

# Charge properties of soils in Malaysia dominated by kaolinite, gibbsite, goethite and hematite

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**Abstract**— Majority of the Malaysian soils in the upland areas of the country are weathered. They are developed from a range of parent materials. These soils, known as Oxisols, are dominated by kaolinite and oxides of Fe and Al (sesquioxides). A study was conducted to determine the charge properties of three common Oxisols in Malaysia. For this study, the mineralogy of the clay fraction of the three soils was determined. It was then followed by the determination of the charge properties, with and without the presence of organic matter and sesquioxides. The results showed that the clay fraction of the soils contained mainly kaolinite, gibbsite, goethite and hematite. The pHo (the pH at which the net charge is zero) decreased with the increase in organic matter contents. On the other hand, it increased with the increase of sesquioxides contents. The negative charge (CEC) increased when soil pH increased. Basalt is a soil amendment. Depending on the rate, its application into the soils had increased soil pH, which concomitantly increased the negative charge of the soils. Simultaneously, the pHo of the soils decreased. This phenomenon further increased the negative charge of the soils under investigation.

**Keywords:** Oxisols, charge properties, sesquioxides

## INTRODUCTION

In Malaysia, many of the soils in the upland areas are highly weathered. These soils which are classified as Oxisols are dominated by kaolinite, gibbsite, goethite and hematite in the clay fraction (Tessens & Shamsuddin, 1983). These minerals are termed as variable-charge minerals (Uehara & Gillman, 1981). Oxisols in the country are developed on shale, schist, basalt, andesite, granodiorite, serpentinite and limestone, but the most weathered of them all are those formed on basalt, andesite and serpentinite. Kaolinite in soils generates negative charge, while the sesquioxides (gibbsite, goethite and hematite) generate positive charge. Another source of variable charge is the organic matter, bearing mostly negative charge. Thus, the study of charge characteristics of Oxisols is mainly based on the charge properties of kaolinite, sesquioxides and organic matter.

The charge in soils dominated by kaolinitic mineral is mainly pH-dependent (variable charge). The point of zero charge (PZC), which is also called pHo, of kaolinite is in the

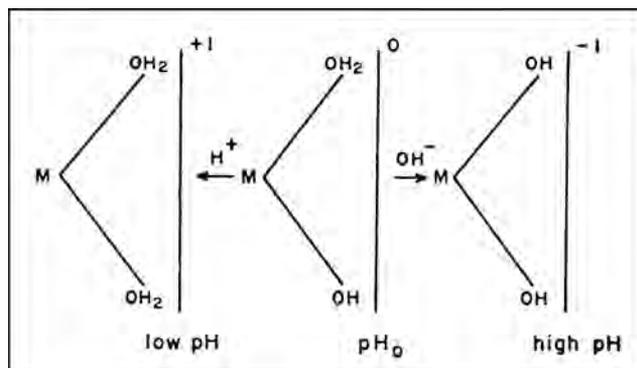
range of about 2.7 to 3.2 (Gallez et al., 1976; Hendershot & Lavkulich, 1983). For sesquioxides, the pHo values for synthetic or soil sesquioxides are in the range of 7.0 to 9.6 (Gillman & Sumner, 1987). The term pHo is fully described in Figure 1. Referring to Figure 1, when the pH is low, the surface of the oxide is positively charged. On the other hand, when the pH is high, it is negatively charged. In other words, sesquioxides have amphoteric properties, i.e. their surface charge can bear either positive charge in an acid condition or negative charge in an alkaline condition. The pH at which the net charge is zero is called pHo. This pHo value for mineral (or soil) can be determined by potentiometric titration (Gillman & Sumner, 1987). However, this method of determining pHo is known to overestimate charge measurements.

The presence of organic matter and sesquioxides decrease and increase pHo values, respectively (Van Ranst et al., 1998). pHo is also decreased by application of silicate (Uehara & Gillman, 1981). The negative variable charge in highly weathered soils, such as those in Malaysia, can be increased by increasing pH and/or decreasing pHo (Figure 1).

This study aimed at determining the mineralogical composition of three Oxisols (derived from basalt, andesite and serpentinite) and the factors responsible for charge development in the three Oxisols under investigation.

## MATERIALS AND METHODS

Three Oxisols, developed from basalt (Beserah, Pahang), andesite (Temerloh, Pahang) and serpentinite (Kuala Pilah, Negeri Sembilan), were selected to represent the common Oxisols in Malaysia. The soils developed from the rocks are respectively classified as the Kuantan,



**Figure 1:** Generation of positive and negative charge by changing pH (Bowden et al., 1980).

Segamat and Sg Mas Series (Paramanathan, 1977; Tessens & Shamsuddin, 1983).

The soil samples were collected from each horizon within the profiles, air-dried, ground and passed through a 2-mm sieve prior to chemical and mineralogical analyses. The relevant chemical properties of the soils were determined by standard methods. The minerals in the clay fraction of the soils were determined by X-ray diffraction analysis (with or without pretreatment). The clay was pretreated with citrate-dithionate-bicarbonate (CDB) to remove iron oxides.

The parameter usually used to assess charge characteristics is pH<sub>o</sub>, which was determined by potentiometric titration, using the method of Gillman and

Sumner (1987). Four pH<sub>o</sub> determinations were performed: (i) pH<sub>o</sub> for all horizons of the three profiles without removal of organic matter and iron oxides; (ii) pH<sub>o</sub> for the topsoil and selected subsoil (Bo2) of the three profiles following pretreatment with H<sub>2</sub>O<sub>2</sub> to remove organic matter; (iii) pH<sub>o</sub> values were measured similar to point (ii) but pretreated with sodium dithionite (SD), in place of H<sub>2</sub>O<sub>2</sub> to remove iron oxides (embedded oxides and oxy-hydroxides); and (iv) pH<sub>o</sub> values were measured with pretreatment similar to point (ii) followed by sodium dithionite (SD). All these pretreatments (ii to iv) were designed to account for factors responsible for the changes in the magnitude of the PZC of the soils.

The magnitude of variable charge was estimated on samples from the A and Bo2 horizons of each profile using a discontinuous back titration method. This method was applied to correct proton consumption resulting from dissolution and hydrolysis reactions. The soils from the A horizon (0-14/20 cm) represent soils having high organic carbon, while the selected Bo2 horizons (40-80 cm) represent soils having lower organic carbon and higher iron oxides.

The soil of Segamat Series, developed from andesite, was treated with ground basalt (at various rates for 15 months) in a pot experiment. Soil pH and pH<sub>o</sub> were determined at the appropriate time.

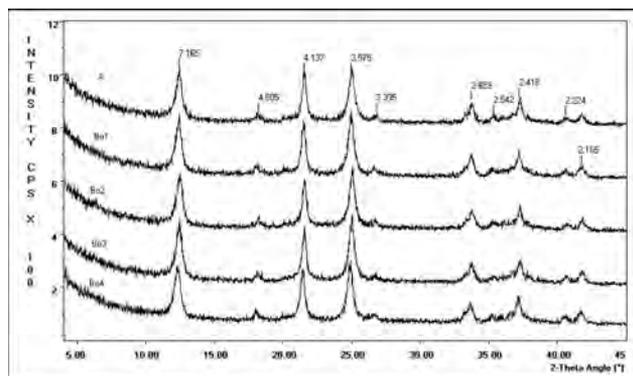


Figure 2: X-ray diffraction patterns of the clay fraction of Sungai Mas soil without iron oxide removal.

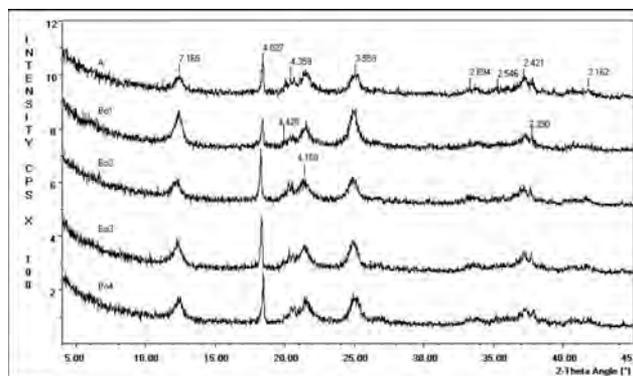


Figure 3: X-ray diffraction patterns of the clay fraction of Kuantan soil without iron oxide removal.

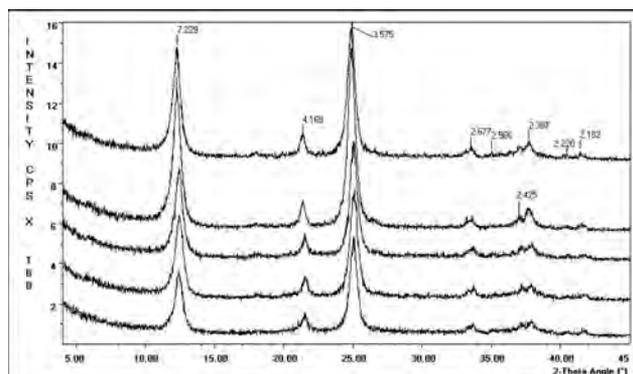


Figure 4: X-ray diffraction patterns of the clay fraction of Segamat soil without iron oxide removal.

## RESULTS AND DISCUSSION

### Mineralogy of the clay fraction

Prior to iron oxides removal, the XRD patterns showed the presence of peaks at 7.17-7.22 and 3.50-3.58 Å within all horizons of the three soils, indicating the presence of kaolinite (Figures 2, 3, 4). The strong peaks at 4.83-4.89 Å, accompanied by weak peaks at 4.35 and 2.39 Å showed by Kuantan and Sg Mas soils indicate gibbsite (Van Ranst et al., 1998). The very strong goethite peak at 4.14-4.19 Å with weak peaks at 2.42 and 2.16 Å was shown by Sg Mas soil (Schwertmann & Taylor, 1989). These peaks were also shown by Segamat and Kuantan soils, but their peak intensity was less than the Sg Mas soil. There is a problem for identification of peak at 2.69 Å because this is the strongest line of hematite (104), but also the goethite (130) line. According to Schwertmann & Taylor (1989), hematite in the presence of goethite can be recognized by the intensity ratio of 2.70 and 2.45 Å peaks, where the ratio is 0.6 if no hematite is present, and it increases with increasing hematite. In the present study, the ratio is about 0.90-1.02, suggesting the dominant contribution of hematite to the 2.66 Å peak. The weak peaks at 2.54-2.57 Å and 2.22 Å further indicate the presence of hematite.

The properties of Fe oxides were further studied by citrate-bicarbonate-dithionite (CBD) treatments (data not shown). Results showed that the goethite and hematite peaks decreased in intensity, but increased in d-spacing values after CBD treatments. The partial collapse of goethite and hematite peaks for Sg Mas and Segamat soils confirms the presence of goethite and hematite. The peaks

of goethite and hematite shifted to the higher values after CBD treatments. For example in Sg Mas soil, the goethite peaks was shifted from 4.137-4.158 Å to 4.173-4.190 Å and that hematite from 2.659 Å to 2.669 Å. This indicates that the small size and/or less crystalline iron oxides were more susceptible to be removed by CBD treatment than the more crystalline materials.

### Point of zero charge (pHo)

pHo values of the three soils are considerably lower in the surface horizons than the underlying horizons (Table 1). The lower pHo for the topsoil is due to the higher organic matter content compared to the subsoil (Van Ranst et al., 1998). Comparing the pHo values of the corresponding horizons within the three profiles shows that horizons of the profile derived from basalt have considerably lower pHo values (4.1-4.9) than those of the profiles derived from serpentinite and andesite (5.6-5.8 and 5.3-6.0, respectively). This indicates that the latter two soils have achieved a more advanced chemical stage of weathering than the former.

The topsoil and selected subsoil (Bo2) samples from three profiles were subjected to H<sub>2</sub>O<sub>2</sub> treatment (to remove organic matter), DCB treatment (to remove iron oxides) and H<sub>2</sub>O<sub>2</sub> and DCB treatments (to remove both organic matter and iron oxides). These were used to assess factors responsible for the magnitude of pHo values.

The removal of organic matter remarkably shifted the pHo to the high values (Table 1). It is considered that only sesquioxides (i.e., iron oxides and gibbsite) and kaolinite mineral control the position of pHo, once the soil organic matter (SOM) is removed. For the topsoil, the removal of organic matter to expose mineral surfaces shifted the pHo position from 5.0 to 6.7, 3.9 to 5.8 and 4.8 to 5.9 for Sg Mas, Kuantan and Segamat soils, respectively. The corresponding shifts in pHo values for the subsoils were from 5.7 to 6.1, 4.5 to 5.3 and 5.7 to 6.2. The unit increase of pHo values was lower in the subsoil than the corresponding topsoil of the three profiles due to lower organic matter in the former. This shows that organic carbon in soils is responsible for lowering the pHo as a result of the creation of negative surface charge and/or masking of positive surface charge. The relationship between point of zero charge (PZC or pHo) is given in Figure 5. It is seen that PZC decreases linearly as the organic carbon increases.

In contrast to organic matter, the removal of iron oxides resulted in a remarkable decrease of pHo values from 5.0 to 2.6 and 4.8 to 3.6 for topsoil of Sg Mas and Segamat soils, respectively, while for Kuantan soil it was only a small decrease (from 3.9 to 3.7) (Table 2). This phenomenon also occurred for the subsoil of the three profiles, but the decrease in pHo was greater in the subsoil than the topsoil for the Sg Mas and Segamat profiles (3.0 vs 2.4 units and 2.8 vs 1.2 units, respectively). For the Kuantan soil, the decrease in pHo values was small; there was only a slight difference between the subsoil and the topsoil (0.8 vs 0.2 units). The greater decrease in pHo values in the subsoil of Sg Mas soil is due to the higher iron oxides in the soil

**Table 1:** The changes in pHo as affected by SOM and Fe removals.

Soil	pHo			
	Natural	OM <sub>rev</sub>	OM-Fe <sub>rev</sub>	Fe <sub>rev</sub>
Sungai Mas				
Topsoil	5.0	6.7	3.6	2.6
Subsoil	5.7	6.1	3.4	2.7
Kuantan				
Topsoil	3.9	5.8	3.9	3.7
Subsoil	4.5	5.3	4.5	3.7
Segamat				
Topsoil	4.8	5.9	3.3	3.6
Subsoil	5.7	6.2	4.0	2.9

OM<sub>rev</sub> = Organic matter removed; OM-Fe<sub>rev</sub> = Organic matter and Fe removed; Fe<sub>rev</sub> = Fe removed.

compared to that of Kuantan and Segamat soils. Although Kuantan has higher iron oxides than Segamat soil (data not shown), the pHo value was lower in the former than the latter after iron oxide removal. This is due to the presence of gibbsite in the Kuantan soil, causing the pHo value to remain high. The removal of iron oxides from Oxisols had resulted in the control of pHo by kaolinite together with gibbsite and organic matter.

The removal of both organic matter and sesquioxides (mainly iron oxides) shifted pHo to lower values than natural condition in both the topsoils and the selected subsoils (Table 1). This shows that once the OM and sesquioxides were removed, the surface of kaolinite minerals, which were presumably coated by organic matter and sesquioxides were exposed and then significantly influenced the position of pHo. For Sg Mas and Segamat soils, the values of pHo were 3.6 and 3.3 for the topsoil and 3.4 and 4.0 for subsoil, respectively. These values are very close to pHo values of kaolinite (2.7-3.2). The pHo values for corresponding horizons of the three soils showed the higher value for Kuantan, followed by Sg Mas (topsoil) and Segamat (subsoil). Although the Kuantan soil contains much higher organic C than the other two soils, the removal of organic matter and iron oxides did not lower the pHo considerably and the values were still higher (3.9 and 4.5) than the pHo value of kaolinite. Examination of the XRD data indicated that gibbsite is present at considerable amounts in the Kuantan, but only at trace amount in Sg Mas soil.

### Variable charge generation

The magnitude of surface variable charge generation as a function of soil pH in the topsoil and subsoil (Bo2) of the three Oxisols derived from different parent materials are shown in Table 2. In all cases, the curves of uncorrected back titration (suspension) showed considerably higher charge generation than the corrected values (suspension – supernatant). The estimate of charge generation was, therefore, drastically decreased after the suspension back titration was corrected for that of the supernatant solution. The charge overestimation was higher in the topsoil than

**Table 2:** The magnitude of variable charge of top- and subsoil at different pH values.

Soil series	Horizon	Corrected charge				VC <sup>§</sup>	CEC	Charge overestimation			
		pH 4.5	pH 5.5	pH 6.5	pH <sup>†</sup> 7.0	pH 4.5-7.0	pH <sup>‡</sup> 7.0	pH 4.5	pH 5.5	pH 6.5	pH <sup>†</sup> 7.0
		cmol <sub>c</sub> kg <sup>-1</sup>									
Sg. Mas	A	1.50	2.10	4.20	5.40	3.90	5.10	160.0	150.0	89.3	63.9
	Bo2	2.10	3.90	5.70	7.50	5.40	3.30	78.6	46.2	55.3	34.0
Kuantan	A	3.50	5.75	10.75	12.25	8.75	14.50	35.7	69.6	37.2	38.8
	Bo2	3.75	4.50	8.95	11.25	7.50	12.20	66.7	94.4	53.6	42.2
Segamat	A	2.80	4.23	6.40	7.50	4.70	7.60	96.4	79.7	57.8	52.0
	Bo2	3.00	4.50	6.90	8.10	5.10	7.50	83.3	71.1	52.2	48.1

<sup>†</sup> Variable charge values were obtained by extrapolation

<sup>‡</sup> The CEC was determined by ion adsorption in 1 N NH<sub>4</sub>OAc buffered at pH 7.0

<sup>§</sup> VC is variable charge generation from pH 4.5 to 7.0

the subsoil of Sg Mas and Segamat soils, but the reverse was true for the Kuantan soil. The charge overestimation varied according to pH values, where in most cases the overestimation decreased with increasing soil pH. At pH 6.5 to 4.5, for example, the respective charge overestimation ranged from 89-160 % and 55-79 % for surface and subsurface horizons of the Sg Mas soil, from 37-36% and 54-67% for the Kuantan soil and from 58-96% and 52-83% for the Segamat soil (Table 2). The high charge overestimation at low pH value (pH < 4.5) indicates the higher dissolution of Al from solid phase and hydrolysis of ion.

The comparison of charge magnitude at any given pH value of corresponding horizons among the three soils indicated the charge generation was highest for soil derived from basalt (Kuantan), followed by soils derived from andesite (Segamat) and serpentinite (Sg Mas). It is seen in this study that at pH 6.5, the charge generation was 10.7, 6.4 and 4.2 cmol<sub>c</sub> kg<sup>-1</sup> in the topsoil for soils derived from basalt, andesite and serpentinite, respectively. The corresponding values for subsoils were 9.0, 6.9 and 5.7 cmol<sub>c</sub> kg<sup>-1</sup>.

For comparison purposes, the negative charge measured by ion adsorption at pH 7.0 has been included in Table 2. With the exception of the subsoil of Sg Mas soil, the data showed a good agreement between corrected negative charges determined by discontinuous back-titration and total negative charges measured by ion adsorption. Other studies had also reported that the cation-anion exchange method yielded identical results to the potentiometric titration method if the solubility of the solid phase is taken into account. The evidence from this study supports the previous studies that the variable charge measurement using potentiometric titration overestimated the magnitude of variable charge due to dissolved solid and hydrolysis of ion. The magnitude of negative charge measured by independent methods (corrected back titration and ion adsorption) showed relatively similar value at corresponding pH values, in which the order was Kuantan > Segamat > Sg Mas. This indicates the surface reactions are controlled by similar soil constituent sites.

The difference in charge generation between the Kuantan soil and the other two soils can be explained by the differences in the type of mineral composition, their

proportion and their particle sizes and organic carbon content. As the pHo values of sesquioxides are 7-10, the variable generation of negative sign developed at pH ≤ 7.0 in this study is derived from kaolinite and organic matter (both having low pHo values). Semi-quantitative estimation (based on XRD method) of minerals showed the proportion of kaolinite in three soils studied was in the order of Segamat > Sungai Mas > Kuantan (data not shown). This indicates the charge generation should be in the order of Segamat > Sg Mas > Kuantan with respect to kaolinite and SOM content. However, this is not the case. The plausible explanation is the nature of minerals; i.e., their crystallinity and particle sizes. The order of crystallinity and particle sizes as estimated by the width at half height (WHH) of XRD lines was Kuantan > Segamat > Sg Mas. Therefore, the nature of kaolinite minerals and the high organic C in the Kuantan soil compared to the Segamat and Sg Mas may be responsible for the higher variable charge creation during a back-titration in the former. The organic carbon content of Sg Mas and Segamat soils at corresponding horizons was similar; hence, the difference in negative charge generation should be the proportion of kaolinite and sesquioxides. The lower negative charge could be related to goethite and hematite which were much higher in the Sg Mas but lower in kaolinite content compared to Segamat soil. In addition, the organic C content of the Kuantan soil is about 2 times greater (for both top- and subsoil) compared to the corresponding horizons of the Sg Mas and Segamat soils.

### The effect of basalt application on pH and pHo

Basalt is known to be an effective soil ameliorant. In this study, ground basalt was applied into the soil of Segamat Series in order to determine its effect on soil pH and pHo. The results on the change in soil pH due to basalt application are given Figure 6. It is seen that soil pH increased with time and that it increased with the rate of basalt application. Increase in soil pH would increase the negative charge of soils containing variable-charge minerals (Uehara & Gillman, 1981). It means that due to pH increase, the overall negative charge in the Segamat soil had increased (Figure 1).

At the same time, the pHo of Segamat soil had decreased

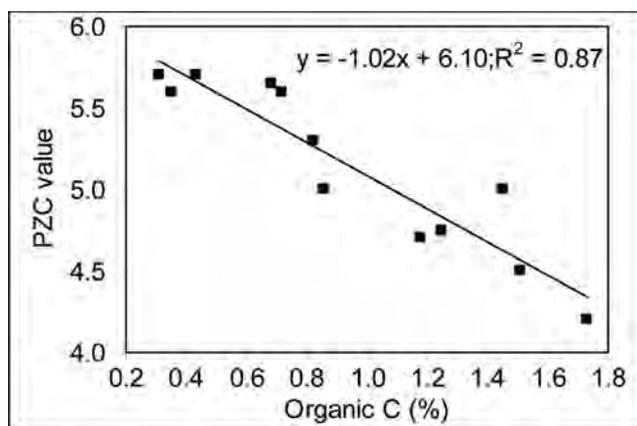


Figure 5: The relationship between PZC (pHo) and SOM.

(Figure 7). The higher was the rate of basalt application the lower was the pHo value. According to Uehara & Gillman (1981), the negative charge on the variable-charge minerals depended on pHo minus soil pH (pHo-pH). When basalt was applied into the soil, pHo decreased with concomitantly increase in soil pH. It means that the difference between pHo and pH was widened. Hence, negative charge increase in the soil due to basalt application was by two mechanisms: pH increase and pHo decrease.

### CONCLUSION

The mineralogy of the clay fraction of Oxisols developed from basalt, andesite and serpentinite in Malaysia is dominated by kaolinite, gibbsite, goethite and hematite. The negative charge on the surface of these minerals increases with increase in soil pH and/or decrease in pHo. The value of the pHo of the soils depends on the presence of organic matter and sesquioxides in the soils. Basalt application can increase soil pH as well as decrease pHo, which in turn, would result in an increase of negative charge of the soil.

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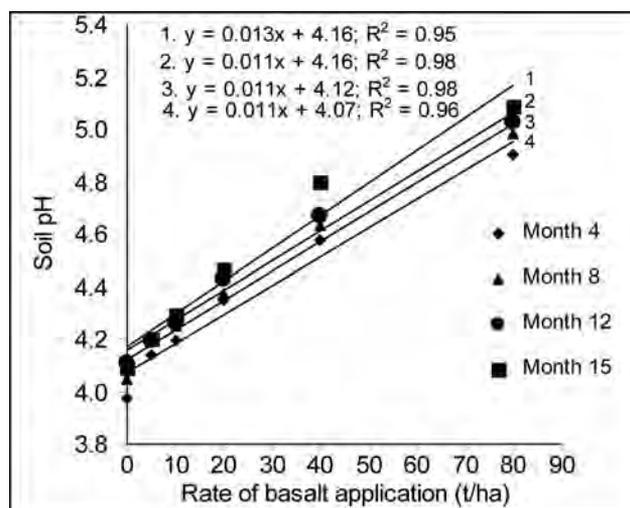


Figure 6: Relationship between soil pH and basalt rate.

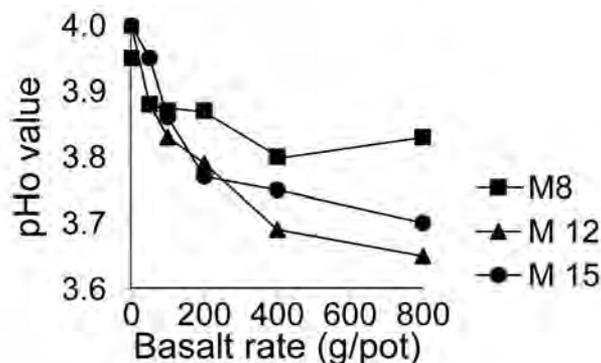


Figure 7: The effect of basalt application on pHo.

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