

Short communication

Liming with CaCO₃ or CaO affects aggregate stability and dissolved reactive phosphorus in a heavy clay subsoil

Gizachew Tarekegn Getahun^{a,*}, Ararso Etana^a, Lars Juhl Munkholm^b, Holger Kirchmann^a

^a Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, SE-750 07 Uppsala, Sweden

^b Aarhus University, Faculty of Technical Sciences, Department of Agroecology, Research Centre Foulum, P.O. Box 50, DK-8830 Tjele, Denmark

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ABSTRACT

A 22-month incubation experiment was conducted to study the effect of lime on clay dispersion, wet aggregate stability (WAS) and dissolved reactive phosphorus (DRP), using a heavy clay subsoil with an initial pH of 7.0 and 7.3 g kg⁻¹ of soil organic carbon. Lime was applied to achieve soil pH values of 7.5, 8 and 8.4. Clay dispersion decreased linearly with increased pH (corresponding to an increase in lime amount) for both lime types ($R^2 = 0.44$ for CaO; $R^2 = 0.53$ for CaCO₃, $P < 0.05$), with a decrease of 2–16 % (CaO) and 3–17 % (CaCO₃) compared with the control.

Both WAS and DRP followed piece-wise linear functions, with an increase and peak around pH 7.5–7.8, and a decline at higher pH (WAS: $R^2 = 0.73$ for CaO, $R^2 = 0.68$ for CaCO₃, $P < 0.001$; DRP: $R^2 = 0.84$ for CaCO₃, $R^2 = 0.33$ for CaO, $P < 0.001$). Wet aggregate stability increased on average by 13 % and 11 % at the lowest and intermediate levels, respectively, compared with the control. At the highest lime application rate, WAS was 6 % (CaO) and 8 % (CaCO₃) lower than in the control. These differences were probably caused by changes in electrical charge and in concentrations of soluble calcium and dissolved organic carbon (DOC) as the pH increased. More studies are needed to understand the processes in detail and to draw conclusions that are more robust.

1. Introduction

Subsoil, commonly below the ploughing depth, often limits root growth due to compaction or poor soil structure. Thus, the availability of nutrients and subsoil water to crops is hindered, thereby causing reductions in crop yield. Established management strategies to ameliorate subsoil problems are limited (Batey, 2009; Kautz et al., 2013). However, using available management options, efforts have been made to ameliorate subsoil constraints to limit the negative effects on root growth and crop yield (Gill et al., 2008). One such management option is the application of lime materials to the subsoil.

Lime is widely used as an amendment to counteract soil acidification. A further purpose with liming soil is to promote soil aggregation and increase soil structural stability (Gardner and Garner, 1953; Goulding et al., 1989). Improvement of soil structure and workability by liming has often been found to be effective at pH below 7.5 (Richards, 1954; Valzano et al., 2001) and in soils with high clay content and high cation exchange capacity (Frank et al., 2020; Keiblinger et al., 2016). Liming initiates a series of chemical processes, including ion exchange, flocculation and pozzolanic reactions (Mallela et al., 2004). The theory is that

addition of lime increases the concentration of calcium ions causing compression of diffuse double layer and flocculation (Ghobadi et al., 2014; Haynes and Naidu, 1998), resulting in the formation of micro-aggregates (Grant et al., 1992; Six et al., 2004).

Liming materials include carbonates, oxides and hydroxides of calcium (Ca), which differ in their effectiveness in improving soil structure (Goulding, 2016; Greipsland et al., 2014). Calcium oxide (CaO) dissolves quickly and the calcium ions released bind to soil particles and enhance flocculation, forming micro-aggregates in soils with high clay content and cation exchange capacity (Keiblinger et al., 2016). Calcium hydroxides are oxide materials that are mixed with water and quickly react with soil. Their neutralizing power, however, is less than that of CaO (Greipsland et al., 2014). Calcium carbonate (CaCO₃) dissolves more slowly (Valzano et al., 2001) and is less reactive.

Studies by Blomquist et al. (2018) and Ulén and Etana (2014) report a rise in aggregate stability following liming. Liming also affects phosphate solubility and has been reported to increase, decrease or have no effect on phosphate solubility (Haynes, 1982). Several mechanisms are involved in the retention of phosphorus in soil. Phosphate can adsorb to the surfaces of aluminum and iron hydr(oxides) and clay minerals. It can

* Corresponding author.

E-mail address: gizachew.tarekegn.getahun@slu.se (G.T. Getahun).

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also form secondary minerals such as Fe/Al-P and Ca-P. Its fixation is highly dependent on soils pH range (Gustafsson et al., 2012; Penn and Camberato, 2019). Minimum phosphate solubility in soil solution has been found close to neutral pH (Gustafsson et al., 2012), contradicting claims that optimum phosphate solubility is reached close to neutral pH (Troeh and Thompson, 1993).

The objectives of this study were to investigate the effect of different rates of CaO and CaCO₃ on soil structural stability and dissolved reactive P (DRP), using a heavy clay subsoil. The research questions addressed were:

- Does the application of lime to subsoil cause changes in clay dispersion and wet aggregate stability?
- Does the application rate of different forms of lime affect phosphate solubility in the subsoil?

2. Materials and methods

2.1. Experimental site and soil characteristics

The soil was a heavy clay subsoil (34–44 cm layer), (Kungsängen) sampled in the vicinity of Uppsala, Sweden (59°83'N, 17°68'E). The soil has been under cropping for more than a century and sampling was performed within the Swedish long-term soil fertility trial at the site. The area has an illite-dominated clay mineralogy and, according to the FAO system, the soil is classified as a *Gleyic Cambisol* originating from glacial deposits. The subsoil (34–44 cm layer), is high in silt and clay, low in organic matter and has neutral pH (Table 1). Before liming, particle size distribution in subsoil samples was measured using the pipette method, and soil organic matter and total nitrogen content were determined by dry combustion (LECO CNS Analyser; LECO Corporation, St. Joseph, MI, USA).

2.2. Incubation experiment and treatments

Samples of subsoil were dried and crushed to pass through 2 mm mesh, and 200 g subsample soil mixed with powdered CaO or CaCO₃ to reach target pH values of about 7.5, 8.0 and 8.4. Lime requirements to achieve these values were pre-determined by mixing approximate amounts and measuring soil pH. Rates ranged from 0.1 to 0.4 Mg ha⁻¹ for CaO and 0.4 to 9.0 Mg ha⁻¹ for CaCO₃. The soil was thoroughly mixed with lime, moistened to about 56 % of water-holding capacity and incubated in 500 mL screw-cap polypropylene containers at 20 °C for 22 months. The containers were uncapped and aerated regularly. On each aeration occasion, the containers were weighed to check for possible water losses and the water content was corrected if necessary. The following seven treatments were compared: control at pH 7, addition of CaO (Alfa Aesar by ThermoFisher (Kandel) GmbH, Germany, p.a.) to attain a pH of 7.5, 8.0 and 8.4, and equivalent treatments with CaCO₃ (Merck KGaA, Darmstadt Germany, p.a.). Each treatment had three replicates resulting in 21 experimental units in total.

Table 1
Selected attributes of the bulk subsoil (34–44 cm) sample.

Soil properties	Value
Sand %	3.2
Silt %	47.0
Clay %	49.8
Soil organic carbon (g kg ⁻¹)	7.3
Nitrogen (g kg ⁻¹)	0.9
pH (H ₂ O)	7.0

2.3. Measurements of clay dispersion, wet aggregate stability and dissolved reactive phosphorus

Clay dispersion was measured as outlined by Pojasok and Kay (1990). After air-drying, the soil samples were gently fragmented by hand and passed through a sieve with mesh size 8 mm. About 10 g of the soil aggregates < 8 mm that had developed inside the containers over the 22-month incubation period were mixed with 80 mL artificial rainwater (0.012 mM CaCl₂, 0.15 mM MgCl₂, and 0.121 mM NaCl; pH 7.82; EC 2.24 × 10⁻³S m⁻¹) (to achieve a soil-water ratio of 1:8 by weight) in plastic bottles.

The bottles were capped and shaken end-over-end for 2 min at around 33 rpm. The suspension was then left undisturbed for 230 min, allowing particles >2 μm to settle. The top 60 mL of the suspension containing particles ≤2 μm (dispersed clay) were carefully siphoned off by pipette and transferred to 100 mL glass vials. Aliquots of the suspension were again transferred to pre-weighed (with accuracy to four decimal places) small glass vials. The glass vials (2 for each sample) were oven-dried at 105 °C to determine the amount of dispersed clay. The remaining pipetted soil suspension of about 40 mL was used to determine dissolved reactive phosphorus. Dissolved reactive phosphorus was determined colorimetrically using the ammonium molybdate blue method (ECS, 1996). A sample of soil (10–15 g) was oven-dried to determine the water content and to allow values allowing results of clay dispersion to be expressed on a dry-weight basis.

Wet aggregate stability (WAS) was determined using a Yoder-type wet sieving apparatus (Yoder, 1936) and soil aggregates <8 mm. A sieve (20 cm diameter, 250 μm mesh size) containing 30 g of soil aggregates that developed inside the containers over the 22-month incubation period was placed in a container filled with 5 L of artificial rainwater. Initially, the sieve was lowered to moisten the soil for 30 s, and then mechanically moved up and down for 2 min to expose the soil for vertical sieving process. The mass of soil aggregates retained on the sieve after the sieving period (stable aggregates) divided by the mass of total aggregates (stable and unstable) provided an index of aggregate stability, expressed as a percentage. Vertical movement of the sieve induced lower disruptive force on the soil compared with dispersion by shaking (Amezqueta, 1999).

2.4. Statistical analysis

The effect of treatments on clay dispersion, WAS and DRP was evaluated using one-way analysis of variance (ANOVA, significance level $P < 0.05$). Statistical analyses were performed using the R statistical package version 4.0.2 (RCoreTeam, 2020). Linear regression was used to test the relationship between clay dispersion and pH. The relationship between WAS and DRP vs. pH was fitted to a piece-wise, two-segmented linear equation using SigmaPlot 14 (Systat software).

3. Results and discussion

3.1. Clay dispersion

Clay dispersion was significantly negatively correlated with soil pH, for both lime types ($R^2 = 0.44$ for CaO; $R^2 = 0.53$ for CaCO₃, $P < 0.05$) (Fig. 1). Clay dispersion was reduced by on average 3, 10 and 17 %, at the low, intermediate and high rate of CaCO₃ and CaO application compared with the control. ANOVA revealed that these differences were not significant compared with the control. However, a trend was detected for reduced dispersion at the highest addition rate of CaCO₃ and CaO compared with the control ($P = 0.07$ and $P = 0.1$, respectively).

The trend for reduced clay dispersion or a linear decrease at increasing pH (corresponding to an increase in lime amount) could be explained by higher calcium concentrations in soil generating mutual attraction between clay colloids and negatively charged organic material. Colloids can then flocculate largely due to electrostatic forces,

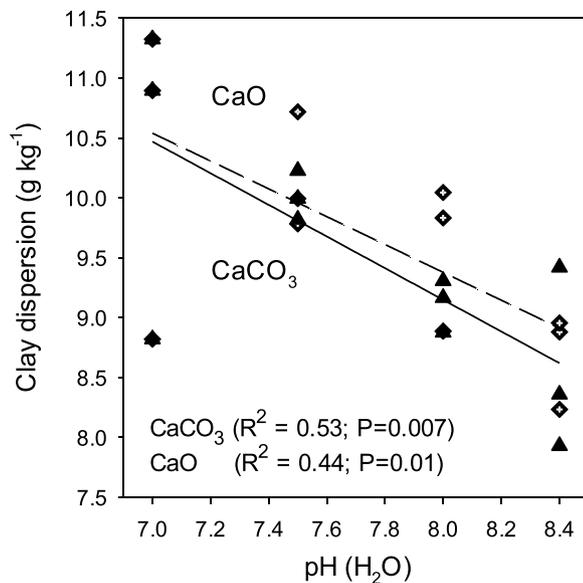


Fig. 1. Linear regression between clay dispersion (g kg^{-1}) and pH after 22 months of incubation with different rates of CaCO_3 (triangles and solid line) and CaO (diamonds and dashed line) (individual observations).

which is the basis for the formation of stable aggregates, and thus the risks of clay dispersion decreases. The role of calcium bridging as a dominant factor in the long-term structural effect of liming was pointed out by Six et al. (2004).

3.2. Wet aggregate stability

Changes in lime amount also affected WAS. The highest WAS value occurred at around pH 7.8, followed by a decrease at pH values higher than 7.8. The response to pH was fitted to a piece-wise regression with a similar breakpoint for both lime types ($R^2 = 0.73$ for CaO , $R^2 = 0.68$ for CaCO_3 , $P < 0.001$) (Fig. 2).

Lime addition increased WAS by 10–13 % at lower and intermediate lime addition rates. Stability at the low application rate was significantly higher from that at the higher application rates for both lime types ($P < 0.05$). At the high application rate, stability decreased to 6–8 % lower than in the control.

According to Tisdall and Oades (1982), soil aggregates $>250 \mu\text{m}$ are mainly held together by organic compounds decomposable by microbes. Chan and Heenan (1998) reported a decrease in structural stability after lime application and enhanced decomposition of soil organic matter. As the solubility of soil organic matter greatly increases with pH (You et al., 1999), the lower aggregate stability at the highest pH could have been induced by higher dissolution followed by increased decomposition of organic matter. The clay dispersion results did not support the above assumption. However, a reduction in wet aggregate stability (breakdown of macro aggregates) may occur without dispersion of smaller aggregates into clay sized particles (Oades and Waters, 1991).

3.3. Dissolved reactive phosphorus

The relationship between pH and DRP was similar to that observed for WAS, with a peak at pH 7.5 and 7.6 for CaCO_3 and CaO , respectively. The best fit to the data was by piece-wise linear regression ($R^2 = 0.84$ for CaCO_3 and $R^2 = 0.33$ for CaO , $P < 0.001$). When the pH was raised to 7.5 by adding lime, the concentration of DRP increased by 24 % and 37 % for CaO and CaCO_3 , respectively, compared with the control. Despite the fact that DRP concentrations were lower at pH 8 than at pH 7.5, they were still 15–17 % higher than in the control. At pH 8.4, DRP concentration was nearly the same as the control. Concentrations of DRP in

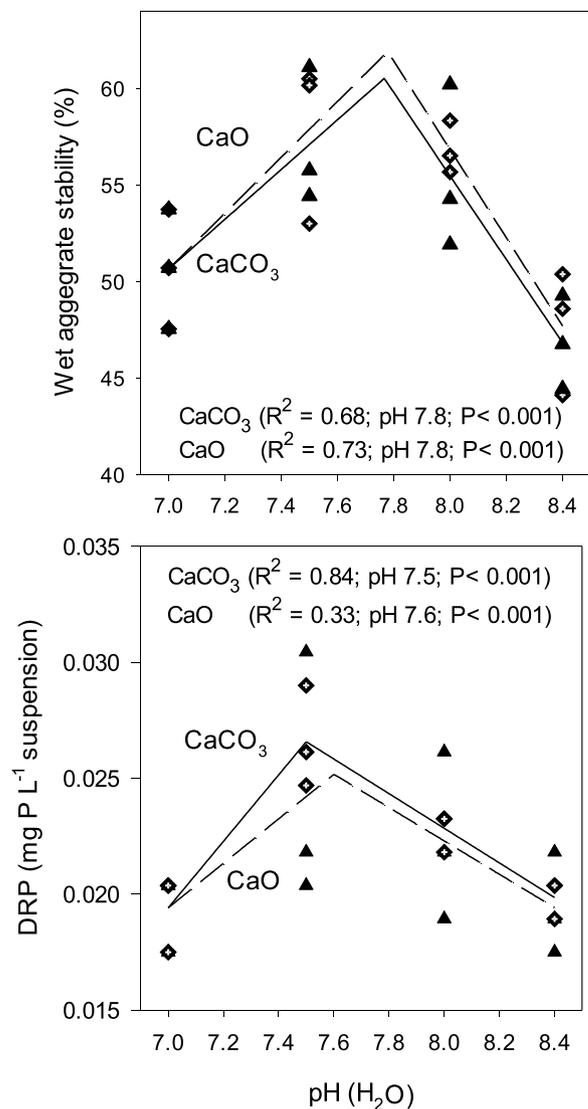


Fig. 2. (Upper diagram) Wet aggregate stability (%) and (lower diagram) concentration of dissolved reactive phosphorus (DRP, mg L^{-1}) as a function of soil pH after 22 months of incubation with different rates of liming materials. For DRP, CaCO_3 (diamonds and solid line) and CaO (triangles and dashed line) and for WAS, CaCO_3 (triangles and solid line) CaO (diamonds and dashed line). The data were fitted to piece-wise linear functions.

CaCO_3 -treated soil were significantly higher at pH 7.5 than in the control ($P < 0.05$).

Gustafsson et al. (2012) found a minimum phosphate solubility (maximum sorption) between pH 6.5 and 7 in a Swedish soil not treated with lime. Sorption of P on hydroxy-aluminium (Al) or an iron (Fe) interlayer of the clay minerals at neutral pH was suggested as a likely explanation for minimum phosphate solubility. The increase in DRP up to a pH breakpoint of 7.5 and 7.6 in the present study was presumably due to increased negative surface charges, whereby more phosphate ions were repelled electrostatically and P solubility increased (Murphy, 2007) and anionic organic compounds may compete with phosphate for sites (Guppy et al., 2005). The decrease in DRP at very high pH indicates that phosphate was withdrawn from solution and most probably precipitated as Ca-P compounds (Haynes, 1982).

4. Conclusions

The two lime types studied (CaO , CaCO_3) had similar impacts on soil structural stability. The decrease in clay dispersion through liming

indicated that flocculation of colloids by calcium took place up to pH 8.4. Bridging of colloids with calcium and formation of flocs took place even at very high pH. A decline in WAS, above pH 7.8 may be attributable to destabilisation through increased dissolution of organic matter at higher pH. These results indicate that organic matter bonds mainly hold macro aggregates together, but organic matter dissolution increases with pH. The net effect observed here was no further stabilisation of aggregates above 7.8 and possibly destabilisation at higher pH. Interactions between changes in electrical charge and concentrations of calcium and dissolved organic matter may explain these results. More studies are needed to understand the processes in detail.

Declaration of Competing Interest

The authors report no declarations of interest.

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