Aquaculture 434 (2014) 282–287

Contents lists available at ScienceDirect

Aquaculture

journal homepage: www.elsevier.com/locate/aqua-online

A bicarbonate titration method for lime requirement to neutralize exchangeable acidity of pond bottom soils

Yangxue Han, Claude E. Boyd *, Rawee Viriyatum

School of Fisheries, Aquaculture and Aquatic Sciences, Auburn University, 203 Swingle Hall, Auburn, AL 36849 USA

ARTICLE INFO

Article history:
Received 8 July 2014
Received in revised form 22 August 2014
Accepted 25 August 2014
Available online 30 August 2014

Keywords:
Lime requirement
Pond liming
Pond bottom soils
Water quality
Bottom soil management

ABSTRACT

The lime requirement of ponds can be determined by direct titration with standard sulfuric acid of the amount of alkalinity neutralized by the exchangeable acidity displaced from a bottom soil sample equilibrated with a solution of 1.0 N in potassium ion and 0.04 N in bicarbonate (2 mg $CaCO_3$ equivalent mL^{-1}). This procedure, called the K-bicarbonate method here, provided precise estimates of lime requirement that were 9.6% to 27.2% (average = 12.9%) greater than those obtained by the method currently recommended for use on pond soils. It is likely that the K-bicarbonate method neutralizes more of the exchangeable acidity in pond bottom soil samples than does the current method recommended for pond bottom soils and thereby provides a more reliable estimate of lime requirement. Moreover, the K-bicarbonate method does not require a hazardous chemical, a mechanical shaker, or a pH meter as does the current method for pond lime requirement. The cost per analysis also is cheaper by the K-bicarbonate method than with the method currently recommended for pond soils.

1. Introduction

Agricultural limestone or other liming materials often are applied to sportfish ponds in the United States and to food fish and crustacean ponds worldwide to neutralize bottom soil acidity and maintain an adequate concentration of total alkalinity in water (Boyd and Tucker, 2014). As there was not a reliable way of determining the amount of liming material needed in ponds, Boyd (1974) slightly modified the Adams–Evans (AE) buffer solution method (Adams and Evans, 1962) often used for establishing liming rates for agricultural crop soils in the southeastern United States for application to sportfish ponds. However, because of regional differences in soil properties and the need for greater total alkalinity in ponds for culture of food fish and crustaceans than in sportfish ponds, the Boyd (1974) modification for ponds of the AE lime requirement method was not applicable outside the southeastern United States. Pillai and Boyd (1985) made changes in the lime requirement method for sportfish ponds that allows its use for pond soils worldwide irrespective of their properties provided they are not pyritic (potential or active acid-sulfate soils).

The lime requirement procedure for sportfish ponds was shown to consistently estimate adequate liming material to raise the pH of bottom soil to 6.0 and total alkalinity to 20–30 mg L^{-1} (Boyd, 1974), and it has been widely used in the southeastern United States. The more general method of Pillai and Boyd (1985)—called the PB method henceforth—raised soil pH in ponds to 7.0–7.5 and provided total alkalinity of 40–50 mg L^{-1}. However, the PB method has not been adopted widely; its use is hampered by the necessity for a specialized and hazardous chemical (*p*-nitrophenol or 4-nitrophenol) and a pH meter capable of measuring to the nearest 0.01 pH unit. There are several other buffer methods in addition to the AE method for use on agricultural soils that could be modified for ponds (Godsey et al., 2007; Lierop and Westerman, 1990; Pagani and Mallarino, 2011; Shoemaker et al., 1961), but the determination of lime requirement by buffer methods requires an accurate measurement of the pH change in the buffer solution caused by the soil sample.

The principle of buffer methods such as the AE method and its modifications for ponds is rather simple. Potassium (K^+) or some other basic cation in the buffer solution exchanges for acidic ions—mainly aluminum ion (Al^{3+})—held on cation exchange sites in the soil as illustrated below:

$$\text{Soil–Al}^{3+} + 3K^+ \rightleftharpoons \text{Soil–}3K^+ + Al^{3+}. \quad (1)$$

Aluminum ion is displaced from the soil and hydrolyses in solution resulting in acidity (H^+):

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3\downarrow + 3H^+. \quad (2)$$

Hydrogen ion released by hydrolysis causes the pH of the buffer to decline in direct proportion to the quantity of exchangeable aluminum ion and other acidic ions (H^+ and Fe^{3+}) on the soil. By measuring the pH change of the buffer, the amount of exchangeable acidity in the soil can be determined.

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* Corresponding author. Tel.: +1 334 844 4078.
E-mail address: boydce1@auburn.edu (C.E. Boyd).

http://dx.doi.org/10.1016/j.aquaculture.2014.08.031
0044-8486/

The pH of soil is related to its base unsaturation that is the ratio of exchangeable acidic ions to the cation exchange capacity (CEC) of the soil (Boyd, 1995). If the graphical relationship of base unsaturation to pH is obtained for soils in a particular region, the base unsaturation at any given pH may be determined (Adams and Evans, 1962). The pH change of the buffer provides an estimate of the exchangeable acidity of the soil, and the amount of exchangeable acidity that must be neutralized to give a particular pH—and a specific base unsaturation—may be calculated:

$$\mathrm{EA_n} = \mathrm{EA_t} \times \frac{\mathrm{BUS_i}}{\mathrm{BUS_i} - \mathrm{BUS_d}} \tag{3}$$

where $\mathrm{EA_n}$ = exchange acidity to be neutralized (mEq kg^{-1}); $\mathrm{EA_t}$ = total exchangeable acidity estimated from pH change in the buffer (mEq kg^{-1}); $\mathrm{BUS_i}$ = initial base unsaturation; $\mathrm{BUS_d}$ = desired base unsaturation for desired soil pH. The quantity $\mathrm{BUS_i} - \mathrm{BUS_d}$ represents the fraction of $\mathrm{EA_t}$ that must be neutralized to provide the desired soil pH.

The acidity to neutralize ($\mathrm{EA_n}$) can be converted to a liming rate (mg $CaCO_3$ kg soil^{-1}) by multiplying by a factor of 50 mg $CaCO_3$ mEq^{-1}. The results may be expanded for the weight of soil to be limed to give a lime requirement. In agriculture, the lime requirement typically is reported as the amount of calcium carbonate necessary to raise the pH of the upper 15-cm layer of soil that weighs about 2,240,000 kg ha^{-1} to the desired pH (Brady and Weil, 2008). The acid-neutralizing value of liming materials in percentage $CaCO_3$ (pure $CaCO_3$ = 100%) must be known in order to adjust the lime requirement to a liming rate for the particular liming material to be applied (Boyd and Tucker, 2014).

Agricultural crops differ in pH preference, and buffer methods allow liming rates necessary to attain specific soil pHs. In pond aquaculture, there is no known reason to attain a specific pH in the bottom soil. The objective is to increase soil pH and allow greater total alkalinity in the water (Boyd, 1995). The PB method was designed to neutralize a large amount of exchangeable acidity and lower base unsaturation as much as possible. This approach has a considerable advantage because a graphical relationship between base unsaturation and pH of soils is not needed. The weight of pond soils is typically less than that of agricultural soils; the average dry weight of the 1 ha × 15 cm layer of pond soil is about 1,500,000 kg ha^{-1} (Boyd and Cuenco, 1980; Boyd et al., 2010).

The basis for the new lime requirement method proposed and tested in the present study involves the use of a potassium chloride-potassium bicarbonate solution rather than the buffer solution containing *p*-nitrophenol of the AE (and PB) methods. The concentration of potassium ion in the solution for the proposed method (henceforth called the K-bicarbonate method) is almost twice that of the buffer solution for the PB method to displace as much exchangeable aluminum ion from the soil sample as possible by exchange for potassium. The solution for the K-bicarbonate method is 0.04 N in bicarbonate (equal to 2 mg mL^{-1} total alkalinity as $CaCO_3$ equivalent). The principle of the method is to displace aluminum ion by potassium ion (as in the AE and PB methods). However, in the K-bicarbonate method, hydrogen ion from hydrolysis of aluminum ion displaced from soil will neutralize bicarbonate, and the decrease in the total alkalinity of the solution—that can be measured by acidimetry—allows a direct estimate of the amount of liming material (as $CaCO_3$ equivalent) necessary to neutralize soil acidity and lower base unsaturation as much as possible. The pH of pond bottom soils has a very low base unsaturation that is typically 7.0 to 7.5 (Pillai and Boyd, 1985).

2. Materials and methods

2.1. Soil samples

Fifteen soil samples (5 cm diameter × 15-cm-deep cores) for use in this study were collected from ponds on the E.W. Shell Fisheries Center (SFC) at Auburn University using a procedure described by Munsiri et al. (1995). Thirty samples from sites representing major physiographic regions and soil groups in Alabama were available from a previous study (Ou, 2013). The soils from the SFC were dried in a mechanical oven at 60 °C and pulverized to pass a sieve with 0.85-mm apertures—the same procedure that was used for the other samples. Dry samples were stored in plastic bags until used in analyses.

The pH of all soil samples was determined in 1:1 mixtures of dry pulverized soil and distilled water (Thunjai et al., 2001). The organic carbon concentration was also determined by sulfuric acid-potassium dichromate digestion (Walkley–Black method) described by Nelson and Sommers (1982).

2.2. Proposed K-bicarbonate lime requirement method

2.2.1. Analysis

1. Prepare a solution 1.0 N in potassium ion and 0.04 N in bicarbonate (2 mg $CaCO_3$ equivalent mL^{-1}) by diluting 71.6 g L^{-1} potassium chloride (KCl) and 4.044 g L^{-1} potassium bicarbonate ($KHCO_3$) to 1 L with distilled water.
2. Mix 20.0 g of dry, pulverized soil sample and 40.0 mL of the bicarbonate solution in a 250 mL Erlenmeyer flask. Place on an oscillating platform shaker (200 rpm) for 30 min.
3. Remove the flask from the shaker and let it stand for particles to settle. Filter the supernatant through a Whatman No. 1 filter paper.
4. Pipette 5.00 mL of the filtrate into a 250 mL beaker and dilute to 50.0 mL with distilled water. Titrate to the methyl orange endpoint with 0.02 N sulfuric acid (H_2SO_4).

2.2.2. Calculation of lime requirement

1. The initial $CaCO_3$ equivalence of the bicarbonate solution is:

$$I_{\mathrm{CaCO_3}} = (V)(C) \tag{4}$$

where $I_{\mathrm{CaCO_3}}$ = initial $CaCO_3$ equivalence of the solution (mg $CaCO_3$); V = volume of bicarbonate solution mixed with soil sample (mL); C = concentration of bicarbonate solution (mg $CaCO_3$ mL^{-1}).

2. The final $CaCO_3$ equivalence $\left(F_{\mathrm{CaCO_3}}\right)$ of the bicarbonate solution is calculated from titration data:

$$F_{\mathrm{CaCO_3}} = (N)(T)(50)\,\frac{V}{v} \tag{5}$$

where $F_{\mathrm{CaCO_3}}$ = final $CaCO_3$ equivalence of the solution (mg $CaCO_3$); N = normality of sulfuric acid (mEq mL^{-1}); T = titration volume for sulfuric acid (mL); 50 = mg $CaCO_3$ mEq^{-1}; v = volume of aliquot of the filtrate of the soil–bicarbonate mixture taken for titration (mL).

3. Estimate the $CaCO_3$ equivalence of the sample:

$$S_{\mathrm{CaCO_3}} = \left(I_{\mathrm{CaCO_3}} - F_{\mathrm{CaCO_3}}\right)\frac{1,000}{W} \tag{6}$$

where $S_{\mathrm{CaCO_3}}$ = sample $CaCO_3$ equivalence (mg $CaCO_3$ kg^{-1}); 1,000 = mg kg^{-1}; W = weight of soil sample (g).

4. Calculate the lime requirement of the pond bottom soil. The upper 15 cm of soil within which lime typically reacts has an average weight of 1,500,000 kg ha^{-1}; thus the factor relating $S_{\mathrm{CaCO_3}}$ to lime requirement is based on the relationship that 1.0 mg $CaCO_3$ kg^{-1} is equivalent to 1.5 kg $CaCO_3$ ha^{-1}:

$$\mathrm{LR} = S_{\mathrm{CaCO_3}} \times 1.5 \tag{7}$$

where LR = pond bottom soil lime requirement (kg ha^{-1}).