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A study of three potassium fertilizers in Californian almond production soils

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A study of three potassium fertilizers in Californian almond production soils

By

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THESIS

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Abstract

Potassium (K) is one of essential elements for plant growth, especially orchard crops, and the third most important macronutrient after nitrogen and phosphorus. Despite the fact that K reserves are relatively abundant on earth, consisting of 2.1 – 2.3% of the earth crust, a large proportion of K is not available for plant uptake due to its uneven distribution. Potassium inputs come from different sources such as irrigation water or soil amendment applications. To supply K replenishment in agriculture, the application of K fertilizer is the most effective to increase K nutrient in soils. Thus, this study will focus on K behavior in the plant as well as dynamics in soil context.

The K pools in soil are solution K, exchangeable K, non-exchangeable K, and structural K. Both solution K and exchangeable K portions are considered plant-available K, although they are usually low in total soil K. A number of factors govern the amount of K pools in soil, including soil texture, cation exchange capacity (CEC), pH, moisture, temperature and clay mineralogy. These factors not only influence the K efficiency of plant uptake, but also affect the K distribution of K availability by soil depths. In terms of precise estimation of available K for crop uptake, the current K fertilizer application recommendations are based on ammonium acetate extraction method, which only measures the solution K and exchangeable K. A novel sodium tetraphenylboron (NaTPB) method was introduced and discussed to help better estimate the plant-available K.

In plants, K is the key component that maintains numerous metabolic functions at all levels. For instance, enzyme activation, protein synthesis, photosynthesis, carbon assimilation and transport, and water balance. Therefore, a lack of K nutrition leads to malfunctions of these processes and eventually reduces the crop yield and fruit quality. In annual crops, K deficiency is

easy to observe. Generally, the most common symptoms of K deficiency firstly occur in the older leaves and include chlorosis and necrosis. While in orchard crops, low K condition in trees does not immediately become visible and result in low yield or reduced quality of harvest. Hence, a regular leaf K analysis is recommended for growers to monitor tree K levels on purpose. For orchard production, a proper K management is especially important to secure yields. However, different orchard crops require different amounts of K. For instance, in almonds 75 kg K was removed in fruit per metric ton of kernel yield. Usually, orchard crops are not sensitive to K fertilizer sources but the application rates. For example, in pistachios, Zeng & Brown (2001) proposed that a K application rate between $110 - 220$ kg ha^{-1} was sufficient to sustain highly productive pistachio orchards with any K sources while excessive K fertilizer (> 220 kg ha^{-1}) was applied, nut yield reduced in the subsequent year.

During the course of weathering, the rate of K release and fixation is highly correlated to the clay mineralogy. Some secondary clay minerals, such as montmorillonite, are high K-fixed, which makes K become unavailable. In addition, the alternate wetting-drying cycle regimes greatly reduce K diffusive flux and K mobility in soil. Thus, proper K fertilizer management and application become crucial in agriculture. In this study, three K fertilizers are discussed – muriate of potash (MOP), sulfate of potash (SOP), and polyhalite (POLY). There is still little information available to describe the properties of K fertilizers and their efficacy for orchard production, especially almond production. To better understand K behavior in the soil system, the experiment was conducted to explore K dynamics using a soil-column experiment by comparing the behavior and distribution of KCl, microfine SOP and POLY in three different soils (Hillgate sandy loam and two different loams San Ysidro and Yolo) obtained from almond orchards in California's Central Valley. Three replicate columns with each K fertilizer along with an

unfertilized control were subject to four wetting events over a two-month period, and different K pools were measured at depth of 0-10, 10-20 and 20-30 cm.

POLY resulted in a higher solution K concentration in all soils. After complete incubation, a large proportion of unaccounted K (e.g. 921 mg K column^{-1}, which is equivalent to 42% of input K in the San Ysidro soil) was observed, perhaps due to movement of K into the non-exchangeable pool. The slow-release characteristic of POLY-K and the additional content of Ca and Mg increased total extractable base cation levels in soils, and increased leaching of base cations after four wetting compared to other two K fertilizers.

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Chapter 1: Literature Review: Potassium source dynamics in agricultural soils

1-1 Potassium demand and availability in cropping systems

1-1-1 Global potassium fertilizer sources in agriculture

Since the 1950s, the global population has increased from two to seven billion. With this trend of rapid population expansion, the food demand of future generations is an emerging issue worldwide. To ensure food security, a massive increase in crop production with minimal environmental impact and concurrently preserving energy-related resources of our earth is crucial (Zorb et al. 2014). Potassium (K) is one of the essential elements in plant biomass and the third most important macronutrient for crop growth in addition to nitrogen (N) and phosphorus (P). Potassium is involved in a number of plant physiological functions and biochemical processes such as photosynthesis, enzyme activation, carbon assimilation and transport, and water relations between the plant and environment. Potassium is a relatively abundant element on earth, comprising about 2.1 – 2.3% of the earth's crust (Schroeder, 1978) and average soil K reserves are quantitatively large, although these are not mostly available for plants (Zorb et al. 2014). The availability of K and its uneven distribution causes K deficiency in some agricultural regions.

Potassium inputs are the total quantity of K, originating outside a given volume of soil, that moves into that volume (Murrell et al. 2021). These inputs encompass atmospheric deposition; irrigation water; soil runoff or erosion transported K from one area to another; K in plant residuals (seeds, cuttings, or transplants); organic fertilizer and soil amendment applications; and

commercial fertilizer sources. Potassium fertilization is essential in many environments to secure optimal yields (Murrell et al. 2021). Consequently, herein we will focus on the K fertilizers in agriculture.

1-1-2 Potassium behavior and availability in soil system

The major K pools in soil are **solution K**, **exchangeable K**, **non-exchangeable K** (also called fixed K), and **structural K** (Sparks & Huang, 1985). Solution K and exchangeable K are both plant-available. However, these two pools account for only $1 - 2\%$ of total K in soil. Barber (1962) proposed that K transport in soil is mainly via diffusion as the K depletion in the vicinity of roots causes a concentration gradient that results in movement of K from high (bulk soil) to low concentration (rhizosphere). The rate at which K is replenished at the plant root surface is an important factor affecting plant growth. In soil, K transport mechanisms vary depending on the site in the soil profile and moisture regimes (Table 1-1-1).

Table 1-1-1 – K transport mechanisms and rates in soil settings.

Situation	Mechanism	Rate (cm day^{-1})
In profile	Mainly mass flow	Up to 10
Around fertilizer placement	Mass flow and Diffusion	< 0.1
Nearby root	Mainly diffusion	$0.01 - 0.1$
Outside clay interlayers	Diffusion	10^{-7}

Source: Tinker, 1978, *Potassium in Soils and Crops*, Potash Research Institute of India, New Delhi.

Soil solution K is generally low (~0.1% of total soil K) and directly available for plant and microbial uptake and can potentially be leached from soils (Mouhamad et al. 2016). The equilibrium between solution and readily exchangeable K depends on soil type, soil moisture,

temperature and the content of other cations (e.g. Al, Ca and Mg) in soil (Spark & Huang, 1985). This equilibrium is subject to the number of binding positions on soil exchangeable sites (Havlin et al. 2016). The most readily available K forms are in the planar position where K^+ held on the outside of soil particle surfaces. The edge position is where K^+ is bonded on the side of soil particles and subject to pH-dependent surface charge. On the other hand, the inner position has a high specificity of K^+ trapped at the interlayer between 2:1 clay minerals. Potassium ions compete with other cations, particularly Mg^{2+}, Ca^{2+} and NH_4^+, in solution for cation exchange capacity (CEC) binding sites on clay minerals or organic matter surfaces via electrostatic attraction. This electrostatic bond is relatively weak, so that a cation can be easily replaced by another cation. For instance, the CEC of vermiculite (~150 meq/100 g) and kaolinite (~15 meq/100 g) clay minerals results in differences in binding sites to hold cations on surfaces (Alexiades & Jackson, 1965). For soil K testing, the NH_4OAc extraction method is widely adopted in laboratories to measure the K concentrations in both solution pool and exchangeable pool.

Nonexchangeable K and structural K are considered unavailable K for plant growth. Non-exchangeable K is the K^+ not held tightly within the crystal structures as part of soil mineral particles. Despite the low availability of nonexchangeable K, when the soil solution K and exchangeable K are depleted by root absorption or lost via K leaching, a portion of non-exchangeable K becomes available to maintain the K balance in soils (Havlin et al. 2016). The K release of non-exchangeable K is often too slow to meet plant need during the growing season.

Potassium reserves in soils arise from K-bearing mica, feldspars and vermiculites, which have different K release mechanisms. For instance, feldspars have K residing throughout its entire 3-dimensional mineral lattice and this K can be released only by destruction of the mineral

structure (Havlin et al. 2016). While for the 2:1 layer mica, most K is strongly bonded within crystal structures between adjacent tetrahedral layers of dioctahedral and trioctahedral layers and the strong binding makes K not immediately plant available (Mouhamad et al. 2016). More discussion will be addressed about K release and K fixation in a later section (1-3-2).

1-1-3 Potassium losses by leaching

Potassium is a moderately mobile cation in agricultural systems. Sparks et al. (1980) observed a downward movement of broadcast K, plowed into a depth of 10 cm, at 83 and 249 kg K ha^{-1} in fine-loamy Dothan soil. The increase of exchangeable K in the subsoil (20 – 58 cm; A2 and B21t), apart from the parent material, was attributed to the leaching of applied K from the Ap horizon (0 – 20 cm). The K in the subsoil may not be available to crops if the rooting depth is limited by unfavorable physicochemical conditions (Sparks et al. 1980). The level of K leaching is mainly influenced by soil texture, soil pH, CEC, type of clay minerals and K fertilization (Rosolem et al. 2006).

In a K column study, Mendes et al. (2016) found that based on the difference of mass of the column irrigated at 100%, a 200% water replacement percentage of the depth necessary to bring the soil moisture to the target field capacity, led to K losses of 8 and 57% of the total K applied in clayey and sandy soils, respectively. It is known that K, Ca, and Mg are antagonistic ions in the soil. Rosolem et al. (2010) stated that in a tropical soil, K availability and dynamics were subject to the ratio of Ca and/or Mg to K. These ratios regulate the K equilibrium between the solution and exchangeable pools. Excessive amounts of one of these cations in soil may induce the deficiency of the others on plant growth. Although a number of studies investigated the

availability and efficiency of applied K in soil, little information about the K dynamics of different K fertilizer sources is available.

1-1-4 Potassium transport in plant, K role in crop quality, and symptoms of K deficiency

Potassium is an essential nutrient in agricultural production required for optimum yield and to maintain crop quality. In plants, K is the most abundant cation and serves as a very important component for many functions at all levels, including individual cells, within tissues, and in a long-distance transport (Marschner, 2012). K-dependent processes include functions such as enzyme activation, protein synthesis, photosynthesis, carbon assimilation and transport, and water balance (Pettigrew, 2008; Mikkelsen, 2017).

The absorption of K in plant roots involves two processes: low-affinity K^+ uptake and high-affinity K^+ uptake (Pettigrew, 2008). The low-affinity K^+ uptake is a passive process which allows K^+ influx into root cells through specific K channels via an electrochemical gradient. This process requires little energy. On the other hand, the high-affinity K^+ uptake requires energy in the form of ATP as K^+ pumps transport K^+ into root cells against an electrochemical gradient. High-affinity K^+ uptake is associated with a concurrent outflow of either Na^+ or H^+ as counter ions. Once K^+ is taken up, it is transported throughout the plant cells via xylem by a series of integral membrane proteins (transporter and cation channels) to allow K^+ ions across the cytosolic membrane (Marschner, 2012).

Potassium deficiency in leaves primarily influences photosynthesis, and synthesis and translocation of enzymes. First, low K status affects the ATP synthesis via photophosphorylation, which is a process to convert ADP molecules to energy-rich ATP molecules using light energy. Potassium is a component of the trans-membrane pH gradient

necessary for the ATP synthesis (Marschner, 2012). The ATP is a crucial energy source required for plant to produce essential compounds like carbohydrates, lipids, and vitamins. Second, the synthesis and activity of photosynthetic enzymes are governed by the K concentration in cells. For instance, K is important in the stroma to maintain a high pH for the optimal RuBP carboxylase activity. To maintain this high pH environment, the influx of K^+ into the stroma is mediated by a H^+/K^+ counterflow (Wu et al. 1991). Third, K^+ influences CO_2 fixation through chloroplasts. Kaiser et al. (1980) demonstrated that the CO_2 fixation was strongly inhibited at low mono-valent cation concentration (about 3 mmol L^{-1}) in spinach chloroplasts. Conversely, the rate of photosynthesis was fully restored or even higher when the K^+ concentrations in the chloroplasts increased to 50–100 mM, which is equivalent to the K^+ concentration in the cytosol of intact cells.

Potassium is an important cation for enzyme activation and protein synthesis. A large number of enzymes are either entirely dependent on or stimulated by K^+ (Suelter, 1970). One of crucial enzyme functions in cells required by K involvement is conformational changes of the specific protein configuration. Generally, these K^+-induced changes in enzymes increase the rate of catalytic reactions, and the affinity for the substrate (Evans & Wildes, 1971). For example, the activity of starch synthase is highly dependent on univalent cations, especially K^+, to catalyze the conversion of sugars (glucose) to starch (Marschner, 2012). Reduced starch accumulation can affect fruit quality.

The most sensitive enzymes to low K supply are pyruvate kinase, phosphofructokinase, and nitrogenase (Lauchli & Pfluger, 1978). When a leaf is K deficient, the cytosolic K^+ concentrations are maintained at a constant level while the K^+ concentrations in the vacuole greatly decreases. However, with prolonged K deficiency, the cytosolic K^+ concentrations also

decline (Marschner, 2012). It is not clear whether reduced enzyme activities and changes in metabolite pattern arise from the direct or indirect effects of K deprivation. An indirect effect would be the failure to maintain the cytosolic pH, which in turn inhibits biochemical processes and plant growth.

For protein synthesis, K^+ is a crucial element and is required in higher concentrations than for enzyme activation. Wyn Jones et al. (1979) illustrated that K^+ is associated with many steps in the translation process, including the binding of tRNA to ribosomes. For instance, RuBP carboxylase is very abundant in the chloroplast of C3 species. Under K deficiency, the synthesis of this enzyme is strongly impaired. Marschner (2012) suggested that the maximum enzyme activation was achieved at 10 mM K^+ in the external solution, whereas a 10 times higher concentration in the chloroplast is required to ensure high rates of protein synthesis.

Assimilate transport in plants requires K^+ for both the loading of sugars and the rate of solute transport, driven by mass flow, in the sieve tubes of the phloem (Marschner, 2012). The loading of sugars in the phloem sieve tubes needs K^+ to maintain a high pH condition for an optimal loading rate. In addition, K^+ controls the osmotic potential and influences water flow rate in the sieve tubes for photosynthates transport rates and loading. Under K-deficient conditions, protein synthesis is restricted. This results in an accumulation of sugars (glucose and fructose) and N-rich compounds in leaf tissues. Translocation of assimilates uses energy from ATP. Thus, the process of CO_2 fixation and assimilation into sugars and carbohydrates requires a lot of energy and K^+ to functionally transport those products to other organs such as fruits, grains and roots for storage or plant growth (Havlin et al. 2016). Moreover, K^+ is a dominant cation in nitrate metabolism. The lack of K^+ leads to a decreased uptake rate of nitrate by roots, and slows nitrate assimilation into amino acids (Mikkelsen, 2017). The long-distance transport for NO_3^- in the

xylem and storage in vacuoles requires K^+ as a counterion (Marschner, 2012). Furthermore, without sufficient K^+, organic acid anions accumulate in plant tissues. The accumulation of photoassimilates due to a restricted assimilate transport as a result of K deficiency in the leaves causes an increased weight of leaves and reduced leaf expansion and leaf size in a given unit of leaf area compared to those leaves with adequate K^+ supply (Pettigrew, 2008). This can lead to a lower supply of assimilates to reproductive tissues or growing points of the plant, eventually compromising crop yield and quality.

The K ion is responsible for water relations in plants by regulating stomatal opening. The influx of K^+ into guard cells results in an increased turgor pressure-driven force (osmotic potential gradient) to draw water into guard cells. In guard cells, the K^+ uptake is governed by the K^+-specific uptake channels and associated with an extruded proton into the apoplast (Hoth et al. 1997). This is a very important process for plant to cool the leaves (water balance) and maintain solute transport in the xylem. Under K deficiency, transpiration is reduced and the plant's ability to withstand water stress is impaired. The malfunction of stomatal opening due to a lower K^+ level results in an inefficient water use of plants, lower rates of photosynthesis, and decreased stomatal conductance (Havlin et al. 2016). At the onset of developing K deficiency in leaves, the decrease in stomatal conductance lowers the efficiency of photosynthesis per unit leaf area (Bednarz et al. 1998). When K deficiency becomes more severe, non-stomatal and other biochemical factors become the principal factors affecting stomatal conductance. To sum up, the osmotic role of K^+ serves as an important regulator for guard cell turgor pressure, supporting plant water relations and cell expansion (Pettigrew, 2008).

Symptoms of K deficiency

Since K is a mobile element in plants, visual K deficient symptoms first appear in the lower and older leaves. With K deficiency progressing, the symptoms also show in top leaves. The typical K deficiency symptoms depend on plant species. In corn, chlorosis and necrosis appear along the edges of older leaves while the midrib remained green (Havlin et al. 2016). In alfalfa, white spots occur along the margin of leaves, sometimes concurrently with a yellowing (or burning) of leave edges. In soybean, chlorosis and necrosis also appear in the lower leaf edges while tissue along the veins and base remains green. Potassium deficient almond trees typically have small, pale leaves, diminished new leaf growth, and burned, curled leaf margins. However, these symptoms may not be visible in orchards at the onset of K deficiency because they take time to become visible. Furthermore, low K concentrations in almond trees do not immediately result in yield loss or reduced quality in the first harvest. However, inadequate K availability will damage the crop in the following years by decreasing the number and growth of fruiting spurs, reducing flowering (Doll, 2009; Mikkelsen, 2017).

Some other K deficiency symptoms are the weakness of straw, small grains, decreasing the load of grains and increased occurrence stalk breakage, which principally take place in corn and sorghum. In citrus, low K availability results in a decreased fruit size, discoloration of fruit skin, reduced peel and skin thickness, and an increase in skin cracking (Havlin et al. 2016). Studies have also shown that crops are more vulnerable to pathogen infections or diseases under K stress, resulting in compromised yields (Wang, 2013). For example, Prabhu et al. (2007) reported that K deficient cotton and other crops were more susceptible to fungal-induced diseases, such as Fusarium wilt and root rot, caused by *Fusarium oxysporum* spp. Adequate K supply before or after planting can greatly minimize this fungal infestation. When symptoms appear, the

application of foliar fertilizer may be a proper measure to instantly supply available K to crops in order to reduce the loss of yields and quality. Regular leaf analysis is a valuable tool to monitor the K status of crops.

1-2 Potassium use in California orchards

1-2-1 Current K demand by orchard crops

In California, orchard production is the most important component of the State's agricultural production. The most common orchard products are almond, pistachio, peach, prune and walnut. Most importantly, almond production accounts for 11% of agricultural output and 80% of the world's total. In general, orchard crops have a high K demand in order to achieve economic yields and high quality. In almonds 75 kg K was removed in fruit per metric ton of kernel yield (Doll, 2009). For almond tree, the critical K leaf value is 1.4% on the dry weight basis (Meyer, 1999), but Muhammad et al. (2017) suggested that leaf K > 1% did not increase yield in their 5-year consecutive field study. They also found that the K sources did not have a significant effect on almond yield. Nevertheless, regardless of K sources, the application K rate of 112 kg ha^{-1} can satisfy crop K demand under conditions of 100-150 mg kg^{-1} soil exchangeable K, which is consistent to Meyer's (1999) result showing that there are no additional benefits to almond yield when K application rate is above 139 kg ha^{-1}.

In pistachios, Zeng & Brown (2001) proposed that a K application rate between 110 – 220 kg ha^{-1} was sufficient to sustain highly productive pistachio orchards with any K sources while excessive K fertilizer (> 220 kg ha^{-1}) was applied, nut yield reduced in the subsequent year. From their 3-year cumulative data, they suggested that the optimal pistachio production for the critical K leaf value is 16.9 g kg^{-1} (1.6% on dry weight basis) and this value has a significant and positive correlation to nut yield during nut fill.

For olive, many published reports related K fertilization recommendations were based on rain-fed olive trees. Additional information about K fertilization in irrigated olive orchard is still

needed. However, generally, the annual K application rates under irrigation for olive are 1000 – 1200 g K_2O per tree or equivalent to 400 – 500 kg ha^{-1} with > 400 trees (Haifa group, 2021), whereas the rain-fed recommendation rate is 200 kg ha^{-1}. With respect to any irrigation strategy, the K deficiency threshold in leaf K is 0.4% in dry matter to ensure K sufficiency. There are contradictory findings on olive response to K fertilization (Zipori et al. 2020). On the one hand, K amount removed was higher than any other nutrient in the pruned material and fruit, showing a high demand of K for olive tree. For instance, on a 5-year average, the amount removal (kg ha^{-1}) for NPK was 40.4, 4.4 and 78.1, respectively. On the other hand, many studies reported that K fertilization had no effect on vegetative growth or yield, even though leaf K concentration was elevated with increasing K levels (Zipori et al. 2020). Rufat et al. (2014) proposed that the mean olive production in the treatment with 0 and 100 kg K_2O ha^{-1} was similar in 2010 (off-year) and 2011 (on-year) but not in 2012 (off-year). They concluded that K application is only useful when both the tree and soil reserves are low (see 1-2-2). For another example, Haberman et al. (2019) described there was no difference in vegetative development between unfertilized olive trees and trees fertilized with 300 kg K_2O ha^{-1} annually for six years. However, in this study, the yield was reported to be significantly higher in the K fertilized trees as a result of higher fruit number per tree and intense flowering.

Apple tree is another orchard crop with high K demand. The macronutrient nitrogen and potassium could affect the vulnerability of apple trees to diseases in two different directions. Consequently, application of K depends during the growth stage of apple trees, but is an efficient management practice to ensure yields. Cheng (2013) proposed that from bud break to fruit harvest, the net gain of total N and total K is 20 g and 36 g per tree, which is equivalent to actual 56 kg N and 101 kg K ha^{-1}, respectively. At harvest, Cheng (2013) also reported that total N and

K in fruit accounted for 37.6% and 71.3% of the total N and K in the new growth, respectively, which suggests apple trees require K nutrient at a much higher amount than N. Depending on the apple rootstock varieties, the desired level of leaf K ranged between 1.35% to 1.85% on a dry weight basis. As apple trees remove a great amount of K at harvest, Cheng (2013) recommended the minimum K_2O application required in relation to fruit yield in "Gala/M.26" for the goal of 1,000 or 1,500 bushels $acre^{-1}$ for 30 and 45 kg K_2O $acre^{-1}$. These application rates varied by apple varieties. In a three-year experiment with 'Jonagold' on M.9 rootstock in British Columbia, Neilsen et al. (2009) found that there was little response of K fertilizer forms to the leaf K concentration under daily fertigation over a six-week period from late June to mid-August. This result showed that regardless of K treatments (KCl 15 g and 30 g; K-Mag 15 g and 30 g; K_2SO_4 30 g; KTS 30 g), the application rates and timing are more important than K sources to apple growth.

1-2-2 Potassium management practices in orchards under irrigation

To conserve water resources and maximize water-use efficiency in orchard production, almond production has shifted from the traditionally rain-fed to the low-volume irrigation systems in those regions where water is scarce. In California, the Almond Board of California (2019) set a vision to help almond growers reduce an additional 20% of water used to grow a pound of almonds by 2025. Traditionally, K fertilizers were applied in orchards by either broadcast or banding under flood or sprinkler irrigation, requiring heavy doses of K fertilizer in order to enrich K in soil solution (Klein et al. 1999). Potassium mobility is however highly limited in soils with high CEC, and these approaches were limited or only efficient directly beneath a sprinkler and within a lateral distance of 30 cm (Neilsen, 1999). Conventional K

fertilization becomes less effective beyond the 30 cm around the emitters. Potassium is also often applied via fertigation along with nitrogen fertilizer. Fertigation is a practice to apply fertilizers via the irrigation system and those fertilizers must be soluble in water. Potassium mobility through fertigation shows a significantly higher distribution in soil K by depth. Since most commercial K fertilizers are soluble, K fertigation is a common practice in orchards. In a four-year 'Spadona' pear field trial, Klein et al. (1999) found that the fertigation of K increased soil K concentration from 0.1 meq L^{-1} to 0.48 meq L^{-1} in the 0 – 30 cm soil layer around the irrigated zone after three years. The use of fertigation through the drip system also considerably lowered the use of K fertilizer and resulted in a more rapid response by the trees compared to the past.

With growing interest in water conservation, K management is usually coupled with water supply to crops. However, although the reduced water application may not affect K supply via fertigation, crop yield is still susceptible to a lack of water supply. Fruit crops with water deficit in biomass usually have a yield loss and reduced fruit quality. The proportion of K fertilizer use and water application requires more attention under irrigation. Rufat et al. (2014) reported that the reduced water supply by 25% during the growing season in a super-intensive Arbequina olive field in Spain led to a yield reduction of 9.6% compared to the full irrigation olive trees. In the same study, Rufat et al. (2014) reported that if there is a low fruit yield year and the K content in the soil is high, soil K is not used by the olive tree for the year. The following year with a high fruit yield, olive trees took up higher K amounts from the soil. When soil K was not adequately supplemented, olive trees consumed K from tree K storage and the remaining soil K reserves, and no differences on K deficit were observed yet. However, in the subsequent year, when the soil K was still not well re-supplied after the depletion of soil and tree K reserves, the yield was greatly reduced. As a result, the authors concluded that K supply is only effective for the

significant empirical effect when both soil K and plant K reserves are low. To maximize the application of nutrients to crops during watering, K fertigation is usually associated with nitrogen (N) fertigation since N is also a highly mobile element in soils. However, the excessive use of NH_4-N fertilizer via irrigation system is likely to induce soil acidification in the irrigated root zone due to release of H^+, thus lowering soil pH and decreasing K availability for crop uptake (Neilsen et al. 1999; See 1-3-1). There is also a concern that higher application of K to soils inhibited the absorption of Ca and Mg by crops. Callan & Westcott (1996) found that excessive K application through drip irrigation suppressed the uptake of Ca and Mg in their cherry tree trial. Drip irrigation in cherries resulted in shallow root growth within the wetted zone leading to limited utilization of other cations at shallow depth, even though drip irrigation provided a satisfactory K nutrition for cherries. Therefore, they suggested that regular leaf analysis to monitor the foliar nutrient status is required to avoid deficiency of plant essential nutrients.

1-2-3 Methods to estimate K availability

Current K fertilizer application recommendations are based on the commonly used ammonium acetate (NH_4OAc; 1 mol L^{-1}) extraction method (Soil Survey Staff, 2004). The NH_4OAc method extracts both soluble K and exchangeable K in the soil. The method may be inadequate to determine K availability in soils with micaceous or vermiculitic mineralogy, as these soils may have a high K fixing potential, making the estimation of K fertilizer needs inaccurate or questionable (Cassman et al. 1990). To reduce uncertainty and the risk of K deficiency as well as to improve the accuracy of the prediction of plant-available K in soil, a sodium tetraphenylboron (NaTPB) method was developed by Cox et al. (1999). The TPB^- anion combines with K^+ in solution and precipitates as KTPB. NaTPB is a reagent that mimics plant root activity by

depleting soil-solution K^+, which triggers the release of exchangeable and a portion of non-exchangeable K^+.

On the east side of the San Joaquin Valley (SJV) of central California, some soils contain K fixing minerals derived from granitic alluvium of the Sierra Nevada. Murashkina et al. (2007) modified the NaTPB method and conducted a large study on K fixation in SJV soils, collected on the west and east side, to develop a more effective method to predict plant-available K in cotton production. They showed that NaTPB was able to extract 50 – 100% more K than NH_4OAc, and there was a stronger statistical relationship than with the NH_4OAc test for extracting K from granitic east side of pedons (high K fixing potential) than from nongranitic west side soils (low K fixing potential). Murashkina et al. (2007) also stated that there still was no clear and indicative relationship to demonstrate the lack of correlation between plant-available nonexchangeable K and K fixation potential in the soils. More information is required to improve the development of current estimated K methods to better predict K fixation in soils.

1-3 Fertilizer sources and soil K dynamics

1-3-1 Soil characteristics that affect K availability

Soil texture and CEC

   Soil particle size distribution is usually related to the level of soil CEC. Generally, fine-textured soils have more exchange sites and thus a higher CEC than coarse-textured soils. Potassium losses via leaching are minimized in fine-textured soils due to their high CEC. However, high exchangeable K does not always result in high solution K, depending on clay mineral types and other factors. High portions of primary minerals like mica and feldspar lead to a greater potential availability of K. Weathering transforms primary minerals (e.g. mica) to secondary minerals (e.g. illite and vermiculite). Illite-rich soils will also have a greater K-fixing capacity, which reduces K availability. Depending on soil texture and type of clay minerals, the same amount of K fertilizer application is not likely to have the same effect on plant-available K levels in different soils. Therefore, a proper K fertilization requires site-specific adjustments.
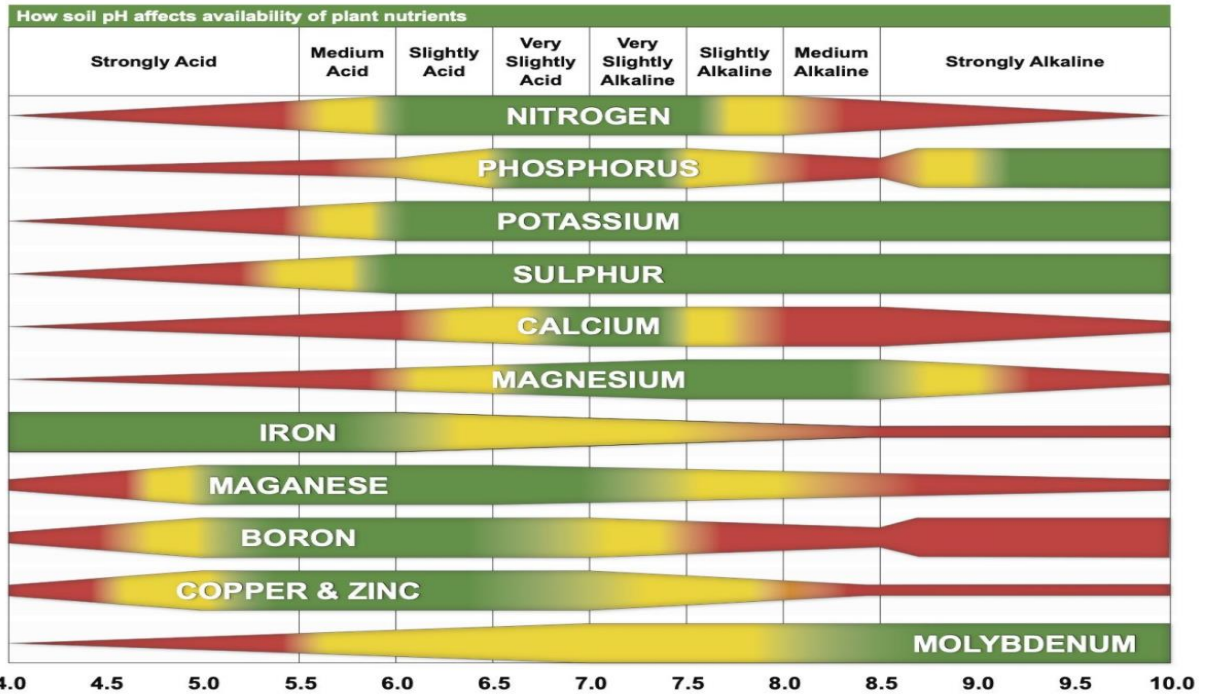
Figure 1-3-1 – Plant nutrient availability by soil pH. (Adapted from Haley, H and Bradley, S. 2021. Soil Testing, Liming, and Fertilizing Wildlife Food Plots).

Soil pH

The K availability is directly associated with soil pH. Potassium is most available for crops when soil pH is above 6 (Figure 1-3-1). Below pH 6, acidic cations become predominant and K^+ is replaced by Al^{3+} and H^+ on soil exchange sites, with more K in solution, the risk of leaching losses is increased. Soil pH also affects K fixation and will be discussed later. Although K availability is high in alkaline soils, very alkaline soils may be unfavorable to plant K availability. In this case, other cations, such as Ca, Mg and Na, become prevalent in soils and compete with K for binding sites.

Soil moisture and temperature

Potassium movement is highly governed by soil moisture levels. Potassium transport via mass flow or diffusion requires water. In soils with a high moisture content, water films are thicker and continuous across soil particles, creating a path for K mobility.

The temperature effect on K availability can be attributed to changes in crop root growth and K diffusion. For instance, Havlin et al. (2016) suggested that the influx of K absorbed by corn roots at 15 °C was < 50% than that at 29 °C. In the same study, the growth of corn roots was eight times greater at 29 °C than 15 °C. Temperature influences the rate of K adsorption in the soil. For example, Mon et al. (2016) showed enhanced K^+ adsorption on kaolin clay at an elevated temperature. They concluded that this may be because of changes in surface charge characteristics at different temperatures for kaolin clay. As a result, at low temperatures, higher amount of K may need to be applied to overcome the adverse effect on K diffusion for crop K uptake.

1-3-2 Potassium release and fixation

The availability of nonexchangeable K in the soil is governed by the rates of K release and K fixation by K-bearing minerals. During the course of weathering, K^+ held at the interlayers of 2:1 silicates is gradually released from the outer bonding sites as a result of the replacement by the water molecules or ions of similar size. When the primary minerals undergo further weathering, more K is released into solution, causing partial physical collapse of the crystal structure. This process results in a formation of hydrated secondary clay minerals at interlayers, leading to a break-up of mineral conformation and thus increasing the CEC of the soil. The different transformed forms of weathering micas are determined by the degree of hydrous status of the clay mineral. Mica has zero CEC when the lattice is intact and dehydrated. At an intermediate weathering stage, mica is transformed to illite with a CEC of 30 – 50 meq/100 g, while at a high level of weathering, illite is transformed to vermiculite with a CEC of 150 meq/100 g (Alexiades & Jackson, 1965). This process requires time. The exchange sites (either dioctahedral or

trioctahedral) on the minerals need exchangeable cation (usually NH_4^+) or water molecules to reach and replace K, and the exchangeable K also needs time to diffuse (Sparks, 1987). The release of K from the nonexchangeable form occurs when the solution K and exchangeable K are removed by crops or being leached into deeper soil layers, but it is generally very slow. During weathering, K release can occur at all interlayer locations from any exchange sites or binding positions in soil particle. At the same time, K fixation can also take place in the mineral nonexchangeable positions to make K unavailable.

There is increasing recognition that soil K fixation is a crucial concern on K fertilization. K fixation is a process where K is re-entrapped between interlayers of 2:1 soil minerals. In contrast, 1:1 soil minerals like kaolinite do not fix K (Havlin et al. 2016). Due to the similar ionic radius of K^+, NH_4^+ can also be fixed into the interlayer. The presence of NH_4^+ will partially alter both K fixation and release from a strong K-fixing soil. K fixation in soil limits K availability for crop uptake. Soils containing high K-fixing minerals such as vermiculite, montmorillonite, hydrous biotite, and biotite mica (weathered micas) at different weathering stages are considered soils with a high K-fixation potential (Page et al. 1967; Shaviv et al. 1985). Many factors affect the degree of K-fixing capacity in soils, including the concentration of K ions and other competing ions, type of clay minerals and their charge density, the weathering phase, soil pH and moisture regimes. The latter will be discussed more detailed below. Martin et al. (1946) found that there was no fixation in a soil with a pH < 2.5; in soil with a pH between 2.5 and 5.5, the amount of K fixation increased rapidly. When pH exceeded 5.5, the increase in K fixation lessened. Studies showed that the K fixation is strongly influenced by charge density when the type of minerals and moisture level are the same. Rich (1968) reported that the K fixation level was significantly higher in montmorillonite-rich soil under adequate soil moisture. This is not only because of the

higher charge density of its natural property, but also a greater opportunity of having more wedge positions in montmorillonite, where the selectivity for K is higher. When solution K and the exchangeable K pools are depleted, some nonexchangeable K may be released from these K-fixing minerals, alleviating K deficiency in soil. The capacity for plants to explore non-exchangeable K in soil considerably relies on plant species and root morphology (Mengel, 1985). It is very important to manage K fertilization under the strong K-fixing conditions. However, for sustainable agriculture, K fixation is not always an unfavorable phenomenon since it conserves K and serves as a long-term K provision to plant growth (Havlin et al. 2016).

1-3-3 Wetting and drying events

Potassium fixation develops when soil moisture regimes alter in mica-rich soils. Havlin et al. (2016) demonstrated that air-drying some soils high in exchangeable K may increase K fixation and reduce in exchangeable K. Conversely, air-drying soils low in exchangeable K, especially subsoils, frequently increases the exchangeable K pool. Zeng & Brown (2000) examined the effects of soil moisture regimes on soil K mobility and K dynamics in drip irrigated pistachio orchard and in pot-grown corn. Their results revealed that K applied to a soil with a constant soil moisture content at field capacity had a higher mobility compared to the wetting-drying (W-D) cycle regime typical of longer cycle irrigation practices. In California orchards, micro-sprinkler irrigation systems, which only irrigate a portion of soil around the trees, are commonly set to irrigate 12 h every 3 - 4 days (Zeng & Brown, 2000). In summer, this causes alternate W-D cycles in the irrigated zone which can greatly influence K diffusive flux. Zeng & Brown (2000) found that pronounced W-D cycles could enhance soil K fixation, especially during the first 2 days after rewetting, and decrease K mobility, thus reducing plant-available K pools. The W-D

effects on K availability is difficult to quantify under field conditions. However, these effects are

also important to soil testing as drying soil samples is a common practice in most soil analysis

procedures (Havlin et al. 2016).

1-3-4 Potassium fertilizer characteristics and effects

Potassium fertilizers from organic sources

Organic K fertilizer sources are usually from organic wastes, such as animal manure or

sewage sludge and crop residues (Andrews et al. 2021). The K content in these sources is

variable, depending on the origin of the raw materials. For example, the K content in animal

waste ranges between 0.2 and 1.2% of dry matter (1.8-18 kg K Mt^{-1} on dry weight); conversely,

the average K content in sewage sludge is 4.5 kg K Mt^{-1} (Havlin et al. 2016). Beyond sources,

the manure handling system of organic sources makes K concentration variable even within the

same materials (Table 1-3-1). For instance, K_2O in beef cattle manure can vary from 5 kg Mt^{-1}

(as a solid manure without bedding) to 17 kg Mt^{-1} (as liquid manure collected in a liquid pit).

Table 1-3-1 – Approximate dry matter (%) and K_2O content (kg Mt^{-1}) of selected manures. (Adapted from Murrell et al., 2021).

Livestock type	Waste handling system	Dry matter %	K_2O content kg Mt^{-1}
Solid handling systems			
Swine	Without bedding	18	4
	With bedding	18	3.5
Beef cattle	Without bedding	15	5
	With bedding	50	13
Dairy cattle	Without bedding	18	5
	With bedding	21	5
Poultry	Without litter	45	5
	With litter	75	17
	Deep pit (compost)	76	22.5
Liquid handling systems			
Swine	Liquid pit	4	9.5
	Oxidation ditch	2.5	9.5

	Lagoon	1	0.2
Beef cattle	Liquid pit	11	17
	Oxidation ditch	3	14.5
Dairy cattle	Lagoon	1	2.5
	Liquid pit	8	14.5
Poultry	Lagoon	1	2.5
	Liquid pit	13	48

Due to the variable K content, it is recommended for growers to regularly determine K concentration with laboratory analysis before applying organic matter amendments to fields. Although, the fertility of K in animal manures with a reasonable amendment rate is generally equivalent to soluble K fertilizers, they are considered low nutrient concentrations and uneconomic for long-distance transport (Murrell et al. 2021). As a result, these organic materials are primarily used near farms where animals are raised to reduce transport costs.

Studies showed that manure applications, besides its mineral content, also improve soil quality, maintain soil fertility, and thus reduce soil degradation (Mikha et al. 2017; Villa et al. 2021). In practice, organic fertilizers are managed to meet either crop N or P demand in order to minimize impacts on surface and groundwater quality (Havlin et al. 2016). Therefore, K inputs with organic fertilizers may not be adequate, especially in K-deficient soils, and further attention to K management is required.

Potassium fertilizers from mineral sources

The materials mined from deposits of K minerals and salts beneath the earth surface or the evaporite of brine lakes and oceans is generally referred as "potashes." (Havlin et al. 2016; Murrell et al. 2021). Depending on the weather and geologic conditions, the compositions of potashes may vary when mined. The term potash is a group of inorganic K sources including many different individual K fertilizers. The products within the potash family (and other commercial K fertilizers) provide growers the greatest accuracy and precision of application to

achieve the target yields. The most common potash sources are: muriate of potash (MOP, also called KCl); sulfate of potash (SOP, also called K_2SO_4); sulfate of potash magnesia (SOPM, also named $K_2SO_4·MgSO_4$); nitrate of potash (NOP, also named saltpeter KNO_3); and Chilean saltpeter, which is a mixture of sodium and potassium nitrate ($NaNO_3 + KNO_3$) (Murrell et al., 2021). This review will focus on the common K fertilizers MOP, SOP and a complex type of mined mineral K fertilizer, polyhalite ($K_2SO_4·MgSO_4·2CaSO_4·2H_2O$), which will be introduced later in this session.

The K content in any type of K fertilizer is conventionally given by its oxide basis (K_2O). The conversion between elemental K content and K_2O is:

$$K\ (\%) = K_2O\ (\%)\ x\ 0.83$$

$$K_2O\ (\%) = K\ (\%)\ x\ 1.2$$

The reserve of potash resources is generally large. According to the US Geological Survey (2020), the global potash reserves were estimated to be 250 billion metric tonnes. This is sufficient for the current demand of potash fertilizers for thousands of years, even when the K fertilizer production was to double (Murrell et al. 2021).

Muriate of Potash is the most common commercial K fertilizer and has a high K content of up to 60% as K_2O. It is a directly usable mining product and is a primary component for producing other secondary K fertilizers. The high solubility of KCl results in a rapid K availability in soil solution for plant uptake. However, the large input of chloride can be toxic and cause an imbalance of plant nutrients. Therefore, MOP fertilizer should be carefully managed and mainly used in low chloride conditions and in chloride-tolerant crops. These limitations make KCl a less favorable fertilizer to most crop production in California including

almonds. The cost of MOP was US$275 per metric ton in 2020, which makes it the cheapest fertilizer per unit K (Creamer Media's, 2020).

Sulfate of Potash contains 50% K_2O and 17% S. It is the second most common potash fertilizer on the market, and accounted for 9% of global K fertilizer sales in 2015. The solubility is one-third of KCl. There is not a large difference of K supply efficiency from other potash fertilizers. SOP is generally used for high-value crops and is a suitable substitution for KCl with the additional benefit of providing S, which is important for protein synthesis and enzyme function. For soils with salinity problems, SOP is an alternative to KCl in order to avoid Cl^- addition. The cost of SOP was nearly double that of KCl at approximately US$500 per metric ton in 2020 (Creamer Media's, 2020).

Polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$) is a multi-nutrient fertilizer consisting of K (14% as K_2O), Ca (17% as CaO), Mg (6% as MgO), S (19%) and many essential trace nutrients. Early research regarding polyhalite can be dated back to the 1930's when a large salt deposit of polyhalite estimated 103,600 square kilometers was discovered in western Texas and New Mexico (Mansfield & Lang, 1929). However, the subsequent discovery of MOP shifted the interest from polyhalite to MOP and polyhalite received little attention since then. Recently, polyhalite has found renewed interest due to the development of improved mining techniques, the high value of polyhalite as a fertilizer with both macro- and micronutrients (e.g. B, Zn, Mo, Fe, etc.), and the overall increased cost of K fertilizers (NASS, 2014). The cost for polyhalite was US$200 per metric ton in 2020.

The plant nutritional properties of polyhalite, particularly its salt index (SI), total elemental content and solubility, were investigated by Barbier et al. (2017). They found that polyhalite is an excellent K source with many favorable chemical properties. In addition, polyhalite was

shown to be as effective as MOP or SOP for corn (*Zea mays,* L.) and sorghum (*Sorghum bicolor,* L.) in a pot experiment (Fraps, 1932), for potato (*Salanum tuberosm,* L.) (Lepeshkov & Shaposhnikova, 1958), and for tea (*Camellia sinensis,* L.) (Wu et al. 2019). These studies showed that polyhalite performed as an effective amendment, producing a better yield and higher quality product than MOP, SOP or SOPM fertilizers. Most studies (Barbarick, 1991; Wu et al. 2019; Molin et al. 2019) have focused on the effect of different polyhalite application rates in comparison with conventional K fertilizers (e.g. MOP and SOP) on crop production. Information on the dynamics of polyhalite K in soil is still scarce.

In a tea plantation study in southeast China, Wu et al. (2019) found reduced soil acidification with polyhalite application compared to the SOP treatment. Even though tea quality was not different between the polyhalite and SOP treatments, the yield with polyhalite was 15.1% and 46.9% higher than with SOP and the unfertilized control treatment, respectively. In the same experiment, the soil pH in the SOP and polyhalite treatments dropped by 0.74 and 0.49 units, respectively, after 3 years. The authors hypothesized that Ca and Mg in polyhalite enhanced the percentage of base cations in soil as because Al and Fe in acidic soil were replaced by these two cations (Yang et al. 2018). This is consistent with the finding that the addition of $CaSO_4$ and $MgSO_4$ can slightly increase soil pH (Fung & Wong, 2004; Jayaganesh et al. 2006). Wu et al. (2019) also observed that in plots fertilized with polyhalite, the exchangeable K, Ca, and S contents were significantly increased in soil in the second and third year after application, and an increased exchangeable Mg content was measured in three consecutive years compared to the SOP treatment in strongly acidic soils in a 3-yr field experiment. Similar results were obtained by Barbarick (1991) and Molin et al. (2019) under acidic soil conditions, where polyhalite had a positive influence on dry matter of sorghum-sudangrass (*Sorghum bicolor,* L.) yield and K

uptake. While polyhalite may be beneficial in acidic soils, in the almond producing regions of California, soil pH is typically basic (pH > 7). Therefore, the effects of polyhalite on physicochemical soil properties and on crop yield may be different from those seen in prior studies.

In a column study, Barbier et al. (2017) confirmed that the leaching of various nutrient elements of polyhalite differed by element and soil type. K, Ca and SO_4 were leached rapidly and completely in sandy soil, while less Mg was leached. They proposed that leaching extent is highly affected by soil properties, such as soil pH, texture, and presence of carbonates. In their column study, nearly 100% of applied polyhalite-K was recovered in the first 600 ml of leachate in fine sandy soil from columns, while only 56, 54 and 92% of applied K was recovered in the same amount of leachate in the MOP, SOP and SOPM treatments, respectively. One possible reason for this result was the influence of Ca and Mg in polyhalite and Mg in SOPM, which affected the mobility of K in the soil low in Ca and Mg. Ca and Mg occupy the same exchange sites as K on clay mineral surfaces. When they are added to soil, a larger proportion of K remains in soil solution.

In conclusion, the value of K nutrition from any organic and inorganic K fertilizers is identical since K is not incorporated into organic molecules. For growers, of utmost importance is the timing and the quantity of K fertilizer applications to fulfill crop need during the growing season. Although there is a number of factors complicating the decision-making for the proper K management, the effective use of K fertilizers in soils would be the most important goal to optimize yields and ensure crop quality.

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Chapter 2: A study of three potassium fertilizers in Californian almond production soils

2-1 Abstract

Potassium (K) management in almond production is a major concern as almond trees have a high demand of up to 336 kg K ha^{-1} yr^{-1} and a K deficit compromises crop yield and quality. Sulfate of potash (SOP) is the most frequently used K source in almonds while other K sources including muriate of potash (KCl), microfine SOP (mSOP) and polyhalite (POLY) are also used. Little information is available to describe the properties of K fertilizers and their efficacy for orchard production. This study explores K dynamics using a soil-column experiment by comparing the behavior and distribution of KCl, mSOP and POLY in three different soils (Hillgate sandy loam and two different loams San Ysidro and Yolo) obtained from almond orchards in California's Central Valley. Three replicate columns with each K fertilizer along with an unfertilized control were subject to four wetting events over a two-month period and different K pools were measured at depth of 0-10, 10-20 and 20-30 cm.

Our results showed microfine SOP resulted in a more uniform K distribution by depth, higher solution K concentrations and the highest K leaching when used in the sandy loam soil following the first wetting event. The leachate from mSOP and POLY applications had a lower electrical conductivity (EC) compared to MOP leachate at an EC of 3.42 dS/m after the initial wetting event across all soil types. After completion of the experimental incubation, K losses for all fertilizers were low in the fine-textured soils with most K retained in the top 10 cm soil layer.

The total amount of leached base cations from POLY also surpassed the other K fertilizers after two wetting events in the clay-loam soil - Yolo, although there was a pronounced increase

on base cation levels in soils. POLY resulted in a higher solution K concentration in all soils. After complete incubation, a large proportion of unaccounted K, ranging from POLY treatment of 921 mg K column^{-1}, or equivalent to 42.0% in the San Ysidro to SOP treatment of 438 mg K column^{-1}, or equivalent to 16.9% in the Hillgate soil, was observed, perhaps due to movement of K into the non-exchangeable pool. The slow-release characteristic of POLY-K and the additional content of Ca and Mg increased total extractable base cation levels in soils, and increased leaching of base cations after four wetting compared to other two K fertilizers. These results offer valuable insights into the K dynamics in orchard soils from different K fertilizers.

Key words: Potassium fertilizer; K pools; polyhalite; sulfate of potash; leaching effect; K budget; soil column; K dynamics; almond production soil

Abbreviation

K: Potassium; MOP: Muriate of Potash; SOP: Sulfate of Potash; POLY: Polyhalite; EC: Electrical Conductivity; BC: Base Cation; TOC: Total Organic Carbon; TON: Total Organic Nitrogen; W-D cycle: Wetting-Drying cycle; SI: Salt Index; RMS: Resin Membrane Strip; NaTPB: Sodium Tetraphenylboron; SJV: San Joaquin Valley

2-2 Introduction

In California, almond is a high-value crop and accounts for 80% of worldwide almond production (Almond Board CA, 2020). Potassium (K) is the key nutrient for almonds, as it increases flowering and fruit set, prevents nut cracking, and is crucial for the development of the hull, shell and kernel (Almond Board CA, 2020). With a typical harvest yield almond trees remove up to 336 kg K ha^{-1} yr^{-1} from the soil (Doll, 2009). Given this characteristic, proper K management is needed to ensure optimal yields and crop quality. To meet this goal, this current study aimed to gain insight into K dynamics and fate in the soil system with different fertilizer materials in soils with different textures.

The mobility of K in soils has been widely discussed in the past (Barber, 1962; Sparks & Huang 1985; Mouhamad et al. 2016). Potassium transport to the roots is mainly through diffusion as a mechanism for K movement from high to low concentrations (Barber, 1962). In this regard, the K replenishment rate to the root zone is an important factor governing root K uptake. In California's Central Valley where almond production is focused, soil pH is typical above 7 (USDA-NRCS & CBI, 2014) with basic cations predominant in the soil. Without a proper K supply in the soil, K eventually becomes deficient by crop removal or leaching. Although, conventional K fertilizers (e.g. MOP and SOP) have long been used, information about K dynamics in an orchards system, such as pistachio (Zeng & Brown, 2001), apple (Cheng, 2013) and olive (Haberman et al. 2019) is limited. While MOP is a widely used K fertilizer by almond growers, the Cl anion is toxic to almond growth because almond trees are sensitive to high salinity levels, e.g. when the soil electrical conductivity (EC) is above 1.5 dS/m (Doll, 2014). Other K fertilizers, which have a lower effect on salinity, such as SOP, potassium thiosulfate (KTS) and polyhalite have been proposed as alternative K fertilizers for MOP. Little

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information about slow-release polyhalite ($K_2MgCa_2(SO_4)_4.2H_2O$) is available for orchard

production and available studies of polyhalite were mainly focused on K leaching (Barbier et al.

2017; Yermiyahu et al. 2017; Huang et al. 2020) in different soils on annual crops such as

tomato (Mello et al. 2018), maize (Sutradhar et al. 2016; Molin et al. 2020) and soybean

(Sutradhar et al. 2016). Comparisons of K dynamics of three K fertilizers (MOP, mSOP and

polyhalite) K and their relative movement in soil and partitioning into different K pools

following the use of various K fertilizers is missing. Polyhalite is unique among these three K

sources in that it contains large amounts of Ca and Mg in addition to K and as such K availability

may be restricted (Sparks & Huang, 1985).

Our experiment was designed to measure the effect of fertilization and irrigation on the

movement and distribution of K into soil fractions following MOP, mSOP, and POLY

application to soil columns of different soil types (coarse vs. fine texture). The objectives for the

present study were to 1) compare the effects of different K fertilizers in three soil types on the K

partitioning at different depths and; 2) assess the effect of K fertilizer type on K, Ca and Mg

leaching under simulated irrigation management. The following hypotheses were tested: (i) K

fertilizer type will alter K distribution (soil solution K, adsorbed K, extractable K, and leached

K), total K distribution, and K leaching; (ii) the low solubility and high Ca, Mg content of

POLY-K, compared to the other two K fertilizers, will increase the total extractable soil base

cation levels (especially K, Ca and Mg) and this will reduce K leaching.

2-3 Materials and Methods

2-3-1 Soil descriptions and collection

Soil samples were collected from three almond orchards in Northern California in fall 2019. The orchards were located in Arbuckle (38°57'29.3"N 122°04'48.8"W), Woodland (38°40'02.9"N 121°53'27.5"W), and Davis (38°31'57.0"N 121°46'30.8"W). Plant residue on the soil surface was removed before soil samples were collected. At each site, the top 30 cm of the soil profile were collected in three separate 10-cm layers into 5-gallon buckets. The samples were air-dried at 60 °C in a drying oven. Each sample was then ground and passed through a 2-mm sieve. The Arbuckle soil was classified as a Hillgate sandy loam (Soil Survey Staff, 1999), the Woodland soil as a San Ysidro loam and the Davis soil as a Yolo loam. Some initial soil physicochemical properties in each layer are summarized in Table 2-3-1.

The three soils had different infiltration rates through the column, decreasing in the order of Hillgate > San Ysidro > Yolo. In general, applied water infiltrated within 24 hours in the Hillgate soil, while it took one week for the San Ysidro soil and two weeks for the Yolo soil.

Table 2-3-1 – Initial unfertilized soil properties at Arbuckle, Woodland, and Davis sites

Site	Layer	pH	EC	Texture (Sand, Silt, Clay in %)	Series	TC[**]	TN	Ex. K[*]	Ex. Ca[*]	Ex. Mg[*]
	cm		dS/m			%		--mmol soil layer[-1]--		
Arbuckle	0-10	7.25	0.17	Sandy loam (62, 29, 9)	Hillgate	1.20	0.13	5.16	22.99	8.84
	10-20	7.31	0.10	Sandy loam (62, 29, 9)		0.52	0.07	4.44	14.53	7.38
	20-30	7.06	0.11	Sandy loam (60, 30, 9)		0.48	0.07	4.93	13.97	7.60
Woodland	0-10	7.52	0.47	Loam (40, 39, 21)	San Ysidro	1.15	0.12	2.66	74.93	16.54
	10-20	7.54	0.42	Loam (40, 38, 22)		0.81	0.09	1.74	56.58	21.17
	20-30	7.56	0.46	Loam (42, 37, 21)		0.56	0.07	1.46	46.65	26.51
Davis	0-10	7.64	0.27	Loam (44, 35, 21)	Yolo	0.85	0.10	7.78	29.48	46.53
	10-20	7.66	0.13	Loam (41, 37, 23)		1.09	0.14	7.53	30.55	49.56
	20-30	7.65	0.14	Loam (41, 39, 20)		0.57	0.08	5.71	31.14	48.85

The initial nonfertilized soil extractable K levels were moderate to low, ranging from 1.46 to 7.78 mmol kg^{-1}. Calcium and Magnesium were the dominant extractable cations in all soils with the San Ysidro soil contained the highest extractable level of Ca (74.93 mmol kg^{-1}). All three sites have been used for almond production for many years; therefore, the nutrient status reflects soil properties as well as nutrient management practices. Total carbon in all three soils was low, ranging from 0.81 to 1.2% in the top 10 cm of the profile. Soil pH was slightly alkaline, ranging from 7.06 to 7.66, which is typical for arable soil in the Central Valley (Richards, 1954). All selected soil types were classified as nonsaline with maximum EC values of 0.47 dS/m.

Table 2-3-2 – The amount of extractable cations and CEC for each soil layer in the unfertilized Hillgate, San Ysidro and Yolo series.

Series	Layer cm	K mg kg^{-1}	Ca mg kg^{-1}	Mg mg kg^{-1}	CEC meq 100g^{-1}	K satur. %	Ca satur. %	Mg satur. %
Hillgate	0-10	226	1032	238	7.9	7.4	66	25
	10-20	194	652	199	5.5	9.1	59	30
	20-30	216	627	205	5.5	10.1	57	31
San Ysidro	0-10	119	3444	456	22.1	1.4	78	17
	10-20	77.8	2600	584	18.9	1.1	69	26
	20-30	65.6	2144	731	17.9	0.9	60	34
Yolo	0-10	363	1411	1336	19.2	4.8	37	58
	10-20	352	1462	1423	20.2	4.5	36	59
	20-30	267	1491	1403	19.9	3.4	37	59

CEC was lowest for the Hillgate soil (5.5 to 7.9 meq 100 g^{-1}), and greatest for the San Ysidro and Yolo soils (17.9 to 22.1 meq 100 g^{-1}) (Table 2-3-2). The Ca saturation was relatively high in the Hillgate (up to 66%) and San Ysidro soil (up to 78%) but low in the Yolo soil averaging 37% while Mg saturation was very high in the Yolo soil (59%).

2-3-2 Incubated column preparation

An acrylic tube (inner diameter: 9.5 cm; height: 40 cm) was cut into four 10 cm long sub-columns. Soil was then packed into each corresponding sub-column. Soils were packed starting with the 20 - 30 cm layer, followed by the 10 - 20 cm and 0 - 10 cm layers. While packing soils into the columns, a resin membrane sheet (5 cm wide; 30 cm long, CMI-7000, Membranes International Inc., NJ) was vertically inserted to serve as a super sink for cations to simulate plant root absorption. A round stick with a flat head was used to compact the soil uniformly to achieve a soil bulk density of approximately 1.3 g/cm^3. Three sub-columns filled with soil and an empty sub-column on top, serving as water reservoir during wetting events, were then glued together with silicon glue into a 40 cm tall column. The gaps between sub-columns were sealed with water-proof tape to prevent any leakage. A hole at the 5 cm height of each sub-column was drilled to fit a rhizotron (Rhizosphere Research Products B.V., NL) for soil solution extraction. A permeable geotextile fabric pad was used to cover the column base and tightened with nylon cable ties in order to hold the soil in the cylinders. The columns were then placed on a wooden shelf with a funnel underneath each column.

The treatments consisted of three K fertilizers (MOP, mSOP and POLY) and an unfertilized control. MOP was purchased from the Voluntary Purchasing Groups, Inc (TX, USA). mSOP was an ultra-fine diamond-K product, with fertilizer size guide number (SGN) 44 mm, produced by Compass Minerals (KS, USA). POLY as a granular multi-nutrient K fertilizer acquired from the Anglo American plc (London, UK) marketed as POLY4. All K sources used in this experiment were sub-sampled and sent to the University of California, Davis Analytical Lab for accurate analysis of nutrient contents. The results are summarized in Table 2-3-3.

Table 2-3-3 – Potassium fertilizer content results analyzed by UC Davis Analytical Lab. The SOP # (Standard Operating Procedure number) is a reference and method summary to the UC Davis Analytical Laboratory method used.

Fertilizer	N (Total) [SOP 522.1] %	P (Total) [SOP 590.2] %	K (Total) [SOP 590.2] %	S (Total) [SOP 590.02] ppm	B (Total) [SOP 590.02] ppm	Ca (Total) [SOP 590.02] %	Mg (Total) [SOP 590.02] %	Zn (Total) [SOP 590.02] ppm	Mn (Total) [SOP 590.02] ppm	Fe (Total) [SOP 590.02] ppm	Cu (Total) [SOP 590.02] ppm
MOP	0.03	<0.010	49.5	1340	2.4	0.078	0.026	<1.0	1.4	54.1	<0.5
mSOP	<0.02	<0.010	42.5	193750	<1.0	0.212	0.273	1.2	5.9	300.6	<0.5
POLY	<0.02	<0.010	11.5	193060	244.6	10.473	3.687	<1.0	2.5	95.5	2.0

The application rate for all treatments was 2.38 g K_2O column^{-1}. With a column area 70.85 cm^2, this amount of K_2O applied corresponded to a band application rate of 336 kg ha^{-1} year^{-1}, which is typical for California almond production. The K fertilizers were applied to the soil surface and incorporated into the top 1 cm of the soil. Water for leaching was collected on two occasions from an irrigation well at a field site in West Davis, CA (38°31'57.0"N 121°46'30.8"W). The concentration of the 1st water collection (used for irrigation events 1 and 2) for K, Ca and Mg was 0.8, 75.1 and 7.1 mg L^{-1}, respectively; while the concentration of the 2nd water collection (used for irrigation 3 and 4) for K, Ca and Mg was 2.6, 16.7 and 8.2 mg L^{-1}, respectively.

2-3-3 Column Incubation and different K pools sampling and analyses

The amount of water applied initially corresponded to the pore volume plus an extra 100 ml of water. Leachate was collected by placing a beaker underneath each column. The leachates were analyzed for K, Mg, Ca, Na and EC after each wetting event. The amount of water application was varied between each wetting event owing to the different evaporation rate and drainage rate by soils. For each subsequent wetting event, the quantity of water applied corresponded to the

amount evaporated since the last event plus an additional 100 ml water (Table 2-8-5, appendix). The weight of each column was recorded weekly. The water application date for each wetting event was on day 0, 14, 28 and 56. Due to the different infiltration rates and water flow rates of the soils, the leachate collection was completed on different days for each soil during wetting events. The soil infiltration rate was in the order: Hillgate > San Ysidro > Yolo.

Three days after applying water, 5 ml of solution were extracted from each rhizotron with a 30 ml syringe. This extract was used to determine K^+, Ca^{2+} and Na^+ concentrations in solution by depth. The first three wetting events were conducted in 2-week intervals, while four weeks passed between the third and fourth wetting event. Every time, the quantity of extracts and leachates was measured on a scale and the samples were stored at 5°C for later analysis. Two weeks after the last wetting event, the columns were unpacked. A sub-sample from each layer of each column was air-dried, homogenized, and manually ground to pass through a 2-mm sieve for later analysis. Resin membrane sheets were cut into 10-cm pieces by depths and extracted as described above for soil to represent the pool of absorbed K.

Soil pH and EC were measured in a 1:2 soil-water suspension. Soil texture was determined by the pipette method (Gee & Bauder, 1986). Cations in a 2-g soil sample were extracted by 1M ammonium acetate (NH_4OAC) at pH 7, filtered through a Whatman Q5 filter paper into a 50-ml centrifuge tube (Gavlak et al. 2005) and analyzed by ICP-OES (iCAP 7000 Series, Thermo Scientific, MA). Extractable K pools consist of solution K and exchangeable K.

2-3-4 Data analysis and results interpretation

The experimental design was a randomized complete block in a 3 x 4 x 3 factorial scheme with three replicates of each column. The factors were three soil types (Hillgate, San Ysidro, and

Yolo), four K treatments (control, MOP, mSOP and POLY) and three soil depths (0 - 10, 10 - 20, and 20 - 30 cm). Statistical analyses were carried out using R-studio (version 1.3.1073, PBC) for ANOVA and SigmaPlot v.14.0 was used to create figures. Depth was considered a repeated measure. The Bonferroni and Tukey methods were assigned for variances evaluation between soils and treatments in the K leachate. The Bonferroni method was used for the cross-group (multiple factors comparison) analysis, while the Tukey method was used for within-group (single factor comparison) analysis. All tests were considered significant at $p < 0.05$. To better address our dataset, a specific statistical method- winsorization- was adopted to eliminate extreme residuals of two outliers in the first leachate collection in the mSOP treatment in Hillgate soil. The winsorization method replaces the highest residual value with the second highest residual value by assigning a lower weight to these extreme variances in order to reduce the influence of outliers and thus increase model normality and robustness (Dixon, 1960). All units were converted to mg K per column to calculate a K budget for each treatment based on the following equations:

$$I = w + f + i \text{ --(1)}$$

$$O = r + s + l + f \text{ --(2)}$$

$$Unaccounted\ K = K\ inputs - K\ outputs \text{---(3)}$$

Where:

I = K inputs; O = K outputs

w = K in irrigation water

f = K in fertilizer. Fertilizer K was zero in the control treatment.

i = Initial NH_4OAC extractable K

r = amount of K adsorbed on resin membrane sheet

s = amount of K in solution collected from samplers

l = amount of K in the leachates

f = Final NH$_4$OAC extractable K in soils at end of study

Leached K percentage was calculated as:

l / (f + w) *100---*(4)*

2-4 Results

2-4-1 Effect of different K fertilizers on various K pools in the selective soils

Solution K in K pools

The three K fertilizers (MOP, mSOP and POLY) showed different behavior and effects on various K pools in the three soils. In some cases, however, behavior was similar in the San Ysidro and Yolo loamy soils. In general, the top soil layer of the Hillgate soil had a higher soil solution K than deeper depths for all K fertilizers (Figure 2-4-1) and POLY resulted in a higher K concentration in the top layer (up to 1506 mg K L^{-1} during the first wetting event) compared to the other two K fertilizers. For the subsequent wetting events, the solution K remained high, averaging 1507 mg K L^{-1}. After the fourth wetting event, the top layer in the Hillgate soil with POLY still had a high K concentration of 637 mg K L^{-1}, suggesting that this fertilizer had a slower K release rate and additional inputs of other cations that resulted in the maintenance of K in soil solution. It is also likely that because the top layer in the Hillgate soil dried out much faster, concentrating the K in a smaller volume of soil solution. A slow, but constant K release was also supported by the observation that POLY-treated columns had a uniform distribution of solution K from the top layer to the middle soil layer. MOP and mSOP treatments displayed a similar gradient though with a much lower solution K than POLY. In the loamy San Ysidro soil, all K sources resulted in high K concentrations in the top layer (Figure 2-4-1). However, while comparing K treatments, POLY had much higher solution K concentration than the MOP and mSOP treatments throughout the incubation. For instance, at the first wetting event, POLY-treated K concentration was 709 mg K L^{-1} and then decreased in the following wetting events, but remained relatively high (266 mg K L^{-1}) even at the fourth wetting event. On the other hand,

the solution K of MOP and mSOP were stable, ranging between 150 to 250 mg K L^{-1}. There was a low concentration of solution K found in the middle and bottom soil layers in the San Ysidro soil. In the Yolo loamy soil, all K fertilizers increased solution K in the top layer, similar to the San Ysidro soil (Figure 2-4-1). POLY showed the highest solution K (804 mg K L^{-1}) and second highest solution K (775 mg K L^{-1}) at the first and second wetting event, respectively. After that, solution K in the POLY treatment decreased, but was still higher than in the MOP and mSOP treatments. At the fourth wetting event, MOP and mSOP increased solution K in the top layer, which may have been due to the longer incubation time between the last two wetting events. There was a low concentration of solution K found in the middle and bottom soil depths in Yolo soil. In this loam soil, K fertilizer effects were pronounced only in the top soil.
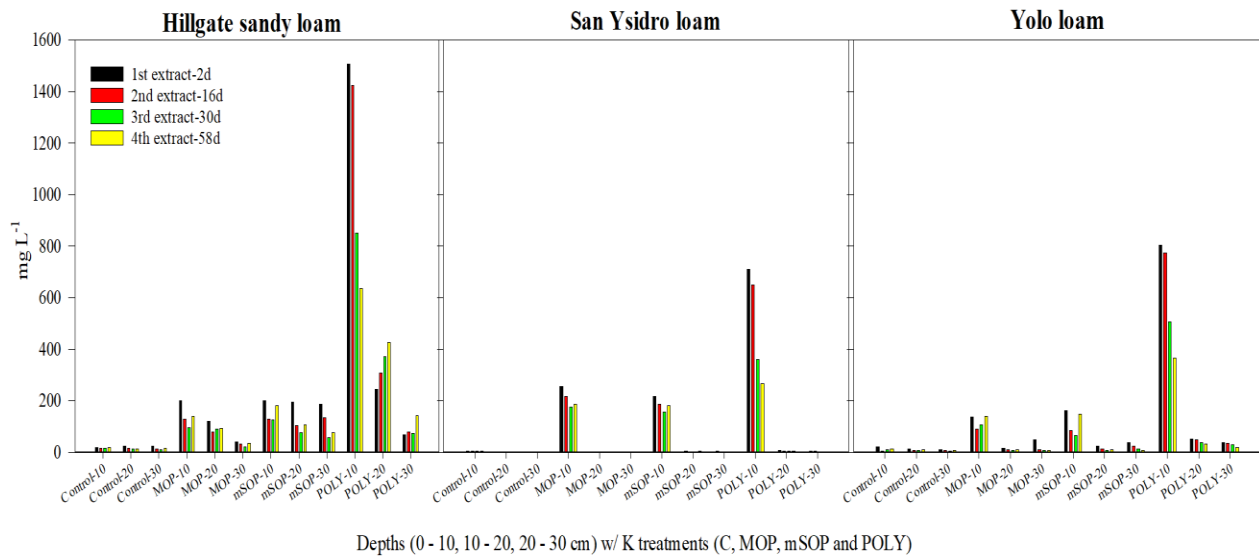

Figure 2-4-1 – Potassium concentration (mg K L^{-1}) in the solution extractors at three depths (T: 0-10; M:10-20; B: 20-30 cm) and four wetting events in the Hillgate, San Ysidro and Yolo soils.

Adsorbed K (Resin membrane strip binding K)

To calculate the total amount of adsorbed K, the resin membrane strip (RMS) in each column was cut into three 10-cm long pieces. The amount of K adsorbed on RMSs was the highest in the topsoil (e.g. up to 60.4 mg K kg^{-1} for the MOP treatment, Figure 2-4-2). The adsorbed K decreased in an order of: MOP > mSOP > POLY. There was no significant difference in adsorbed K across K fertilizers in the San Ysidro soil. The three fertilizers increased adsorbed K on RMS to about 9 mg K kg^{-1} in the top layer. All K sources in the Yolo loam soil exhibited a similar adsorbed K pattern as the San Ysidro soil (Figure 2-4-2). There was no statistical difference across K treatments. Most K was adsorbed by RMS in the top layer, ranging from 15 to 18 mg K kg^{-1} for the fertilized K treatments in the Yolo soil.

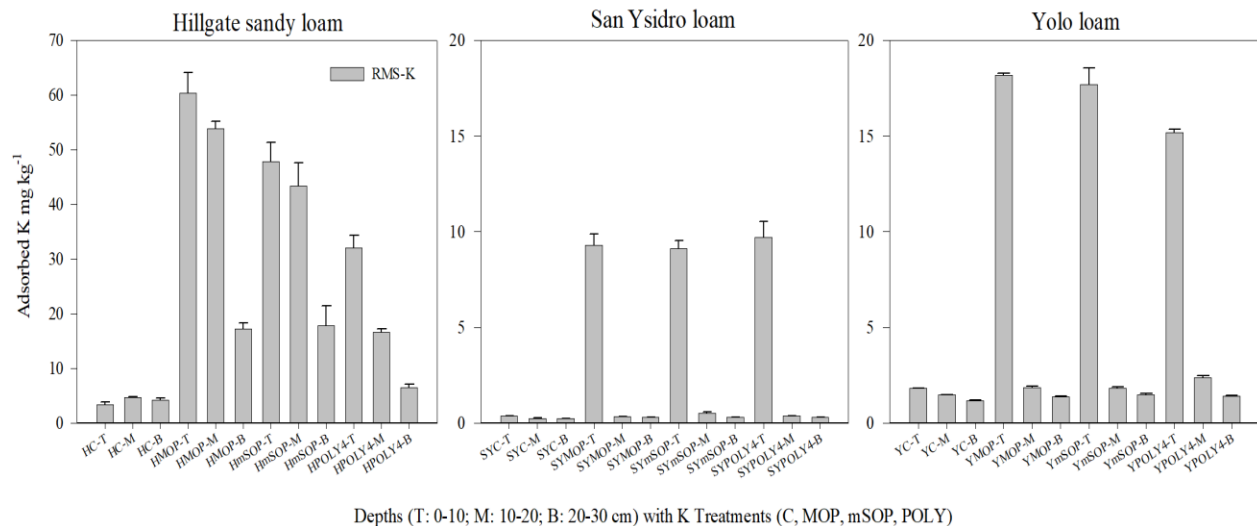Depths (T: 0-10; M: 10-20; B: 20-30 cm) with K Treatments (C, MOP, mSOP, POLY)

Figure 2-4-2 – Potassium adsorption (mg K kg^{-1}) by a cation resin membrane strip (5 cm x 30 cm) at three depths (0 - 10, 10 – 20, 20 - 30 cm) in the Hillgate, San Ysidro and Yolo soils at the end of experiment. Adsorbed K mean ± S.E.

Extractable soil K in K pools

The net change in extractable K did not differ significantly across fertilizer treatments in the Hillgate soil, besides the control (Figure 2-4-3). In the San Ysidro soil, all K inputs greatly increased extractable K after incubation mainly within the top layer (Figure 2-4-3). However,

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there was no statistical significance between K fertilizers in the total extractable K level. The highest combined extractable K level was observed in the mSOP treatment with 1098 mg K column[-1]. All K inputs greatly increased extractable K in the Yolo soil, predominantly within the top layer (Figure 2-4-3). Still, there was no statistically significant difference between K fertilizers in the total extractable K level. The highest extractable K level was observed in the mSOP treatment with 1397 mg K column[-1] in the Yolo soil. In general, the total extractable soil K between soil types were statistically different (p = 0.002). When taking soil depth into account, extractable K increased in all layers in the Hillgate under the K applications. In the fine-textured San Ysidro and Yolo loam soils, the extractable K mostly remained in the top layer, which is consistent with lower K leaching.
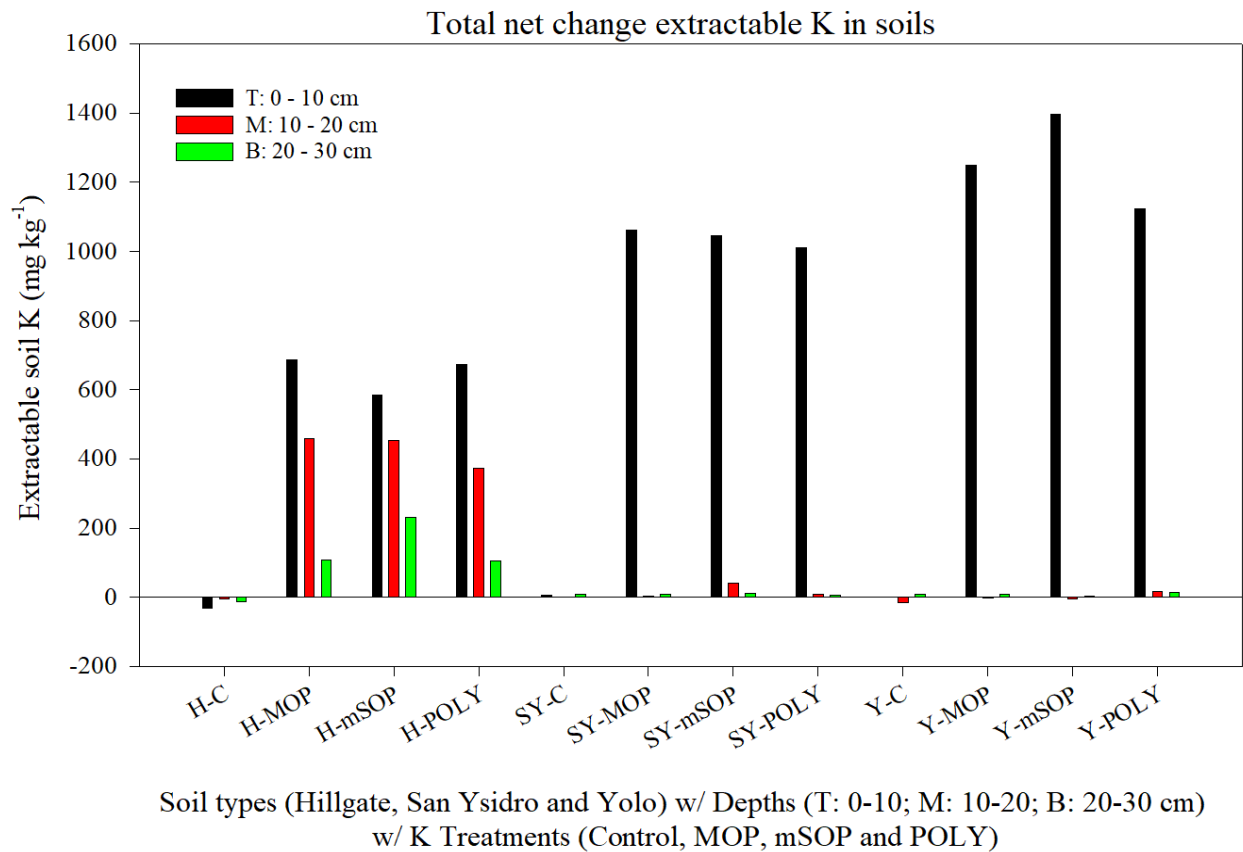

Figure 2-4-3 – Total net change in extractable K at three soil depths (T: 0-10; M: 10-20; B: 20-30 cm) with different K treatments (Control, MOP, mSOP, and POLY) in the Hillgate, San Ysidro and Yolo soils over four wetting events. The net extractable K level was calculated by subtracting the initial extractable K from the final extractable K.

Leached K in K pools

The K fertilizers exhibited different patterns of K leaching through the experiment, with the most marked differences observed at the initial wetting event, ranging from a low of 13.5 (POLY) to a high of 48.0 mg K kg^{-1} (mSOP) (Figure 2-4-4). POLY had significantly lower leached K at the first wetting event compared to the mSOP ($p < 0.001$) and MOP ($p = 0.001$) treatments but, at the end, mSOP had a highest cumulative leached K after four wetting events, with 76.7 ± 24.8 mg K kg^{-1}, which was about double than the total leached K of POLY or MOP. In addition, leached K in the mSOP treatment was rapidly leached in the first and second wetting events while MOP only showed a rapid leaching of K in the first wetting event. Total cumulative leached K with POLY and MOP, 32.7 ± 2.38 and 39.3 ± 7.26 mg K kg^{-1}, respectively, was significantly less than with mSOP (76.7 ± 24.8 mg K kg^{-1}). According to the statistical model, cumulative leached K in the mSOP treatment was significantly higher than in the POLY ($p = 0.0002$) and MOP ($p = 0.0021$) treatments. Low levels of K were leached in the San Ysidro soil (Figure 2-4-4) with < 1 mg K kg^{-1} in all three K inputs, with no significant differences across treatments. Likewise, there was no statistical difference between K treatments in the Yolo loam, with the highest accumulative leached K being 11 mg K kg^{-1} for POLY. K fertilizers in the Yolo loam also had a small leaching potential with less than 0.5% of added K.
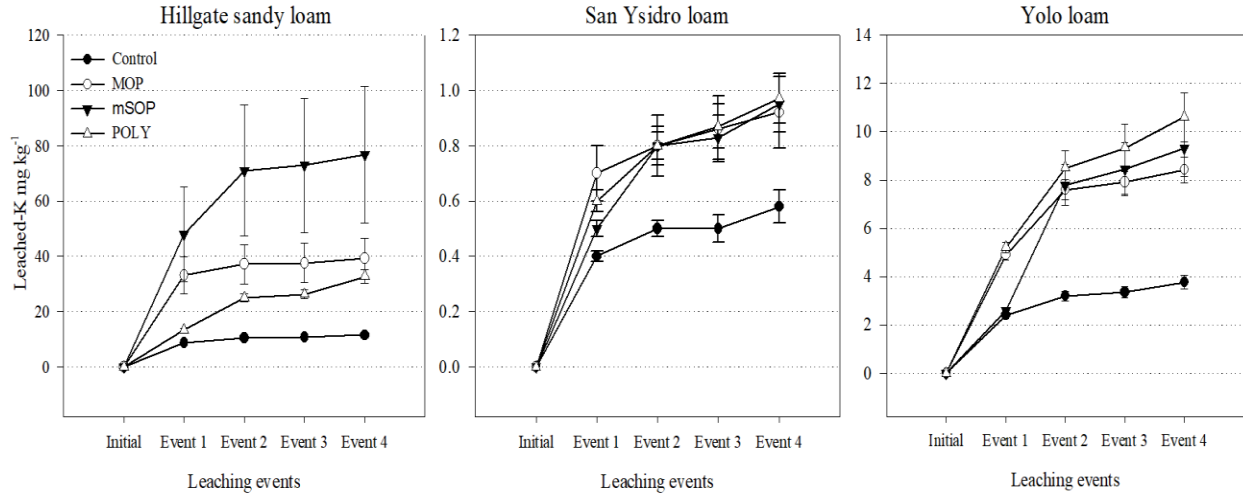
Figure 2-4-4 – Cumulative leached K (mg kg^{-1} dry soil) over four leaching events with MOP, mSOP and POLY treatments and the control in the Hillgate, San Ysidro and Yolo soils. Leaching event 1, 2, 3 and 4 were collected 1, 15, 29, and 57 days, respectively after the start of the incubation.

2-4-2 Potassium budget and leaching potential in the system

The different K pools, expressed in mg K column^{-1}, are presented in Table 2-4-1. The amounts of added K fertilizers in this study were slightly different, which was because of small discrepancies between the label K_2O content and the actual K_2O content. The POLY-treated Hillgate soil had lower adsorbed K, higher soil solution K, less leached K, and less extractable K at the end of experiment. There was a large pool of unaccounted K, calculated as the difference between K inputs and K outputs, in soil columns with K fertilizers application (Table 2-8-6, appendix). K inputs were calculated as the sum of the initial K in soil (sum of extractable K and fertilizer K) plus the K applied with water in every wetting event (eq. 3). K outputs were calculated as the sum of the various K pools after incubation. After the incubation, some POLY fertilizer granules were still on the soil surface. These undissolved POLY residuals contributed to the high unaccounted K at the end. In the Hillgate sandy loam soil, mSOP had a very high leached K (201 mg K column^{-1}). Interestingly, in the San Ysidro and Yolo loam soils, mSOP had

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the lowest K leaching (2.47 and 23.5 mg K per column, respectively). mSOP-K leached readily

in the coarse-textured soil but was minimized in the fine-textured soils.

Unlike the high leaching of mSOP-K in the coarse-textured soil, POLY had notably low

leached K (86 mg K column^{-1}); however no statistical difference of leaching potential across K

fertilizers was seen in the San Ysidro and Yolo loam soils.

Table 2-4-1 – K budget results across soil types and K treatments in different measured K pools on the basis of the equation (1) and (2). Unit in mg K per soil column.

	K in irrigation water	Fertilizer K	Initial extractable soil K	Resin membrane binding K	K in solution collected from samplers	K in leachate	Final extractable soil K
	-- mg K column^{-1} --						
Hillgate Sandy Loam							
Control	3.91	0	567	12.29	0.69	32	519
MOP	3.55	1950	567	131.50	3.48	105	1821
mSOP	3.76	2023	567	109.03	7.67	201	1838
POLY	3.69	1964	567	55.12	16.2	86	1720
San Ysidro Loam							
Control	4.07	0	229	0.83	0.19	1.54	243
MOP	4.25	1950	229	9.91	4.00	2.40	1302
mSOP	4.02	2023	229	9.92	4.16	2.47	1327
POLY	4.01	1964	229	10.34	9.92	2.53	1253
Yolo Loam							
Control	4.39	0	820	4.44	0.68	9.41	815
MOP	5.16	1950	820	21.38	3.30	21.2	2074
mSOP	5.17	2023	820	20.97	2.22	23.5	2214
POLY	4.62	1964	820	18.97	13.1	26.5	1974

Table 2-4-2 – K leaching rate in different soil types and K treatments. Unit in mg K column^{-1}.

	Leached K	K fertilizer	Water K input	Leached K over K inputs
	--mg K column^{-1}--			%
HC	32.0	0	3.91	820
HMOP	105	1950	3.55	5.39
HmSOP	201	2023	3.76	9.92

HPOLY	85.7	1964	3.69	4.35
SYC	1.54	0.0	4.07	37.8
SYMOP	2.39	1950	4.25	0.12
SYmSOP	2.47	2023	4.02	0.12
SYPOLY	2.53	1964	4.01	0.13
YC	9.41	0.0	4.39	214
YMOP	21.2	1950	5.16	1.09
YmSOP	23.5	2023	5.17	1.16
YPOLY	26.5	1964	4.62	1.35

All treatments values are corrected for the background control to represent the fertilizer effect (Table 2-4-3). K inputs equal water plus fertilizer, K recovery is the sum of resin K, extractable K and leached K. Extractable K is the sum of solution and exchangeable K.

Table 2-4-3 – Summarized K budget across soil types and K treatments. Values presented are fertilizer effects where the difference between treatment and control was calculated at the block level.

Soil Type	Fertilizer	K Inputs	K Recovery	Resin K	Extractable K	Leached K
				mg K column-1		
Hillgate sandy loam	MOP	1954	1494	131.5	1257	105
	SOP	2027	1589	109.03	1279	201
	POLY	1968	1310	55.12	1169	86
San Ysidro loam	MOP	1954	1089	9.91	1077	2.40
	SOP	2027	1115	9.92	1102	2.47
	POLY	1968	1047	10.3	1034	2.53
Yolo loam	MOP	1955	1300	21.4	1257	21.2
	SOP	2028	1441	21.0	1396	23.5
	POLY	1969	1213	19.0	1167	26.5
p-values	Fertilizer		0.347	0.065	0.753	0.034
	Soil Type		0.048	0.967	0.410	3.1x10-6
	Fertilizer*Soil Type		0.976	0.999	0.997	0.014

In this study, fine-textured soils had a low leaching potential, ranging from 0.12 to 1.35% of the total amount of K applied with fertilizer and irrigation water (Table 2-4-2). In comparison,

the leaching potential was relatively high, reaching 9.92% in the Hillgate soil. When comparing

different K inputs, the leaching potential of mSOP was more than twice that of the POLY

treatment (9.92% vs. 4.35%) in the Hillgate coarse textured soil.

2-4-3 Comparison of total extractable base cation level change in soils

On average, all K sources increased total extractable base cations in the San Ysidro and Yolo

loam soils, but despite this observation there were no significant differences among K fertilizer

treatments in these two soil types (Figure 2-4-5). However, in the Hillgate sandy loam, the base

cation levels were significantly higher in the POLY treatment, compared to the control (p =

0.032) with higher concentrations of K, Ca, and Mg. Although the increase in extractable soil K

in the Hillgate soil across K treatments was similar, this significant increase of total extractable

base cation level was due to the additional cation inputs by the POLY mineral. In the POLY

treatment, Mg contributed more to the total extractable base cation level than Ca which leached

easily. In summary, the effect of different K treatments on total base cation levels in the fine-

textured soils was not large. In the Hillgate sandy loam soil, POLY significantly increased total

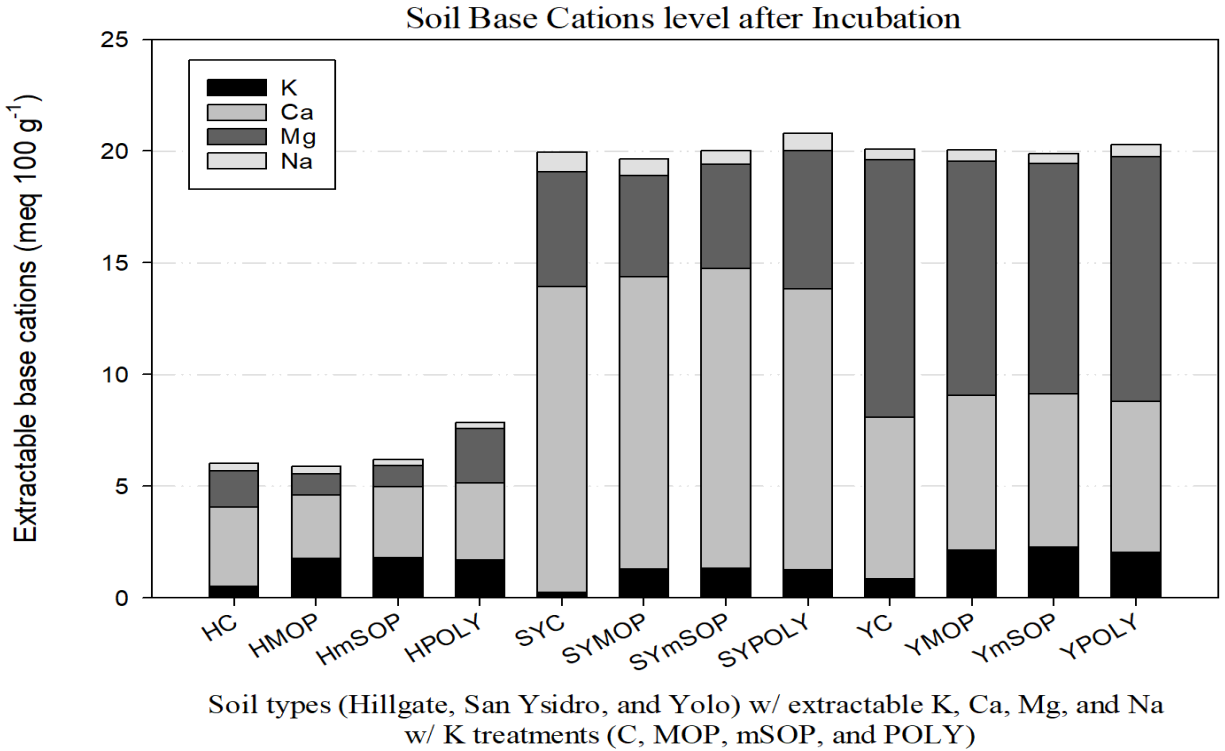extractable base cation level compared to the control.

Figure 2-4-5 – Total extractable soil base cation levels after two-month incubation under the three soil types (Hillgate, San Ysidro, and Yolo) and four K treatments (control, MOP, mSOP, and POLY).

2-4-4 Electrical conductivity of leachates

The EC of leachate from all three soils was highest following the first wetting event. The commercial MOP had the highest EC values across all soil types in the first leachate collection in comparison to the other treatments, reflecting its high solubility in water and the input of Cl (Fig. 2-4-6). The EC values of MOP were much lower after the second wetting event and remained very stable through the duration of this experiment, suggesting that most Cl was leached with the first wetting event. In the Yolo soil, the leachates in the MOP treatment reached 3.42 dS/m. This high value reflected a potential negative effect of salinity (2.1 – 4.0 dS/m, Smith & Doran, 1996) of the leachate solution on crop growth. In comparison to the EC curve of MOP, the EC trend of mSOP was inconsistent across soil types, but all values fell within the non-saline level. For

POLY, the EC values were relatively constant at a non-saline level, although there was a slight

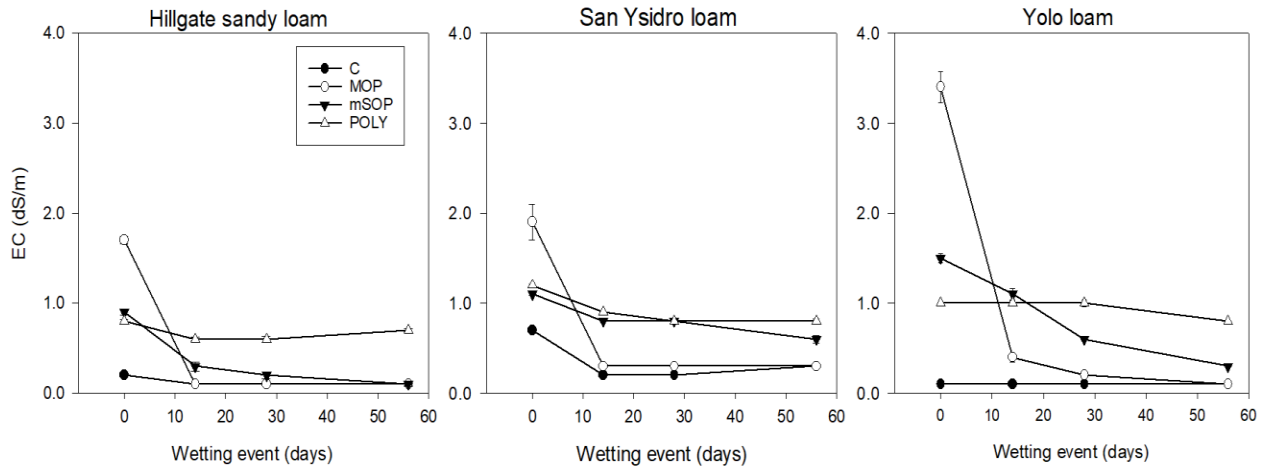increase in the fourth wetting event in the Hillgate soil.

Figure 2-4-6 – EC (dS/m) value of leachate changed over the two-month incubation time with MOP, mSOP and POLY treatments, and the control in selected soils (Hillgate, San Ysidro and Yolo). Each value is the mean of three replicates ± standard error.

2-5 Discussion

2-5-1 Different K supply patterns, evenness of K distribution and K leaching potential in soils

The Hillgate soil is a sandy loam soil with a low CEC. Potassium in this soil was readily leached and also had a more uniform distribution in the profile compared to the fine textured soils. Our result was supported by the K leaching effect in the field study conducted by Rosolem et al. (2010), showing that K distribution was more even below 20 cm in the long run with adequate K fertilization in the lighter-textured soil profile than the heavier-textured soil. The amount of K losses of the different K fertilizer treatments exceeded the control by 54-169 mg K column^{-1}, which corresponds to 2.75 – 8.35% of applied K fertilizers in the Hillgate soil. Kleinhenz (1999) reported that K applied as KCl is more susceptible to K leaching in soils as compared to the K from SOP. However, in a K fertilizer evaluation study for pineapple growth conducted in a tropical soil with a low CEC in Brazil, Teixeira et al. (2011) observed that there was no difference across different K sources for K downward movement in the soil profile. In contrast, our results showed that microfine SOP had the highest K leaching in the Hillgate sandy loam soil approximately double the amount of leached K from applied MOP. These contradictory results of K leaching may be reasonably ascribed to the different properties of the specific soil site and also the size of granules of K fertilizers (Mehring, 1935).

Barbier et al. (2017) found that the behavior of MOP and mSOP fertilizers with a typical particle size range of (SGN between 85 to 100) had a very similar K movement in their intensive leaching soil column study. Furthermore, our results suggested that the particle size of fertilizers is also one of the main factors influencing K leaching. The ultra-fine size of mSOP solubilizes

faster into water than the granular MOP, even though the solubility of mSOP is one-third of MOP (IPIN, 2010). According to Mehring et al. (1935), decreasing particle size results in increasing surface in the proportion to the mass. In our study, the microfine SOP, may even have been washed into the soil profile at the beginning of first wetting event. Because of that, K in mSOP moved further in the soil than MOP and resulted in a higher amount of K leaching. The above hypothesis is supported by the high K concentration of extracts in the whole soil profile after the first wetting event. Since mSOP-K moved fast into the 20-30 cm soil layer during the first wetting event, the high K concentration in this layer also caused greater K leaching with the second wetting event.

The EC of the leachate in the MOP treatment was high in the first wetting event, but low in the following events, suggesting that most of Cl was leached during the first wetting event. When an anion is leached, the solution or leachate need to be electrically neutralized with equivalent amounts of cations (Lehmann & Schroth, 2002). Chloride in the MOP moved faster than the K through the column. Therefore, in order to maintain electrical neutrality, the leached accompanying cations were those already present in the soil. Based on our extractable cations results, the leached accompanying cations were predominantly Ca, followed by Mg, which is in line with a Havlin et al. (2005) study which demonstrated that in sandy soils, considerable amounts of Ca and Mg could be leached after the applications of MOP or mSOP. In the mSOP treatment, Ca most likely formed ion pairs with SO_4 as $CaSO_4$ in the soil profile or transported downward through water movement as a Ca^{2+} cation plus SO_4^{2-} anion in the solution (Barbarick, 1991). The formation of $CaSO_4$ accordingly opened up the exchange sites on clay particles, allowing the K to bond to those available sites. Without this process, the K leaching effect could have been even more pronounced in the mSOP treatment. Our results suggest that the free

exchange sites due to the formation of $CaSO_4$ in the soil with a higher CEC and Ca saturation reduced K leaching. Moreover, our results showed that the process of $CaSO_4$ formation is the case particularly with the fine-textured soils for San Ysidro and Yolo. The K leaching and the formation of $CaSO_4$ in the mSOP-treated column no longer exceed the K losses with the KCl treatment, as it did with the coarse-textured soils. There was very little K leaching observed in San Ysidro columns. The amount of leached K in the fertilizer treatments only exceeded the control by 1 mg K column^{-1} or 0.05% of the added K with no difference across fertilizers. The K leaching in the San Ysidro soil was much lower than the other two soils. This is likely due to its higher CEC and low K content throughout the profile resulting in a higher opportunity for K binding to the exchange sites. The initial K saturation accounted for < 1.5% of the total base saturation.

According to our results, all K fertilizer treatments significantly increased the extractable soil K in the 0 – 10 cm layer and there was no pronounced effect below that depth. This was supported by the very low K concentration of the leachates. The dominant cations in the leachates were mainly those already in the soil. Rosolem et al. (2010) reported similar findings of significant increase on K distribution in the lighter textured soil profile with no excess water application in the presence of soybean roots. In an intensive leaching soil column study, Barbier et al. (2017) also found that leached K was reduced with increasing proportions of fine-textured soil. Most cations were leached during the first wetting event in the San Ysidro loam, which was similarly found in the Hillgate soil. Especially in the MOP treatment, since Cl is a very mobile ion in soils, there needs to be equivalent accompanying cations to maintain the electrical neutrality in solution. This result is evidenced by the high levels of leached cations in the first wetting event.

The Yolo soil had a similar soil texture and CEC to the San Ysidro soil. Therefore, K in solution also mainly remained in the 0 – 10 cm layer and hardly increased at the 10 – 20 cm and 20 – 30 cm layers. This was also the case in the San Ysidro soil, suggesting that the amount of added K with fertilizers did not exceed the capacity of K adsorption on exchange sites in the top layer, even though the initial K saturation was higher in the Yolo soil than in the San Ysidro soil. It is not surprising that the K leaching is also minimal in the Yolo soil. Although the initial extractable soil K was higher than the San Ysidro soil, which led to more K being leached, the amount of leached K accounted for less than 0.5% of the added K with fertilizers. However, the initial proportion of Mg was much higher in the Yolo soil than in the other two soils, resulting in a higher Mg concentration in the leachates.

2-5-2 POLY effect on total extractable soil base cation levels and total leaching potential

In the POLY treatment, the low K leaching during the initial wetting event was due to its slow solubility (Huang et al. 2020). This effect was likely most pronounced in the Hillgate soil, with the fastest infiltration rate. This means that the water flowed down quickly and the POLY on soil surface dried quickly without enough time to dissolve into solution. POLY also contains SO_4, as well as Ca but these two ions have already paired within a complex crystal structure in the polyhalite (Weck et al. 2014). As a result, K behavior is different because mineral composition of $CaSO_4$ in POLY dissolved slowly and the system was not flooded with SO_4 as was the case in the mSOP treatment. This result is in agreement with Yermiyahu et al. (2017) investigation on comparison of release and transport of leached elements in powdered polyhalite to the equivalent soluble sulphate salts treatment in the tested dune sand soil. However, our results differed the granulation size of K fertilizer from their study, which was a factor considered in the current

study. In the San Ysidro soil, the initial Mg saturation was low. The input of Mg with POLY greatly increased extractable Mg content (about 206 mg Mg column^{-1}, data not shown) in the top 10 cm of the column after a two-month incubation and there was clear movement of Mg to the 10-20 cm layer.

Surprisingly, the high soil solution K in POLY treatment was not reflected in higher adsorbed K on the RMS. This result was likely a consequence of the higher quantity of Ca, Mg adsorbed to the RMS with the POLY treatment (Figure 2-8-5, 2-8-6 and 2-8-7, appendix). The total amount of leached base cations in the POLY treatment surpassed the amount of the other K fertilizer treatments after only two wetting events in the Yolo soil, while more than four wetting events would have been required for other soils. This might be explained by the slowest infiltration rate of Yolo soil and that a portion of water remained on the top of the column surface for a longer time period than the other soils, which helped with the dissolution of POLY. Substantial K, Ca and Mg leaching occurred in the Yolo soil under the POLY treatment, especially during the second, third and fourth wetting event. The same trends were observed in the other two soils. A similar leaching pattern was observed by Huang et al. (2020), who found that the nutrient losses in the slow-release polyhalite treatments following simulated rain-led leaching events were smaller, especially at the first leaching event of the trial in sandy soil, than that of the equivalent application of soluble sulfate salts. Interestingly, Barbier et al. (2017) reported that with 24 intensive leaching events, the slow-release characteristics of polyhalite became insignificant and resulted in a higher cumulative amount of leached K of about 20% with only 4% and 7% of K added as MOP and mSOP, respectively, in a fine-textured calcareous soil. As a result, we assumed that with more additional wetting events in the current study, the leached K, Ca and Mg of POLY treatment would have exceeded the amounts of the same cations

with MOP and mSOP treatments in the other two soils. Compared to MOP and mSOP, the amount of total leached cations was greater with the POLY treatment because when the same amount of K was applied, additional Ca and Mg were also added into the column due to polyhalite's natural composition (Yermiyahu et al. 2017). This resulted in a higher cation content in the POLY leachates and also a higher K replacement on the exchange complex. This finding refuted our hypothesis (ii) as we presumed the POLY will increase total base cation level in soils and have a less leaching potential. Therefore, it is possible to assume that in a severe leaching environment and in the absence of plant roots uptake, K likely moves more evenly and faster in the profile when applied as POLY compared to MOP and mSOP. This may either cause K leaching losses or a better distribution of K in the root zone, depending on irrigation management (Yermiyahu et al. 2017) and rainfall (Huang et al. 2020), as well as soil properties and crop specific factors.

2-5-3 General observations of applied K fertilizers in soils

The potassium ion competes with Ca and Mg ions in the soil solution exchange complex (Spark & Huang, 1985). As Ca and Mg are divalent cations, there is a stronger electrostatic force to adsorb to exchange sites compared to the K ion, which is monovalent (Brugman et al. 2020). As Ca and Mg are preferentially adsorbed in soils, the addition of these two ions with POLY displaced K binding to soil particles and resulted in more K in solution. There was also an increase of extractable Na in the soils; this may have resulted from the release of Na from the resin membrane strips because the strips were Na-saturated.

The unique aspect of this study is that the K budget from various individual K pools and leached K were obtained in conjunction with Ca and Mg (Table 2-4-3). Whereas in the study by

Vale (2016), mainly Ca and Mg were emphasized and in the paper by Barbier et al. (2017) only leached base cations and SO_4-S were investigated. Our results showed that there were large proportions of unaccounted K after incubation in all soils. These results suggest that K entered the non-exchangeable K pool in soils. Thus, K was captured into the soil clay interlayers. However, some of the non-exchangeable K is still in equilibrium with the exchangeable K pool. Studies have shown that K uptake efficiency of crops or plant species is divergent on K-fixing soils (Wang et al. 2011; Zorb et al. 2014). The capacity of plants to utilize non-exchangeable K is not only attributed to the efficiency of absorption, but also to root exudates, which can mobilize this K pool (Zorb et al. 2014). These root exudates are usually organic acids, such as citric and oxalic acids released by maize (Kraffczyk et al. 1984). In addition, El Dessougi et al. (2002) found that on K-fixing soils, sugar beets took up 3–6 times more K per unit of root length than wheat and barley. Therefore, there is still a need for the development of more efficient methods to better estimate the availability of non-exchangeable K.

2-6 Conclusion

Depending on the soil type, granulation and solubility of K fertilizers, K behavior varied. In the coarse-textured Hillgate soil, microfine SOP had a more uniform distribution by depths but with the highest leaching potential at the first two wetting events. On the other hand, MOP had the highest EC level at the first wetting event due to the presence of Cl. Surprisingly, K in the POLY treatment had a large proportion retained as solution K in this soil profile. In the fine-textured soil types, all K treatments had a high solution K at top soil layer with little leaching potential. However, POLY had the highest total leached base cation levels after the second wetting events in the Yolo soil. This could be ascribed to the additional inputs of base cations in

POLY mineral. A large proportion of unaccounted K was found after incubation across all K treatments, especially in the POLY treatment, suggesting that K entered to the non-exchangeable pool or did not fully dissolve due differences in granule sizes.

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2-8 Appendix (Supplementary Tables and Figures)
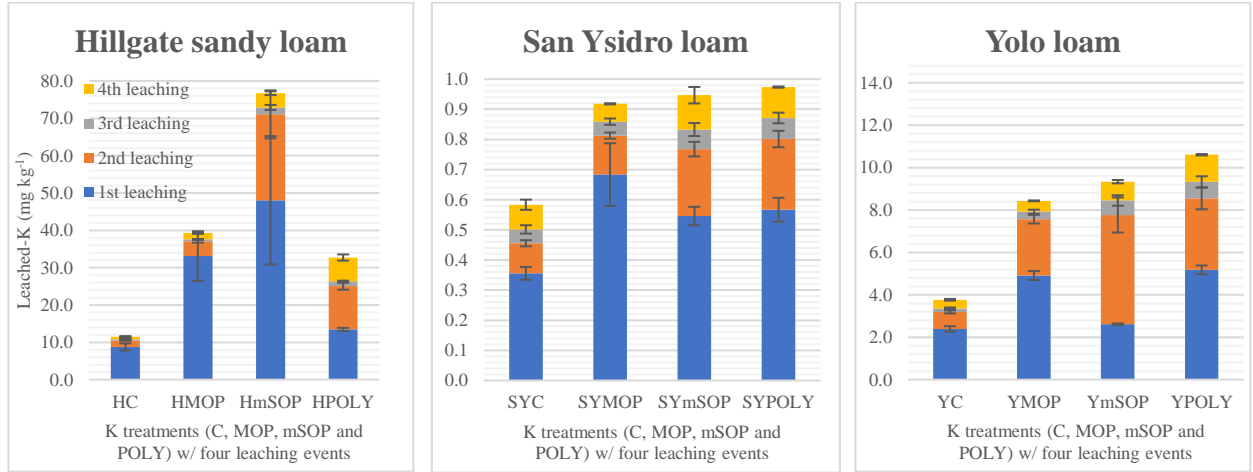
Figure 2-8-1 – Each K treatments of mean leached K (mg kg^{-1} dry soil column) ± S.E. over four leaching events in the Hillgate, San Ysidro and Yolo soils.
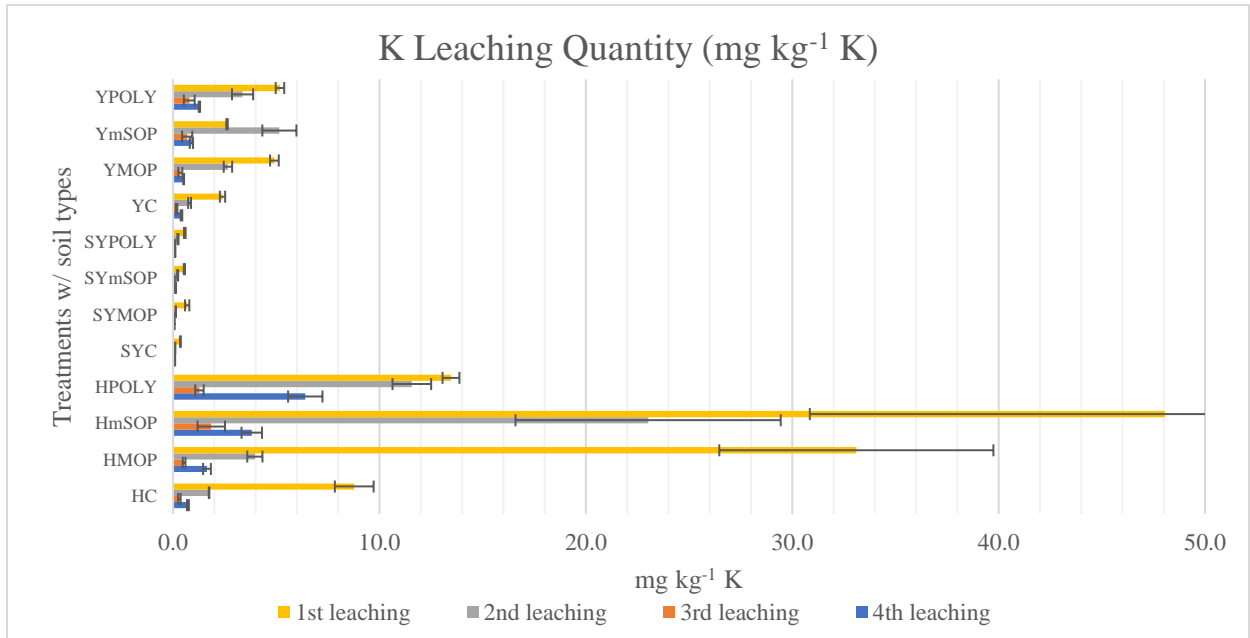

Figure 2-8-2 – Mean of leached-K (mg kg^{-1}) ± S.E. for the control, MOP, mSOP, and POLY in three soil types (Hillgate, San Ysidro and Yolo) under four leaching events.

Table 2-8-1 – ANOVA results of leached K for the first leaching event. Log value represented a better fitted normality in the model.

	Df	Sum sq	Mean Sq	F value	Pr (>F)	
trt	3	3.916	1.305	22.2446	4.109e-07	***
soil	2	79.760	39.880	679.5771	2.2e-16	***
trt : soil	6	3.068	0.511	8.7139	4.314e-05	***
Residuals	24	1.408	0.059			

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 2-8-2 – Tukey test of leached K of different K treatments for the fourth leaching event in the Hillgate soil.

soil = H: Treatment	lsmean	SE	df	lower CL	upper CL	group
C	-0.333	0.127	24	-0.6741	0.00774	a
MOP	0.484	0.127	24	0.1431	0.82491	b
mSOP	1.319	0.127	24	0.9783	1.66008	c
POLY	1.839	0.127	24	1.4986	2.18041	d

Results are given on the log (not the response) scale.
Confidence level used: 0.95
Conf-level adjustment: sidak method for 4 estimates
p value adjustment: tukey method for comparing a family of 4 estimates
significance level used: alpha = 0.05

Table 2-8-3 – ANOVA results for the comparison of net change of extractable K to other factors.

Analysis of Deviance Table (Type II Wald chisquare tests)				
Response: sqrt (Knet)				
	Chisq	Df	Pr (>Chisq)	
trt	30.2637	3	1.215e-06	***
soil	12.4608	2	0.001969	**
depth	237.2054	2	< 2.2e-16	***
trt : soil	1.9706	6	0.922384	
trt : depth	32.4242	6	1.353e-05	***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
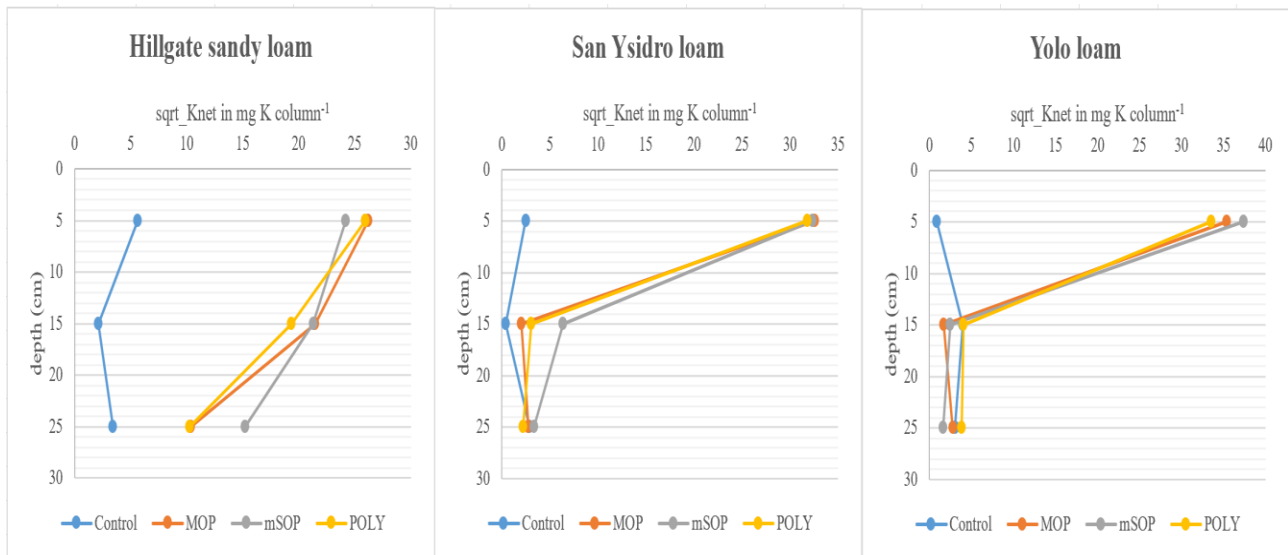
Figure 2-8-3 – Total net extractable K (mg K column^{-1}) level change by depth in three soil types (Hillgate, San Ysidro and Yolo) with different K treatments over the two-month leaching incubation. x-axis: square root of net extractable K per column; y-axis: soil depth (cm).
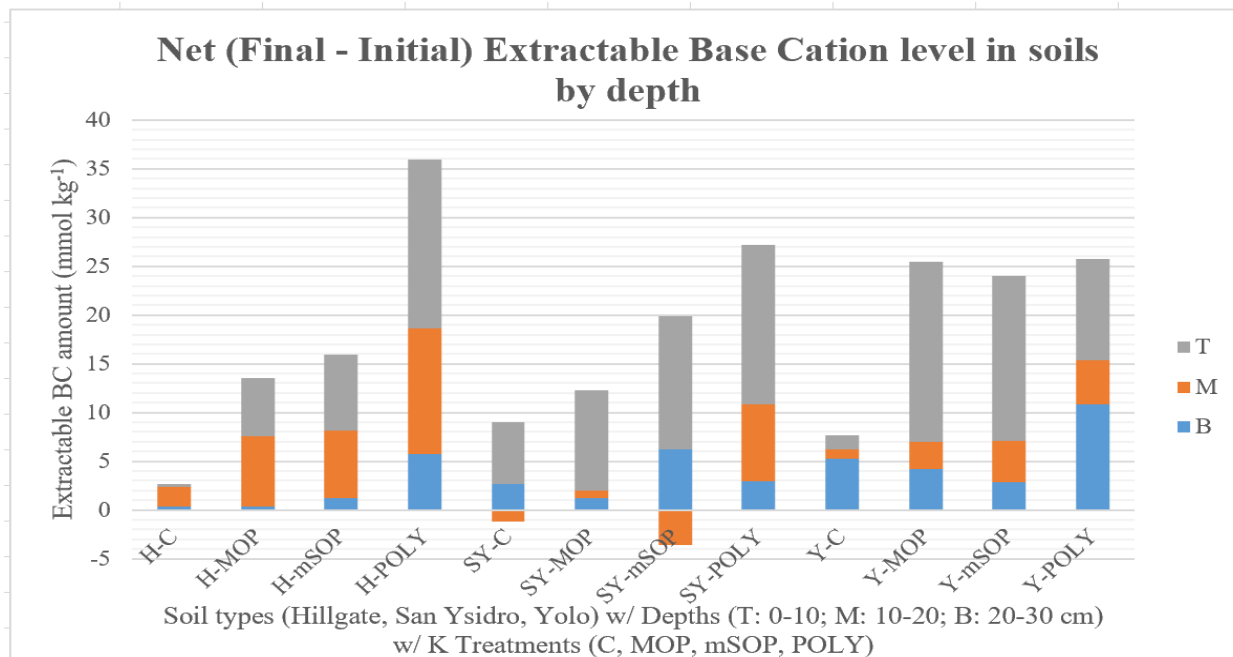
Figure 2-8-4 – Total net extractable base cation (mmol kg^{-1}) change by depths in three soil types (Hillgate, San Ysidro and Yolo) with different K treatments over the two-month wetting incubation. T: 0 – 10 cm; M: 10 – 20 cm; B: 20 – 30 cm.
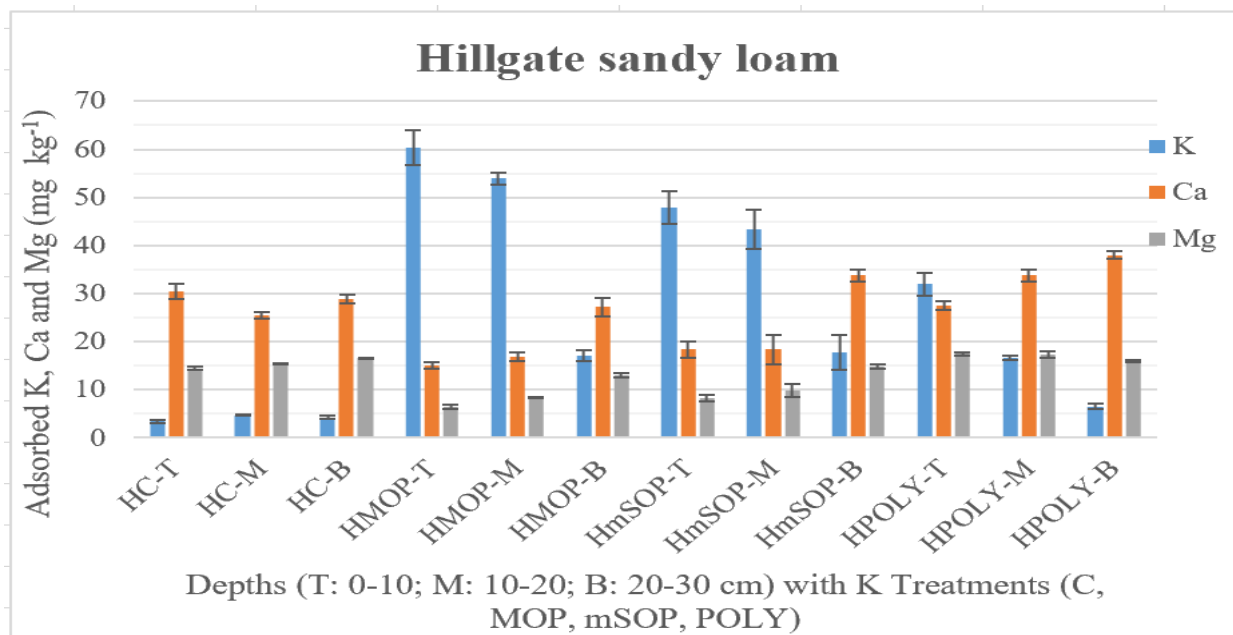

Figure 2-8-5 – Potassium, Calcium and Magnesium adsorption (meq 100g^{-1}) by a cation resin membrane strip (5 cm x 30 cm) at three depths (0 - 10, 10 – 20, 20 - 30 cm) in the Hillgate soil at the end of experiment. Adsorbed K mean ± S.E.
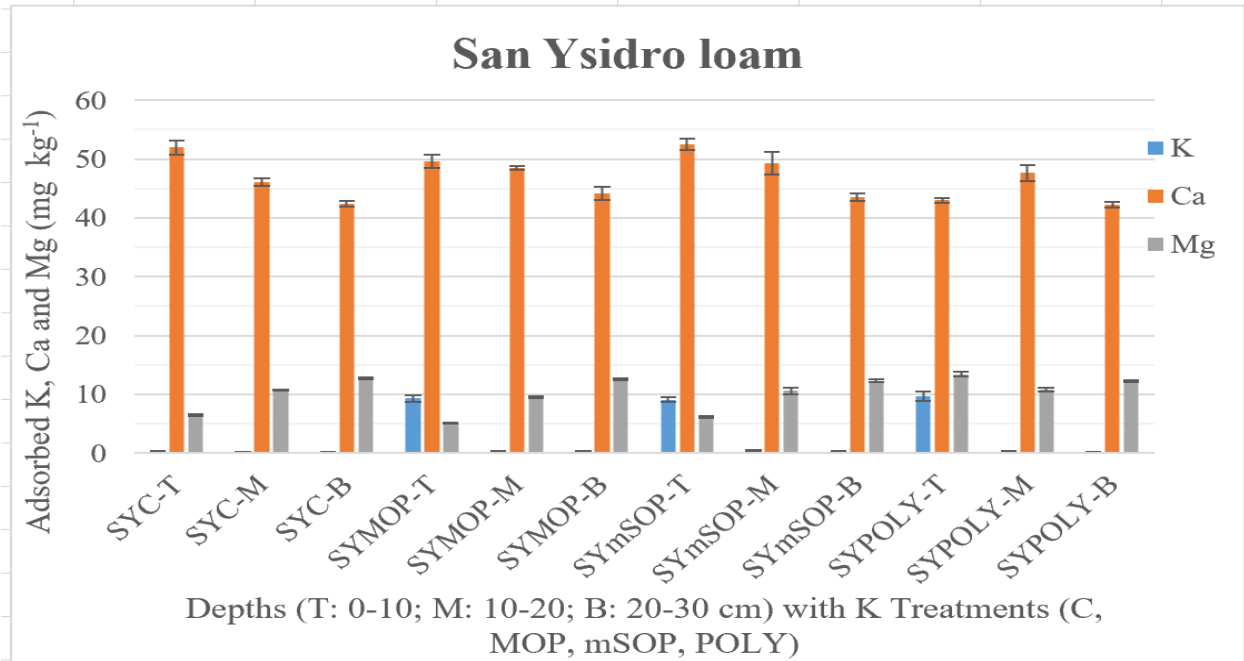
Figure 2-8-6 – Potassium, Calcium and Magnesium adsorption (meq 100g^{-1}) by a cation resin membrane strip (5 cm x 30 cm) at three depths (0 - 10, 10 – 20, 20 - 30 cm) in the San Ysidro soil at the end of experiment. Adsorbed K mean ± S.E.
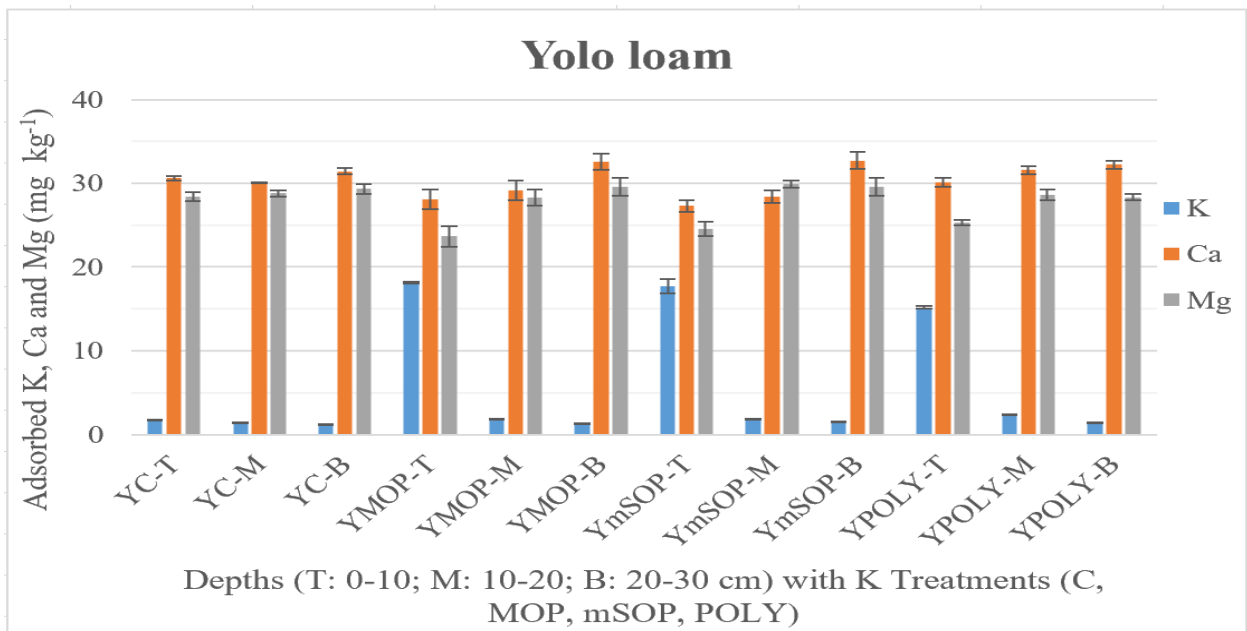

Figure 2-8-7 – Potassium, Calcium and Magnesium adsorption (meq 100g^{-1}) by a cation resin membrane strip (5 cm x 30 cm) at three depths (0 - 10, 10 – 20, 20 - 30 cm) in the Yolo soil at the end of experiment. Adsorbed K mean ± S.E.
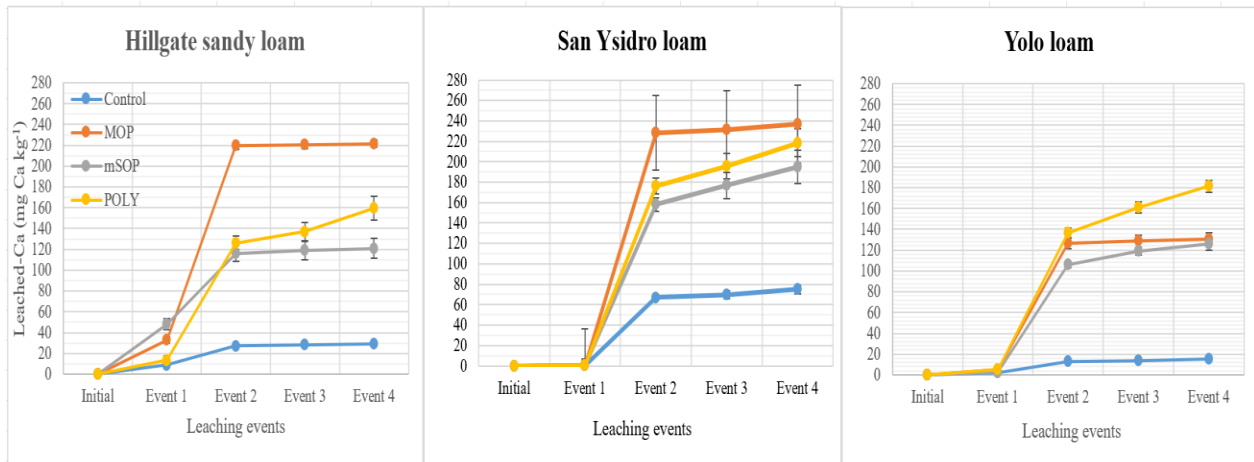
Figure 2-8-8 – Cumulative leached Ca (mg kg^{-1} dry soil column) over four leaching events with MOP, mSOP and POLY treatments and the control in the Hillgate, San Ysidro and Yolo soil. Leaching event 1, 2, 3 and 4 were collected on 1, 15, 29, and 57 days respectively after the start of the incubation.

Figure 2-8-9 – Cumulative leached Mg (mg kg^{-1} dry soil column) over four leaching events with MOP, mSOP and POLY treatments and the control in the Hillgate, San Ysidro and Yolo soil. Leaching event 1, 2, 3 and 4 were collected on 1, 15, 29, and 57 days respectively after the start of the incubation.
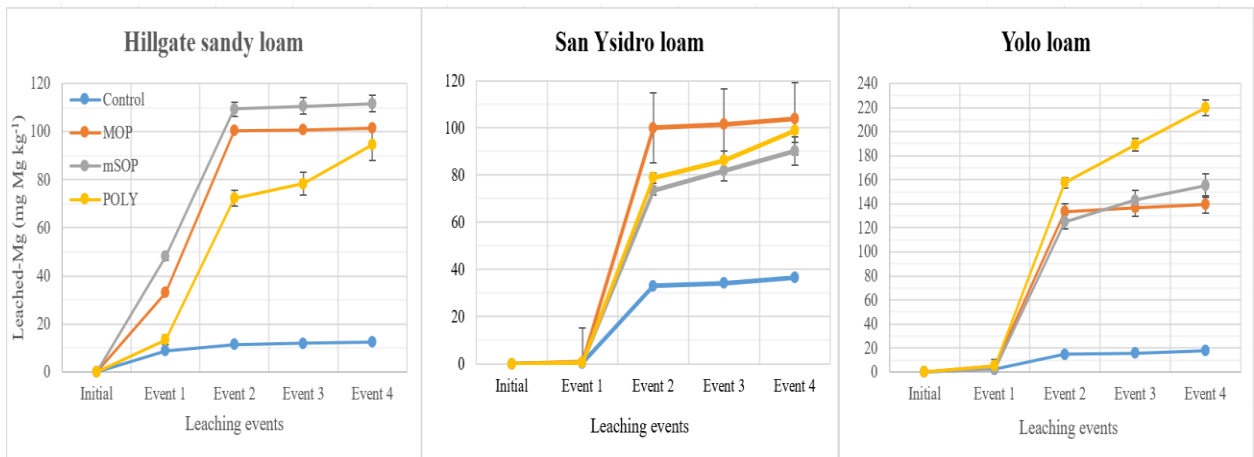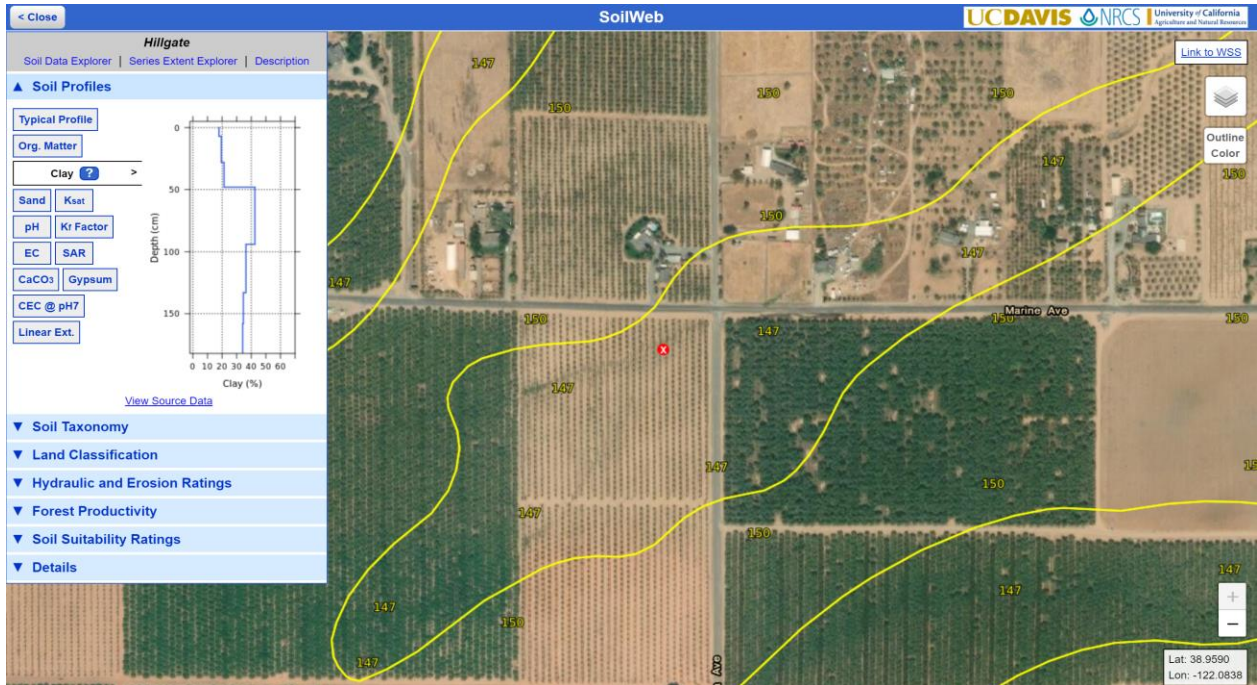
Figure 2-8-10 – Arbuckle (Hillgate series) sampling site. Location: 38°57'29.3"N 122°04'48.8"W.
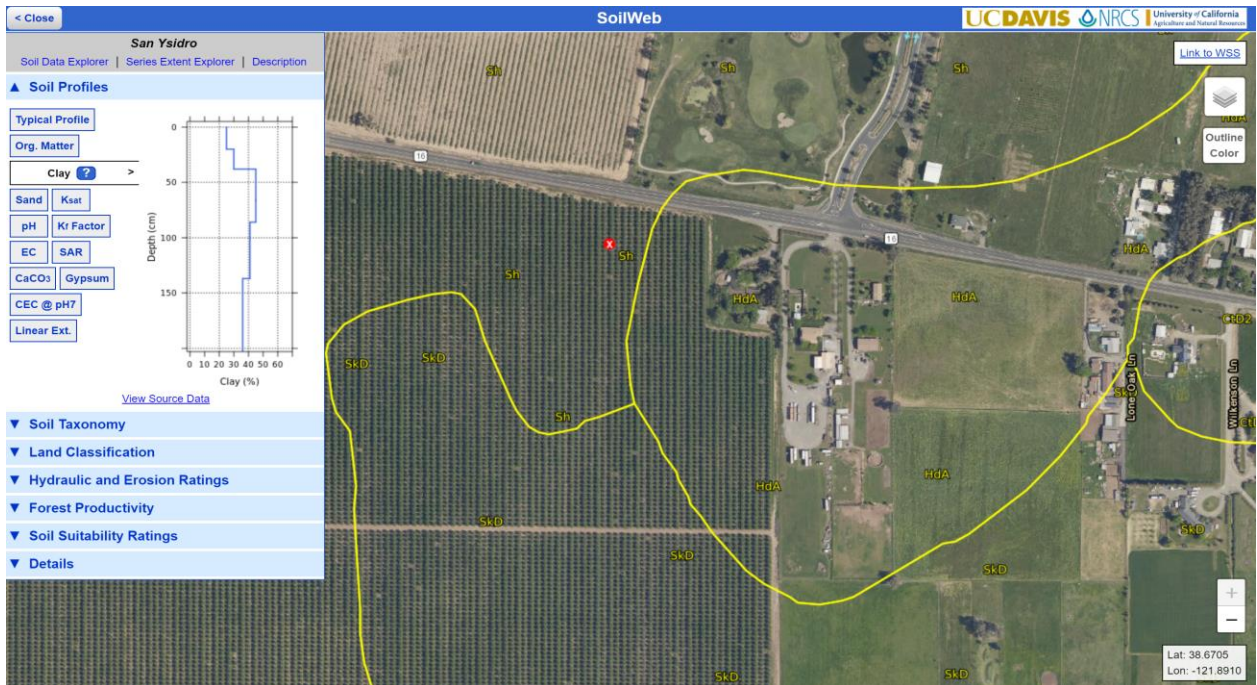

Figure 2-8-11 – Woodland (San Ysidro series) sampling site. Location: 38°40'02.9"N 121°53'27.5"W.
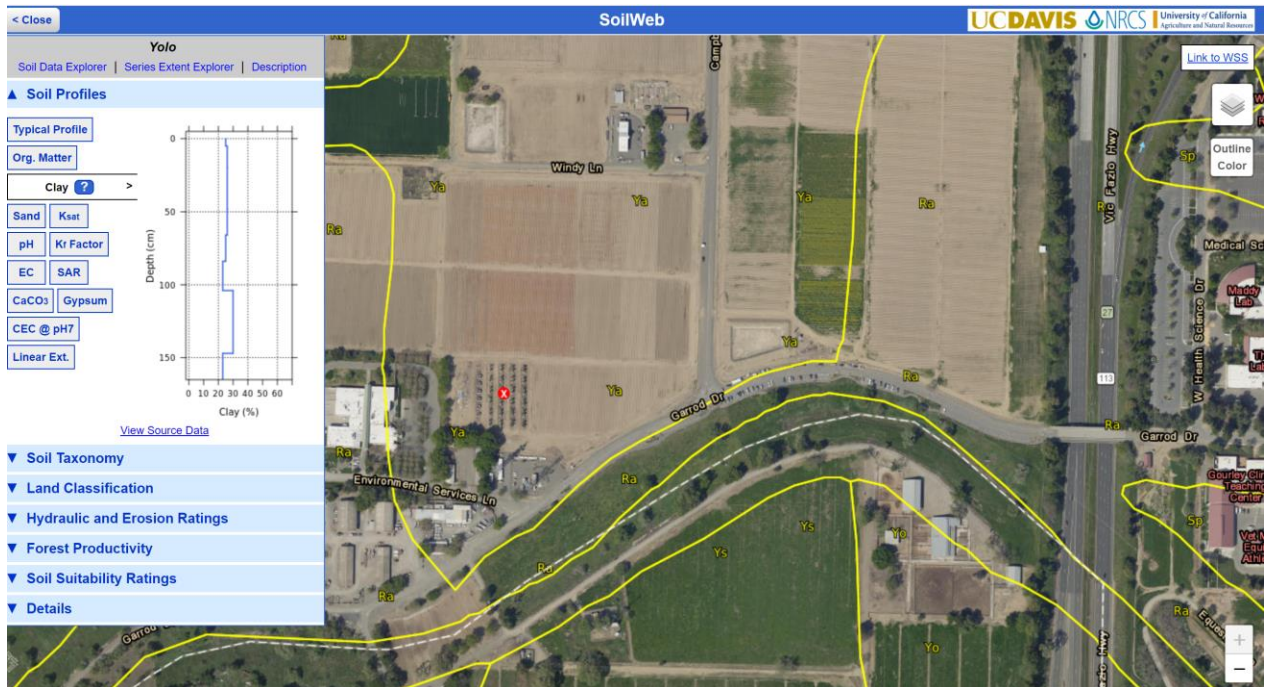
Figure 2-8-12 – Davis (Yolo series) sampling site. Location: 38°31'57.0"N 121°46'30.8"W.

Table 2-8-4 – Tukey test of EC values of different K treatments for the first leaching event in soils.

Contrast	Estimate	SE	df	Lower CL	Upper CL	t ratio	p value
C - MOP	-2.014	0.0648	24	-2.193	-1.8350	-31.078	< .0001
C - POLY	-0.663	0.0648	24	-0.842	-0.4842	-10.232	< .0001
C - mSOP	-0.842	0.0648	24	-1.021	-0.6637	-13.001	< .0001
MOP - POLY	1.351	0.0648	24	1.172	1.5295	20.846	< .0001
MOP - mSOP	1.171	0.0648	24	0.993	1.3501	18.077	< .0001
POLY - mSOP	-0.179	0.0648	24	-0.358	-0.0007	-2.769	0.0489
Results are averaged over the levels of: soil							
Confidence level used: 0.95							
Conf-level adjustment: tukey method for comparing a family of 4 estimates							
p value adjustment: tukey method for comparing a family of 4 estimates							

Table 2-8-5 – Amount of water addition (ml) by wetting event in each column. Water addition = water field pore space at 60% WFPS + extra 100 ml water.

| Soil Type	1st water addition (ml)	2nd water addition (ml)	3rd water addition (ml)	4th water addition (ml)
Hillgate sandy loam				
HC1	1277	384	453	558
HC2	1256	391	431	588
HC3	1252	370	371	560
HMOP1	1271	367	346	503
HMOP2	1268	395	370	497
HMOP3	1280	394	360	454
HmSOP1	1288	406	431	510
HmSOP2	1296	377	326	548
HmSOP3	1302	401	404	527
HPOLY1	1306	350	344	564
HPOLY2	1313	320	327	534
HPOLY3	1333	354	354	569
San Ysidro loam				
SYC1	1260	449	404	600
SYC2	1268	463	424	608
SYC3	1291	450	432	602
SYMOP1	1295	492	467	610
SYMOP2	1280	539	470	604
SYMOP3	1318	532	447	598
SYmSOP1	1283	451	422	611
SYmSOP2	1268	423	410	633
SYmSOP3	1277	390	386	581
SYPOLY1	1272	407	387	598
SYPOLY2	1301	458	399	592
SYPOLY3	1283	431	421	614
Yolo loam				
YC1	1378	451	487	615
YC2	1356	478	512	627
YC3	1327	498	517	586
YMOP1	1353	579	613	787
YMOP2	1337	555	636	825
YMOP3	1349	561	568	736
YmSOP1	1352	523	555	739
YmSOP2	1347	577	612	816
YmSOP3	1340	564	621	840
YPOLY1	1361	500	556	654
YPOLY2	1348	495	576	657
YPOLY3	1335	464	525	637
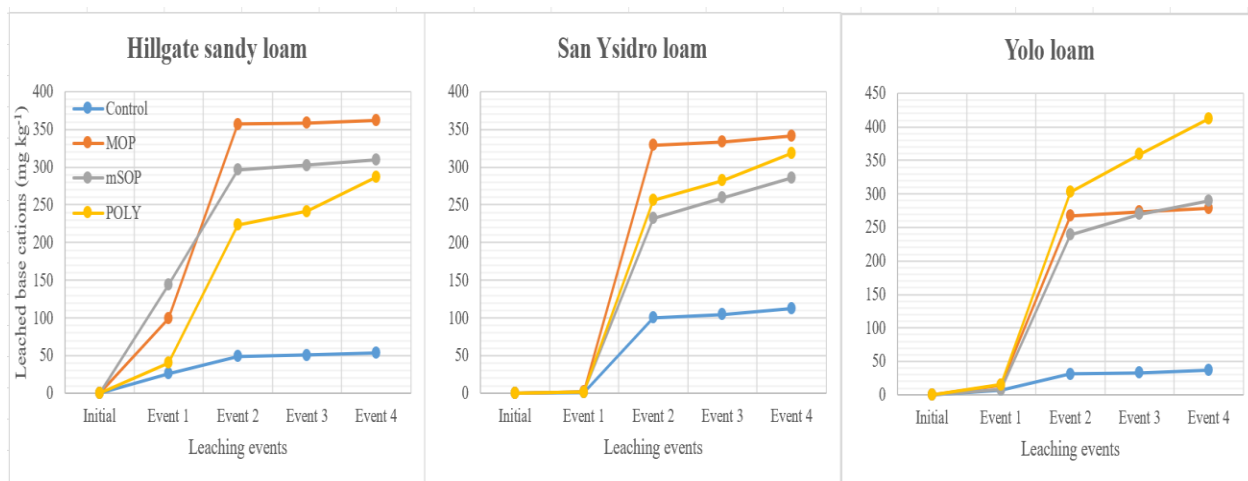
Figure 2-8-13 – Cumulative leached base cations (mg kg^{-1} dry soil column) over four leaching events with MOP, mSOP and POLY treatments and the control in the Hillgate, San Ysidro and Yolo soil. Leaching event 1, 2, 3 and 4 were collected on 1, 15, 29, and 57 days respectively after the start of the incubation.

Table 2-8-6 – Unaccounted K in the K budget results based on the equation (3). Unit in mg K per soil column.

	K inputs	K recovery	Unaccounted K
	-- mg K column^{-1} --		
HC	571	564	6.45
HMOP	2520	2061	460 (18.3%)
HmSOP	2593	2156	438 (16.9%)
HPOLY	2534	1877	658 (26.0%)
SYC	233	246	-12.9
SYMOP	2183	1318	865 (39.6%)
SYmSOP	2256	1343	913 (40.5%)
SYPOLY	2197	1276	921 (42.0%)
YC	824	829	-4.64
YMOP	2775	2120	655 (23.6%)
YmSOP	2848	2260	588 (20.6%)
YPOLY	2789	2033	756 (27.0%)

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