



Ionic Mobility of Cations as Affected by Redox Status of Two Different Soil Textures

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Abstract

Movement of ions within the soil plays a key role in nutrient availability as well as soil management. Various reactions in the soil contribute to soil ionic mobility and consequently nutrient availability, one of which is the oxidation-reduction reaction. Hence, this study sets out to evaluate the effect of redox status of the soil on ionic mobility of cations. A 3x2x2 factorial experiment was set up on two different soil types (clay loam and sandy clay loam), arranged in a Randomized complete Block design (RCBD) with three replicates. The treatment combination involved three levels of poultry manure (0 tha^{-1} , 6 tha^{-1} and 8 tha^{-1}), two levels of NPK 15-15-15 (0 gha^{-1} , 200 kgha^{-1}) and two water regimes (field capacity and waterlogging). Twelve treatments were obtained giving rise to different redox potential. Redox potential was measured using a redox meter, electrical conductivity using a conductivity meter; Ionic mobility was calculated using the mobility equation.

Results from this study show that ionic mobility was highest under highly reduced conditions, also ionic mobility was highest in sandy clay loam than clayey loam and potassium ion has the highest mobility while magnesium has the lowest mobility. It was concluded that soils can be subjected to reduction process to increase the mobility of cations hence their availability to plant. However care must be taken to avoid the loss of highly mobile ions like potassium.

Keywords: ionic mobility, redox, cation, soil, nutrient availability, movement

Introduction

Essential mineral nutrient elements are taken into the plant system by the roots and they exist in soil solution as ions (Singh and Schulze, 2015). These elements can only be used by plants in their ionic forms. Cation and anion absorption by the plant root is determined by both root physiology and the movement of ions in the soil itself and within the soil solution. The nature of the mobility of these ions in the soil solution affects plant growth, crop yield, and product quality (Ehsan et al., 2010). Mobility of ions could be in form of mass flow, diffusion as well as root interception, these processes determine the availability of these ions for plant uptake. Anions and cations in solution are moved mostly by diffusion, and it involves the movement of ions within water that exist around soil particles, the driving force being the ion concentration gradient, always moving from an area with higher concentration

to an area of lower concentration (Drew et al., 1969). Redox reactions involve the transfer of electron from one compound to another. This type of reaction involves an oxidant and a reductant, the oxidant is the electron acceptor and in most cases, is the soil components while the reductant is the electron donor which includes various soil additives. Over the years, pH has been considered as the major soil reaction (Brady and Weil, 2010; Simek and Cooper, 2002), however in recent days, the concept of redox potential or electron flux is gaining attention as a soil chemical reaction. The redox process affects many biogeochemical processes of anaerobic systems like lakes, waterlogged soils, sediments and groundwater (Heron et al., 1994). It also affects the behavior of nutrient elements and is involved in the solubility and toxicity of heavy metals in the soil (Chuan et al., 1996) as well as the chemistry of living organisms (Dietz, 2003; Falkowski et al., 2008; Greenberg, 1998). Redox potential has been used in many disciplines that deal with living organisms, such as microbial ecology (Alexander, 1964), limnology (Reddy and DeLaune, 2008), bioenergetics (Guérin, 2004; Mathis, 1995), soil science (Chadwick and Chorover, 2001), physiology and ecophysiology (De Gara et al., 2010; Dessaux et al., 2009; Dietz, 2003; Foyer and Noctor, 2005; Lambers et al., 2008). The activities of soil microbes are dependent on the soil reaction and oxidation-reduction potential (Falkowski et al., 2008), it also has effect on the development of microorganisms. Bacterial growth is directly correlated to changes in redox potential (Kimbrough et al., 2006) while microbial and enzymatic activities are negatively correlated with redox potential in anaerobic soils (Brzezinska, 2004; Kralova et al., 1992). Furthermore, the redox state of nodules is regarded as a referee of legume-rhizobium symbiosis (Marino et al., 2009) and nitrogen fixation by *Azospirillum* spp. is governed by soil redox fluctuations (Charyulu and Rao, 1980). The source of electrons for biological reduced environment is organic matter (Oglesby, 1997; Chadwick and Chorover, 2001; Lovley et al., 1998). Redox potential and pH mainly influence the form under which N is assimilated by plants. In plant nutrition, the availability of P is greatly influenced by both redox potential and soil pH (Kemmu et al., 2006; Phillips, 1998; Sallade and Sims, 1997; Vadas and Sims, 1998).

Recently, researchers have emphasized using fertilizers from organic sources in agronomic practices (Timisina, 2018) or a combination of both organic and inorganic fertilizers to boost productivity and soil fertility (Roba, 2018). Organic manure from poultry sources has been found to improve the yield of maize and soil infiltration dynamics (Akingbola et al., 2017). Organic residues from tithonia have also been found to improve soil chemical properties and Okra yield (Amodu et al., 2019). This practice has a direct influence on the soil redox status and, consequently on ionic mobility. However, researches that have looked into soil redox potential have not given much information on its effect on movement of ions which plays a vital role in nutrient availability and plant nutrition. Hence, the objective of this research is to investigate the ionic mobility of cations as affected by the redox status of two different soil textures.

Materials and Methods

The site of the experiment was at Apatapiti layout around the west gate of the Federal University of Technology, Akure (FUTA) Ondo State Nigeria. It lies within the tropical rainforest belt in southwestern Nigeria within latitude 5° 16'N -5° 22'N and longitude 15° 11'E -15° 16'E.

The study was conducted using two soil types, the soils used are Alfisols according to USDA classification. They were formed under forest and have a subsurface horizon with clay accumulated, however, both fall under different textural classes according to the textural triangle. Site 1 is a sandy clay loam having a sand content of 54.8%, silt content of 20.5% and clay content of 24.7%. The soil at site 1 has an organic carbon content of 0.92%, total nitrogen of 0.19% and available phosphorus of 15.2 ppm. Site 2 is a clayey loam having a sand content of 48.0%, silt content of 21.4% and clay content of 30.6%. The soil has an organic carbon content of 1.37%, total nitrogen of 0.17% and available phosphorus of 28.8 ppm.

Experimental Design and treatments combination:

A 3x2x2 factorial experiment was set up on two different soil types (sandy clay loam and clay loam), arranged in a randomized complete block design (RCBD) and replicated three times. The treatment combinations involved three levels of poultry manure (0 tha^{-1} , 6 tha^{-1} and 8 tha^{-1}), two levels of NPK 15-15-15 (0 gha^{-1} , 200 kggha^{-1}) and two water regimes (field capacity and waterlogging). A total of twelve treatments were obtained, which gave rise to different redox potential they include; oxidized soils (Eh >300), moderately reduced soil (Eh range 200-300), reduced soil (Eh range -130 to -100) and highly reduced (Eh <-200).

Soil Analysis and Sampling:

Samples of the soil were randomly collected from the experimental site from 1 week after incubation (WAI) to 12 weeks after incubation (WAI) at an interval of 4 weeks (1WAI, 4WAI 8WAI and 12WAI). Samples collected were analyzed for redox potential and electrical conductivity from which ionic mobility was calculated. In analyzing for redox potential, a method similar to that described by Rabenhorst et al., 2009 was used, 20g of the soil samples were collected, soaked in water from bottom to top so as to prevent entrapment of air during saturation and allowed to mix for 30 minutes after which 50 ml of the solution was collected and taken to the laboratory for reading. In the laboratory, redox potential (Eh) was measured using a pH/Redox combined meter. Voltage was measured every 10 seconds for 60 seconds and the mean values of the collected measurements were calculated. The electrical conductivity was analyzed using the method of Rayment and Lyon (2011), 20g of soil was mixed with 50ml of distilled water and stirred at the interval for 30 minutes. The solution was then read with a conductivity meter. Particle size analysis was done to determine the textural classes of the soils used using hydrometer method. Ionic mobility was calculated using the electrical mobility equation.

$$D_i = \frac{\mu K_B T}{q}, \text{ Making } \mu \text{ the subject of formula } \mu = \frac{D_i q}{K_B T}$$

Where; D_i = Diffusion coefficient of ion, q = Electrical conductivity, K_B = Boltzmann's constant= $1.380649 \times 10^{-23} \text{ J K}^{-1}$, T = Temperature and μ =Ionic mobility. Textural class analysis was done using the hydrometer method.

Statistical Analysis

Data obtained from this study were subjected to statistical analysis using Statistical Package for the Social Sciences (SPSS) to obtain mean value and level of significance while graphs were generate using Microsoft excel 2010 edition so as to show the trends of findings.

Results

Table 1 presents the treatment combinations, their respective redox potential and their corresponding electrical conductivities; it also shows their respective oxidation-reduction status. T₁, T₃, and T₇ are oxidized soils, T₅, T₉ and T₁₁ are moderately reduced soils, (T₂ and T₄) are reduced soils and T₆, T₈, T₁₀ and T₁₂ are highly reduced soils. T₁₂ has the highest electrical conductivity for both soils while T₁ has the lowest.

Table 1. Classification of Treatment Based on Eh Range and their corresponding Ec

Treatments	Treatment Description	Eh Range	Eh Class	Ec (Soil 1)	Ec (Soil 2)
T ₁	0 t ha ⁻¹ PM + 0 kg ha ⁻¹ NPK + FC	200 to 370	Oxidized	480l	385k
T ₂	0 t ha ⁻¹ PM + 0 kg ha ⁻¹ NPK + WL	-120 to -100	Reduced	707j	473j
T ₃	0 t ha ⁻¹ PM + 200 kg ha ⁻¹ NPK + FC	260 to 430	Oxidized	582k	732h
T ₄	0 t ha ⁻¹ PM + 200 kg ha ⁻¹ NPK + WL	-130 to -100	Reduced	815i	715i
T ₅	6 t ha ⁻¹ PM + 0 kg ha ⁻¹ NPK + FC	200 to 290	Moderately reduced	913h	787g
T ₆	6 t ha ⁻¹ PM + 0 kg ha ⁻¹ NPK + WL	-240 to -210	Highly Reduced	1395f	1200cd
T ₇	6 t ha ⁻¹ PM + 200 kg ha ⁻¹ NPK + FC	280 to 310	Oxidized	1260g	1005f
T ₈	6 t ha ⁻¹ PM + 200 kg ha ⁻¹ NPK + WL	-230 to -200	Highly Reduced	1646b	1215c
T ₉	8 t ha ⁻¹ PM + 0 kg ha ⁻¹ NPK + FC	230 to 300	Moderately Reduced	1407e	1104e
T ₁₀	8 t ha ⁻¹ PM + 0 kg ha ⁻¹ NPK + WL	-240 to -230	Highly Reduced	1642c	1500b
T ₁₁	8 t ha ⁻¹ PM + 200 kg ha ⁻¹ NPK + FC	230 to 300	Moderately reduced	1426d	1182d
T ₁₂	8 t ha ⁻¹ PM + 200 kg ha ⁻¹ NPK + WL	-240 to -230	Highly Reduced	1740a	1605a

PM = Poultry Manure, NPK = NPK 15-15-15, WL= Waterlogged, FC= Field Capacity.

Figures 1 to 4 presents the effect of redox potential on ionic mobility of soil cations over a period of 12 weeks. Oxidized soils (T₁, T₃, and T₇) are represented with blue lines, moderately reduced soils (T₅, T₉ and T₁₁) by green lines, reduced soils (T₂ and T₄) by red lines and highly reduced soils (T₆, T₈, T₁₀ and T₁₂) by black lines. Similar trend was observed for all the cations throughout the trial period and on the two soil types. Highly reduced soils had the highest values throughout the trial period, followed by moderately reduced soils, oxidized soil and then reduced soils. Although T₁ is one of the treatments subjected to oxidation, it recorded the lowest ionic mobility throughout the trial period. In all the treatments, there was

a slight increase in mobility between 1WAI to 4WAI; between 4WAI to 8WAI there was a considerable increase in mobility of all the elements (Ca, Mg, Na, and K). At 12WAI however, there was a decline in mobility for all elements across all treatments. The highest mobility was observed at 8WAI while the lowest at 1WAI. Generally, mobility of all elements was highest at T_{12} and lowest at T_1 .

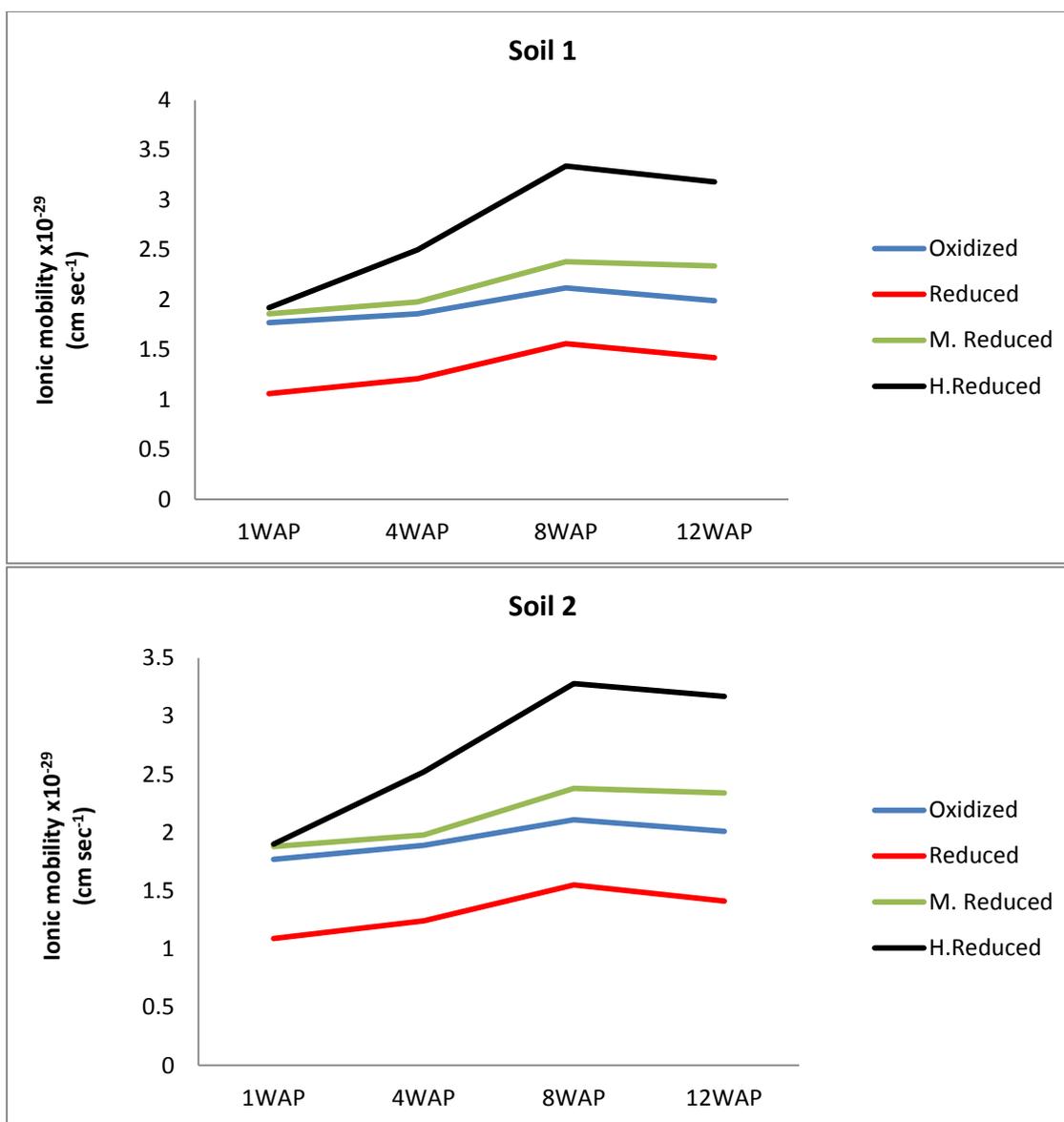


Figure 1. Effect of Redox Potential on Calcium Mobility over 12 Weeks

Figures 5 compares the mobility of exchangeable cations in the soil under oxidized and reduced conditions at 12 weeks after incubation. Calcium ion is represented by blue lines, magnesium ion by red, sodium ion by green and potassium ion by yellow. Throughout the trial period, potassium ion recorded the highest values for mobility across all treatments, followed by sodium, then calcium and magnesium recorded the lowest ionic mobility. Figures 6 to 9 compare the ionic mobility between the two soils used during the trials. Figure 6 shows the calcium ion mobility, figure 7 shows that of magnesium ion, figure 8 shows sodium ion mobility and figure 9 shows potassium ion mobility. Soil 1 was a sandy clay loam and is

represented by blue lines on the graph while soil 2 was a clayey loam represented by red lines on the graph. Mobility was faster in soil 1 than soil 2 on all treatments at all levels.

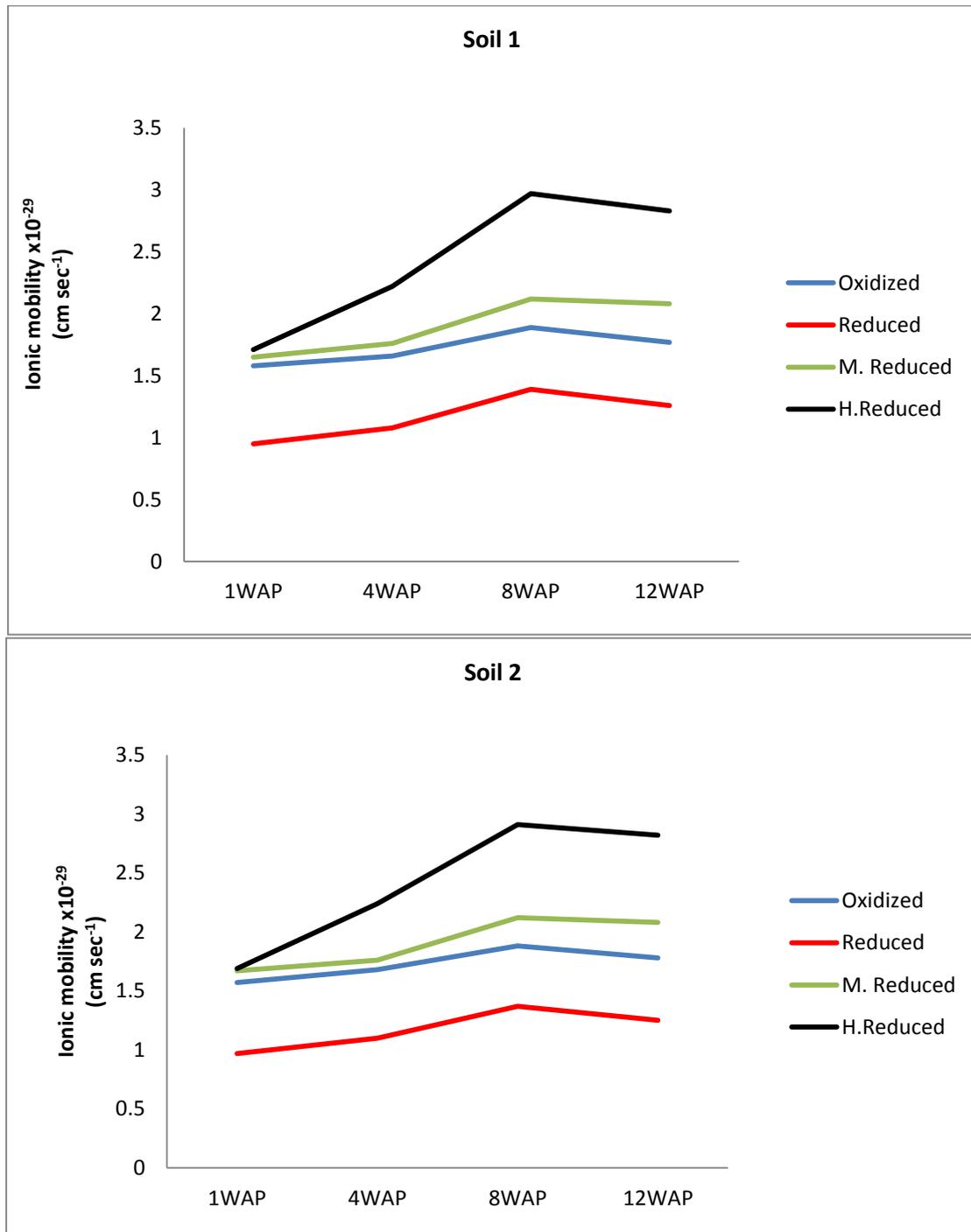


Figure 2. Effect of Redox Potential on Magnesium Mobility over 12 Weeks

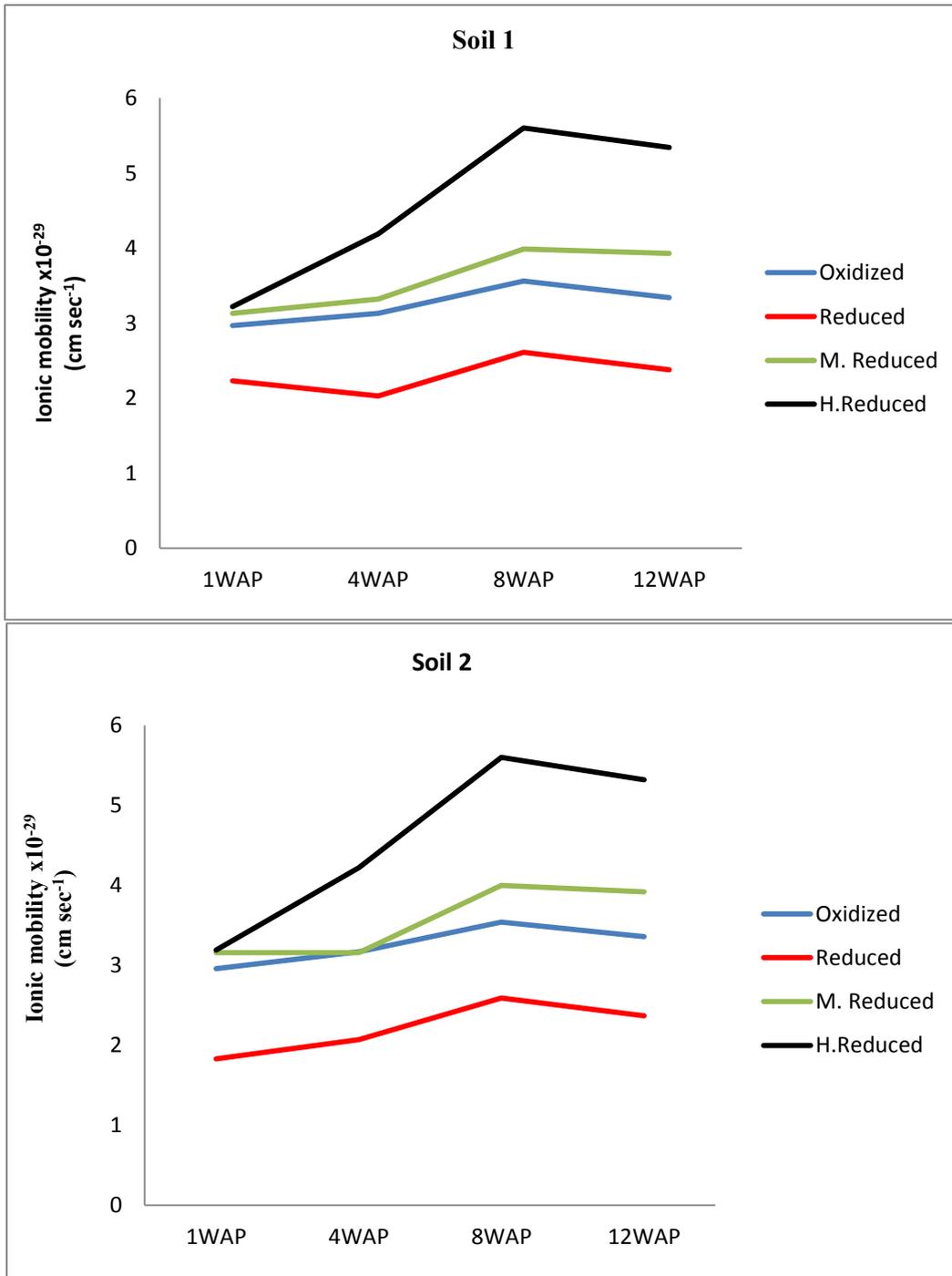


Figure 3. Effect of Redox Potential on Sodium Mobility over 12 Weeks

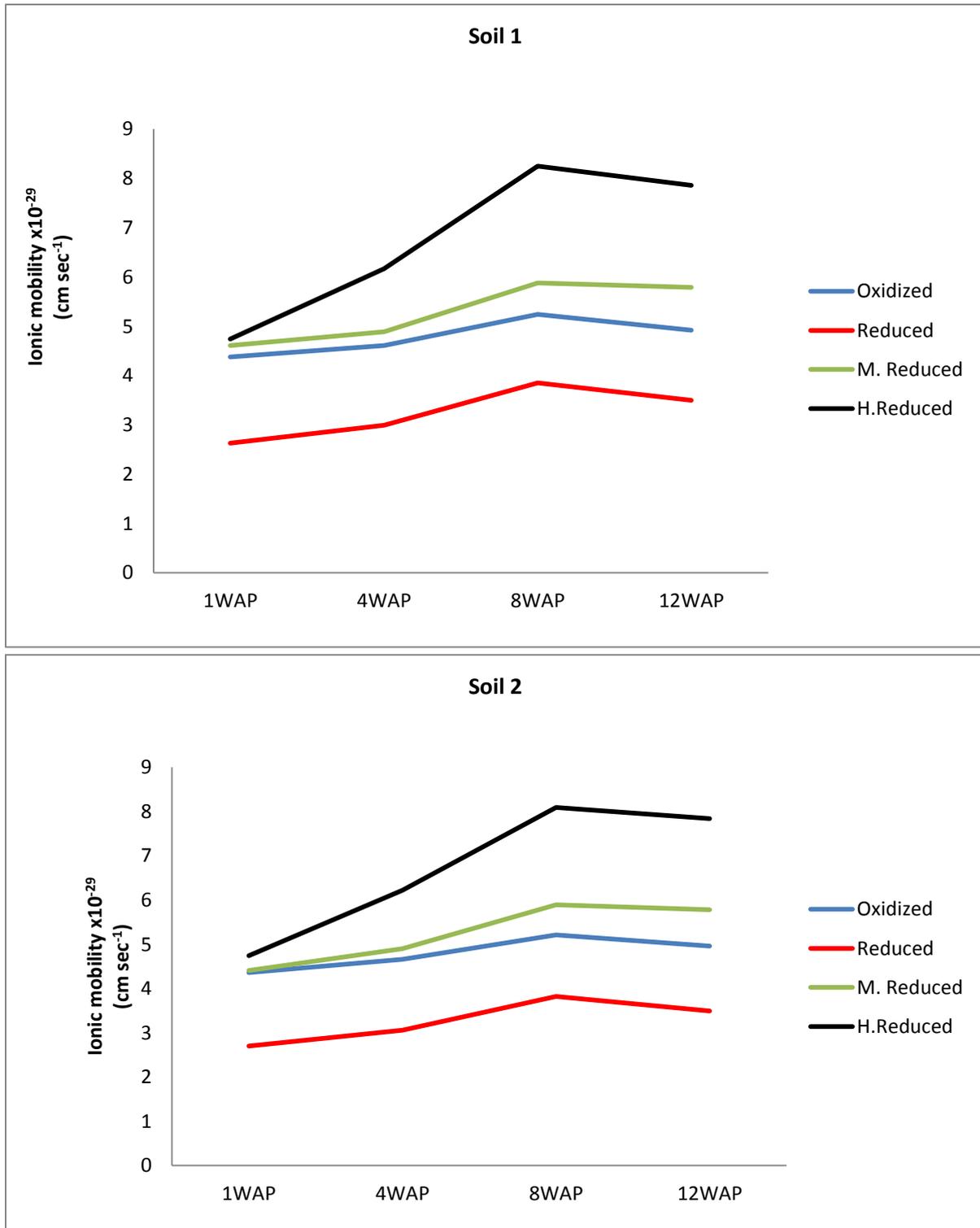


Figure 4. Effect of Redox Potential on Potassium Mobility over 12 Weeks

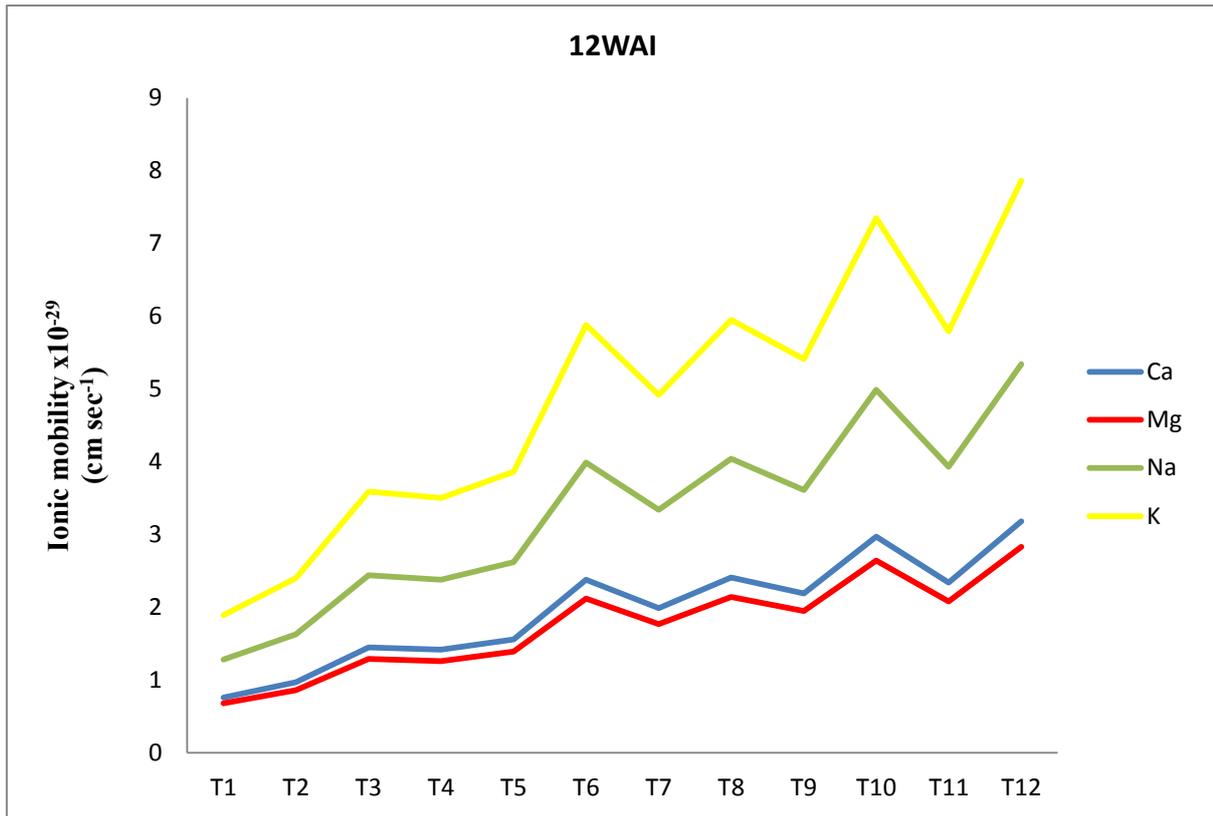


Figure 5. Comparing Soil Cation Mobility at 12WAI

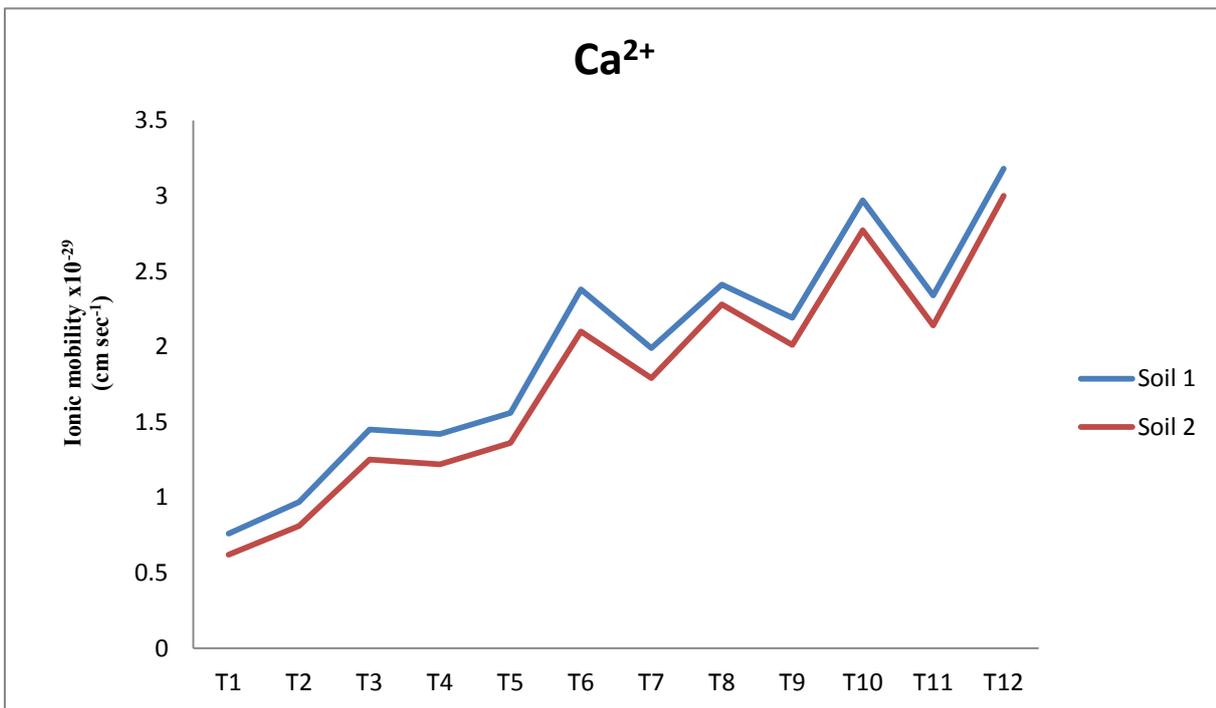


Figure 6. Comparing Ionic Mobility between the two Soils (Ca²⁺)

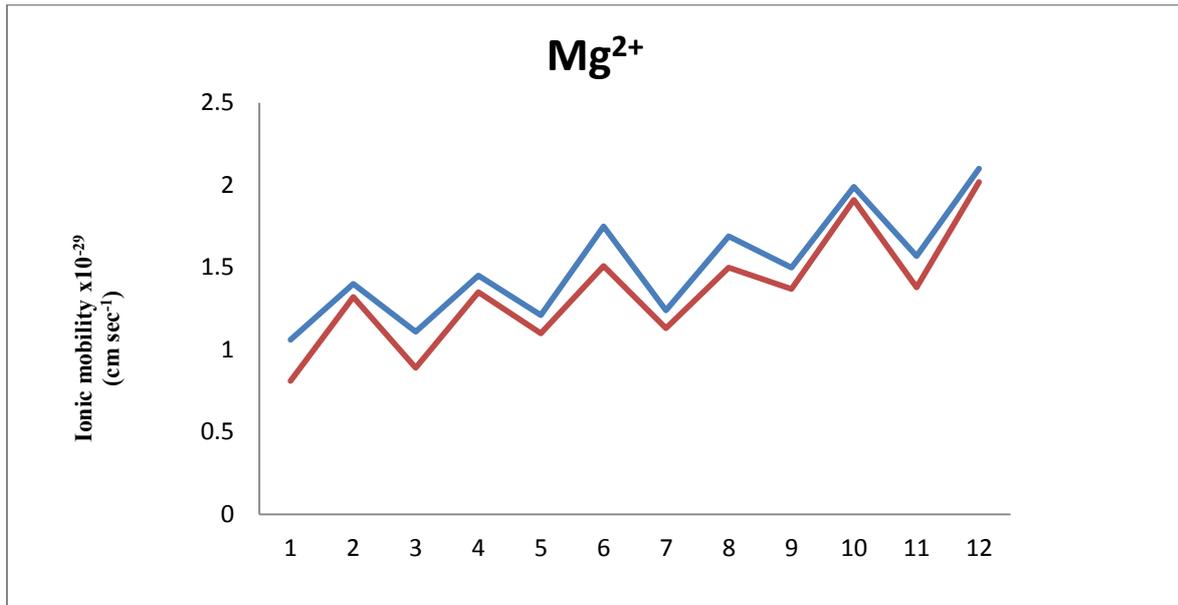


Figure 7. Comparing of Ionic Mobility between the two Soils (Mg^{2+})

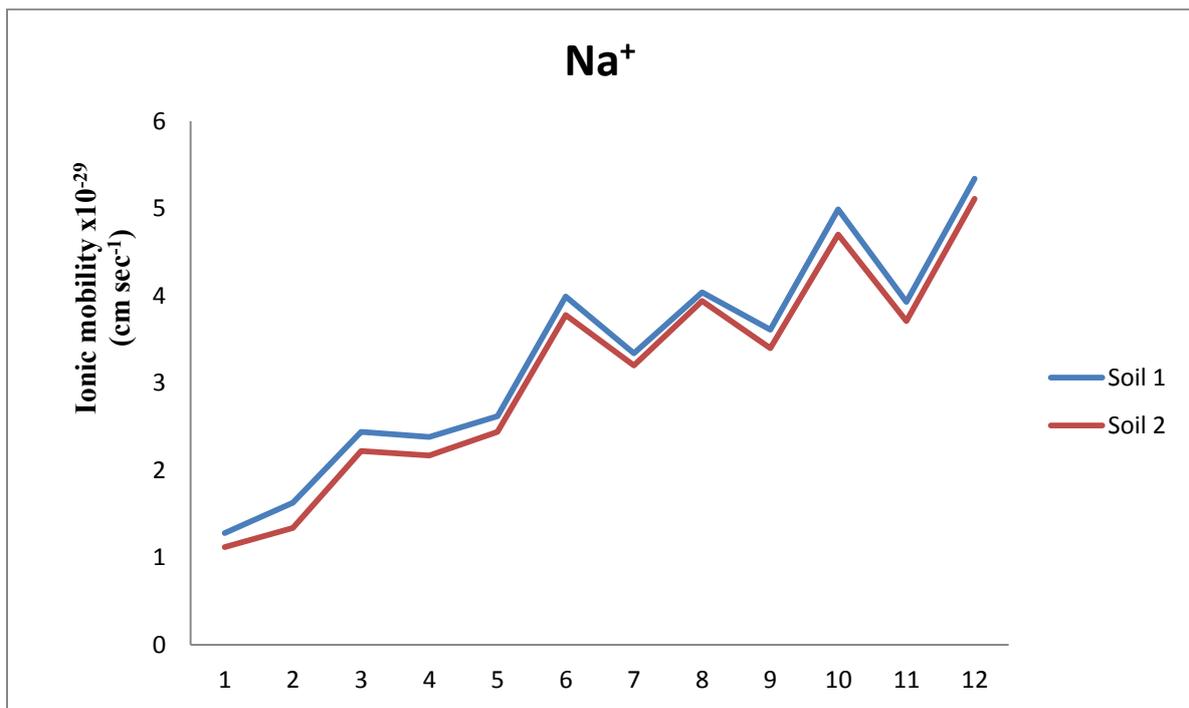


Figure 8. Comparing of Ionic Mobility between the two Soils (Na^{+})

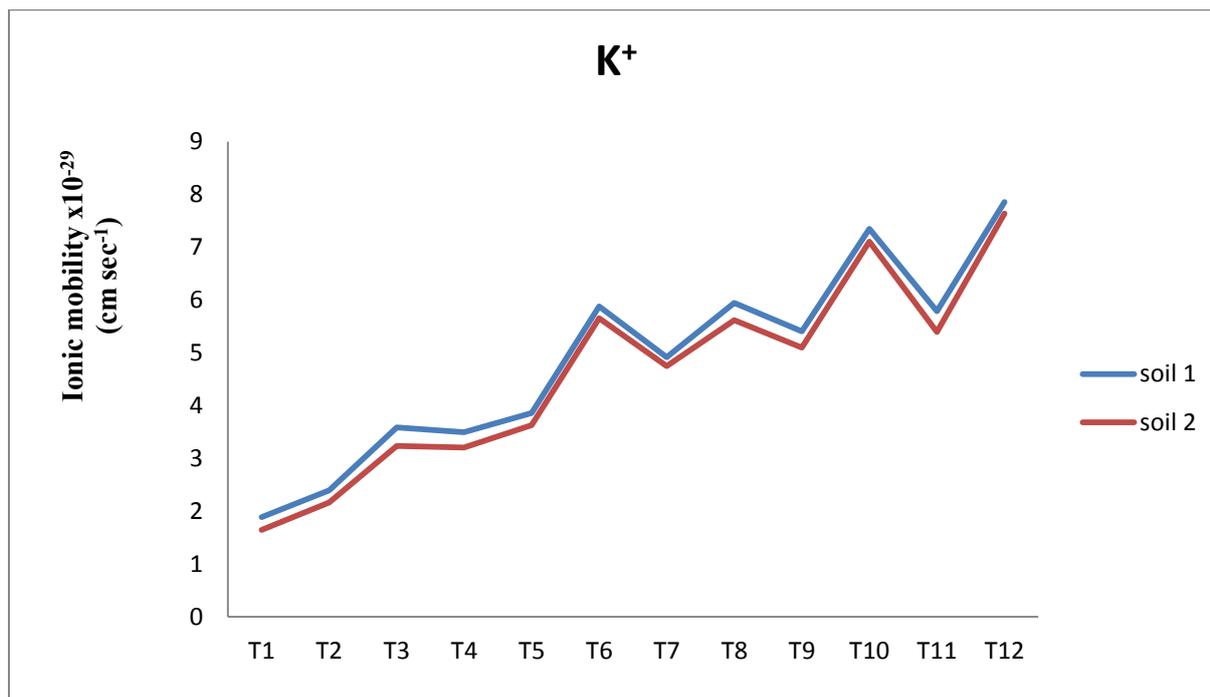


Figure 9. Comparing of Ionic Mobility between the two Soils (K^+)

Discussion

Ionic mobility is the average velocity with which an ion drifts through a specified gas under the influence of an electrical field. The results from this study showed that reduction processes favor mobility of ions in the soil. When an electric field is applied to ions in a medium (a phenomenon called electrophoresis), it causes the positive ions to move with the electric field (Dibyadeep, 2010). Under reduced conditions, electrons are transferred from organic matter to the soil components (Bi et al., 2013), these process of electron transfer generates electric charges in the soil solution which in turn creates an electric field (Bhadra, 2015). It then follows that the more reduced the environment becomes, the greater the electric field and consequently, the faster the ions move along the electric field created. This is because the electric field will exert a force that accelerates the charged particle (Daniel, 2014). This agrees with the work of Secco 2011 who stated that among other things, charge carrier concentration contributes to ionic movement. It was also found out that potassium ion K^+ had the highest movement in the soil solution followed by sodium ion Na^+ followed by calcium ion Ca^{2+} and the slowest is magnesium ion Mg^{2+} . This can be attributed to the fact that electrical currents are created during electron transfer (Bhadra, 2015), when the soil environment is more negatively charged, the ionic radii of the cations increase and the ions become bigger in size (Socratic, 2014). The size of ions is a crucial factor that determines the mobility of ion. In water, these ions are surrounded by water molecules because water is a dipole which is attracted towards positive charges of these ions (Bert, 2018).

With increase in size, hydration power or tendency for ion to be hydrated decreases, however, as the ion gets smaller their surface area increases and the tendency for it to be hydrated or attract more water molecules increase (Aftab, 2020). Due to more water molecules surrounding it, its mobility in water is impeded because it will have to carry water

molecules with it as it moves. Potassium according to the periodic table, is the largest of the cations and becomes even bigger under reduced conditions because it has lesser amount of proton in its nucleus (Earles, 2015), this makes the force of attraction between its orbital electron and nucleus not as strong as obtained in other cations. This is followed by sodium then calcium and lastly magnesium which is the smallest. Mobility was also found to be higher in sandy clay loam than clay loam. Another major factor that affects ionic mobility is the amount of free spaces in the soil aggregate. The more compact a soil is, the lower the movement of ions and the less compact a soil is, the faster the ions move. This agrees with the work of Murawski, (2017) who stated that ionic conductivity is affected by size of particles, ionic mobility is a function of conductivity. Given that sandy clay loam has more pore spaces than clay loam, it makes it faster for ions to move in them than the clay loam. This also corroborates the findings of Nawaz et al., 2012 who concluded in their work that compaction of soil reduces mobility.

Conclusion

This study has confirmed that redox status of soil influences soil ionic mobility. Agricultural practices that encourage the use of organic matter as soil amendments can induce reduction processes and hence ionic mobility of cations in the soil. The study further revealed that potassium is the most mobile element in the soil and as such readily available to plants however care must be taken to avoid it leaching out of the vadose zone of the soil because of its high mobility. Sodium was also found to be highly mobile under reduced conditions; this knowledge can be used in the remediation of sodic soils to reduce the salt content. However, it is recommended that this experiment should be repeated for other soil elements under other textural classes as this would be relevant in soil management and conservation.

Declaration of Interest Statement

I declare that there is no conflict of interest of any kind between the authors of this manuscript.

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