE_{CE} vs. CEC with buffered extractant.

Hello Al, Good-bye H

- ▶ From a 1928 symposium: The Application of Base Exchange Methods (annual meetings of the American Society of Agronomy): 'Acid soils do not contain an appreciable amount of exchangeable Fe and Al' (Parker 1929).
- ▶ But exchangeable Al was finally widely accepted in the 1950s (even though it was reported as early as 1904).
- ▶ For example, Coleman et al. (1959) found that 'Al predominated' acid soils of the North Carolina piedmont and 'there were negligible amounts of electrostatically-bonded H in any soil' studied (acidic or not).

Some Definitions

- ▶ CEC: Cation Exchange Capacity
 - CE_{CE}: effective CEC measured at current pH
 - CE_{CEbuf}: projected CEC measured with a buffered solution (either pH 7.0 or 8.2)
- ▶ Base Cation: really should be 'base-forming' cation
 - calcium, magnesium, potassium
- ▶ BS: Sum of base cations / CEC

Variable Charge

- ▶ Most early work was done on soils high in clay minerals with little pH-dependent charge (structure of clays was unknown).
- ▶ [Sante Mattson, working both in New Jersey and Sweden, published a long series on the 'laws of soil colloidal behavior' in Soil Science (Mattson 1929-1937) that clearly showed variable charge]
- ▶ With the demise of exch. H^+ in the late 1950's, pH-dependent charge became widely recognized.
- ▶ Important in soils high in OM and/or Fe, Al oxides

But can we find it in forest soils?

- ▶ Even though it is easy to demonstrate in the lab, it is difficult to actually find forest soils that show a pH effect on CEC.
- ▶ Acid-precip impacted Swedish beech forest soils developed a pH gradient with distance from tree trunk and lower pH soils had lower charge per unit C (Fig. 3a). This was expected.
- ▶ However, most studies in the US found results similar to Fig. 3b and c, in which there was little or negative change in charge per unit C with higher pH. The concentration of organically-bound (non-exchangeable) Al increases but not the CEC. This was not expected.

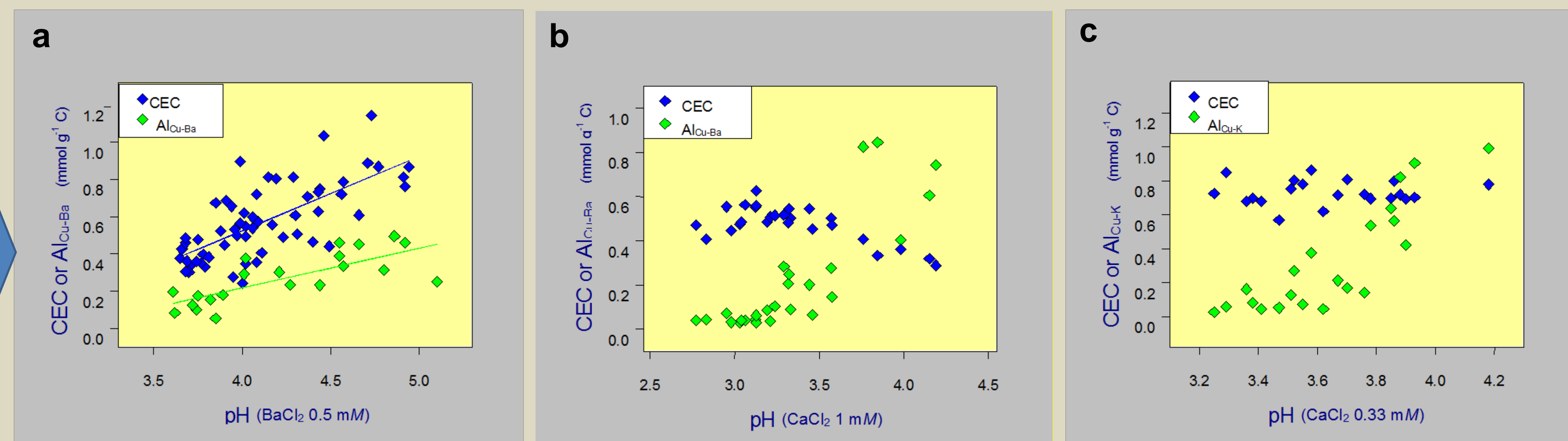


Figure 3. Soil pH vs. CEC per unit C (blue) and organic-Al per unit C (green). The latter was calculated as the difference between Cu-extractable and Ba-extractable Al. In soils that have not been intensely acidified (b and c), CEC does not decrease at low pH but organic Al does. Study 'a' was in a highly acid precipitation impacted beech forest in southern Sweden (Matschonat and Falkengren-Grerup 2000). Study 'b' was in the Brush Brook watershed, Vermont (Ross and Bartlett 1995). Study 'c' was of spruce-fir soils in the northeast USA (David and Lawrence 1996).

Al as a base cation

- ▶ The pK for the first hydrolysis step of Al^{3+} is 5.0. Thus, at pH 4.0 well over 90% of ionic Al is found as Al^{3+} .
- ▶ Therefore, in highly acidic forest soils (usually high-OM surface horizons), Al is not an acidic cation—it does not hydrolyze.
- ▶ In fact, adding Al^{3+} can raise the pH by displacing H^+ .
- ▶ The most acidic forest soils are usually low in Al and high in OM.

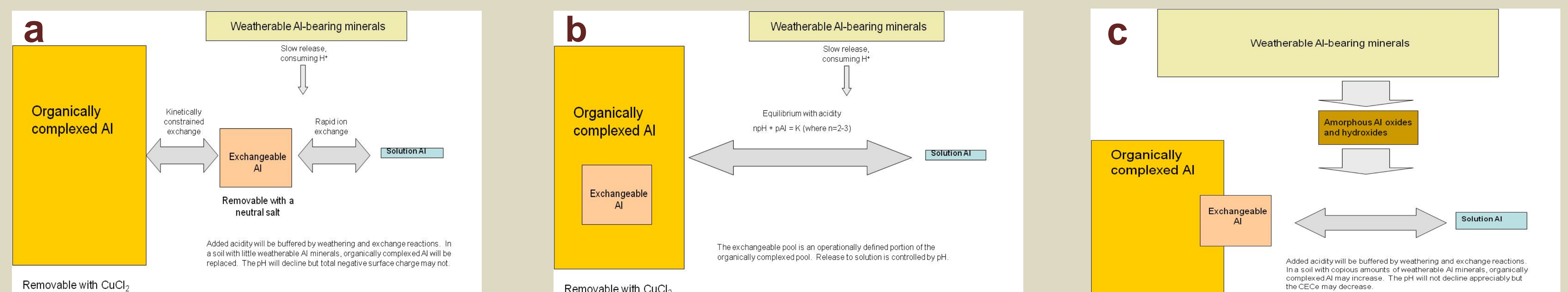


Figure 4. Three models of Al behavior in acid forest soils. a) In this model for low pH high-OM horizons, the organically-complexed and exchangeable Al pools are operationally defined but considered distinct. b) Alternate but more realistic schematic of Al behavior in very acid, high-OM forest soils. The organically-complexed and exchangeable Al pools are indistinguishable. c) The more traditional view of Al behavior that occurs in higher pH (about 4.5), and lower-OM, forest soils. Weatherable Al-bearing minerals buffer inputs of acidity and provide a plentiful supply of exchangeable and organically complexed forms.

Base Saturation:

- ▶ The concept of base saturation was developed during the time period when neither exchangeable Al nor pH-dependent charge was recognized.
- ▶ Higher BS status theoretically demonstrates less acidification. This interpretation will hold true with soils in the pH range of Al hydrolysis but not below.
- ▶ For example, an Oa horizon can have a pH of 3.5 and a BS of 75%.
- ▶ Base cation saturation calculations in the pH range below ~4.5 do not provide a useful metric and, in fact, pH is better modeled if Al^{3+} is considered a base cation.
- ▶ But pH may not be as meaningful as Al saturation.

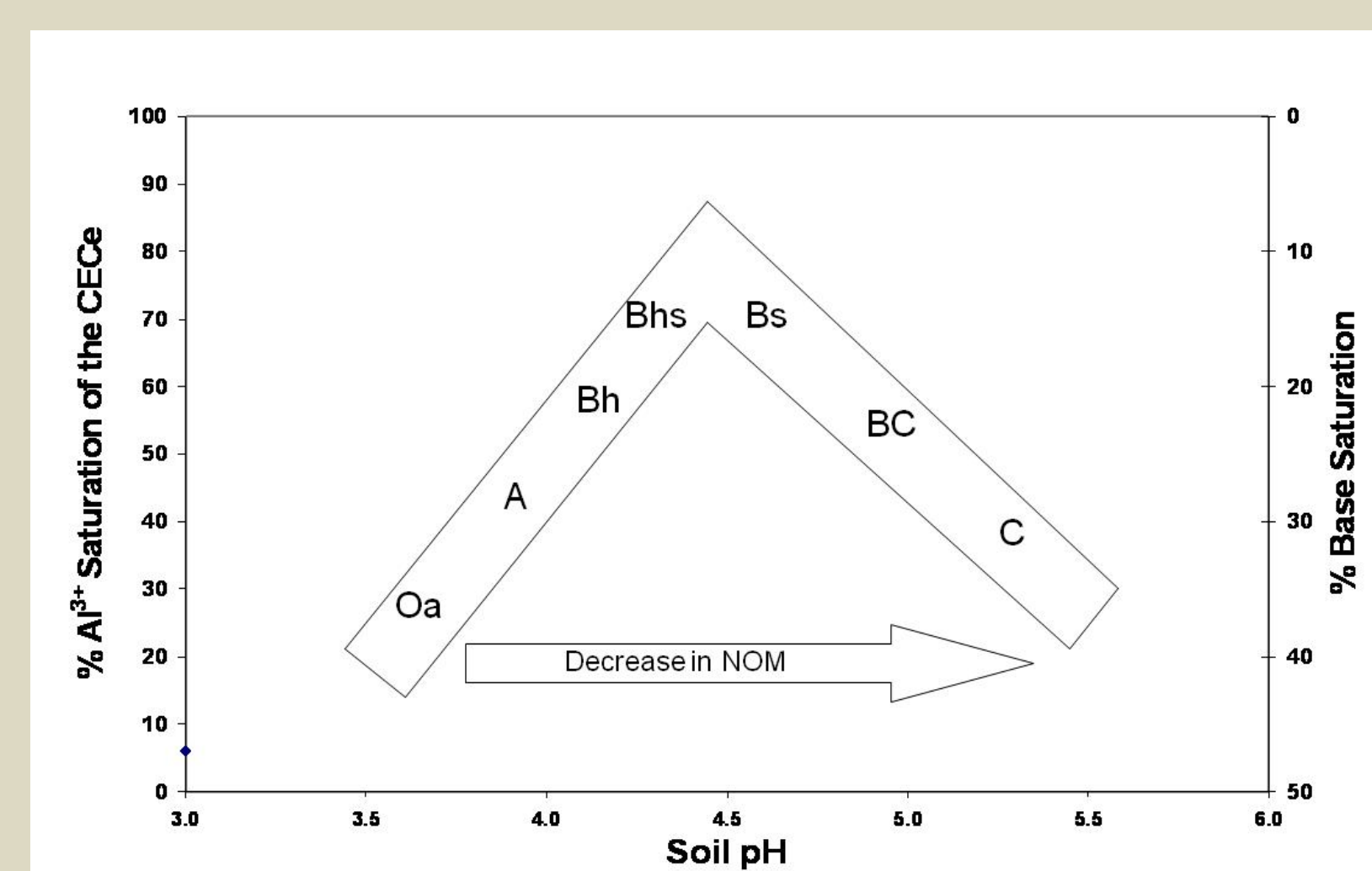


Figure 5. Generalized relationship between exchangeable Al saturation of the CE_{CE} and pH in a forested Spodosol (Ross et al. 2008). Low saturation will be found both in low-pH high-carbon surface horizons and high-pH low-carbon C horizons.

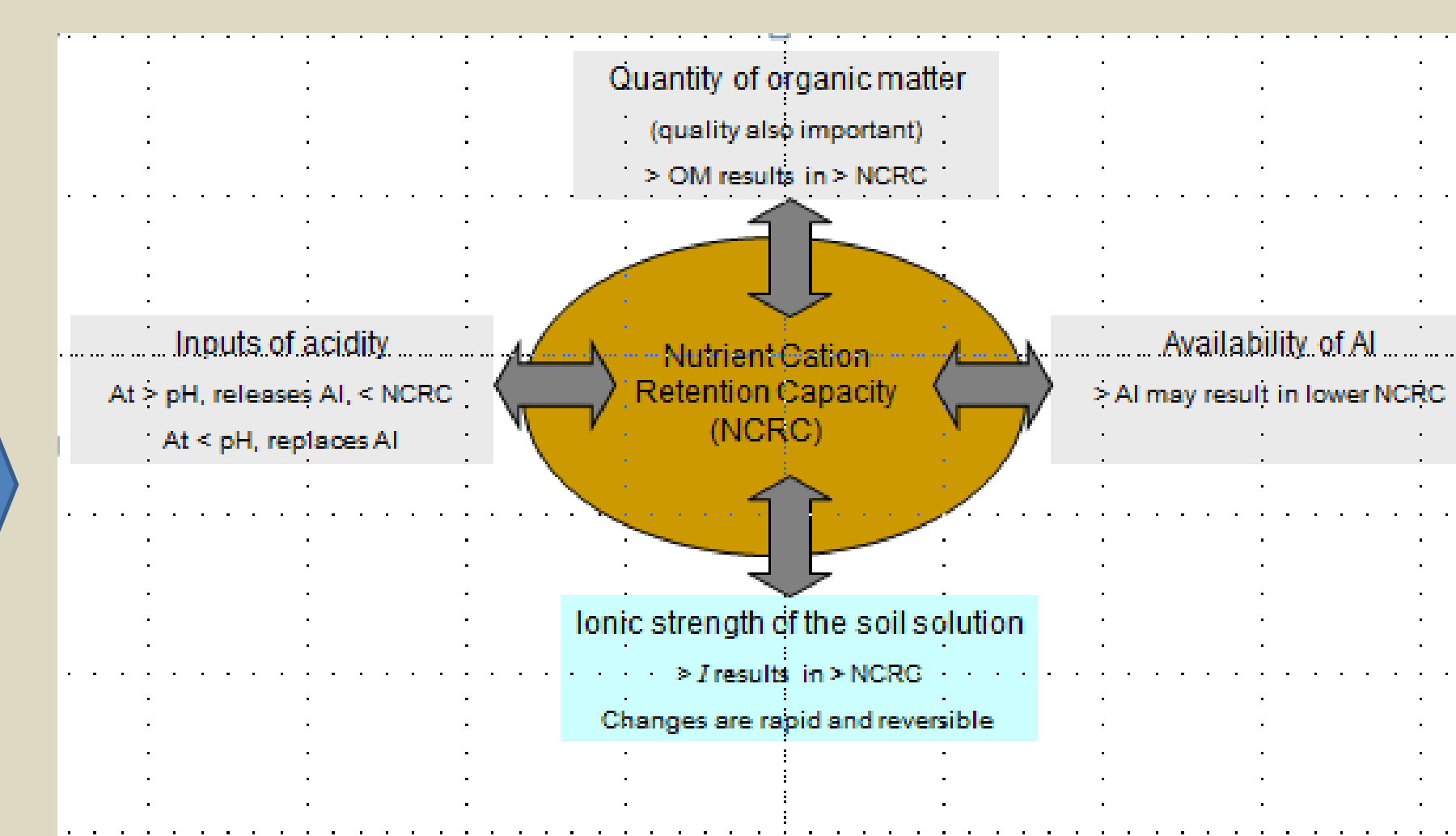


Figure 6. The major factors influencing nutrient cation retention in acid, high-OM forest soils (from Ross et al. 2008). Changes in the amount of OM (e.g. increasing or decreasing forest floor) will also have an effect on BS and CEC.

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