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Effect of potassium and calcium fertilizations on potassium K X-Ray structure in maize saplings

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ABSTRACT

Precise evaluation of K X-ray peak energies of potassium in maize saplings from a pot experiment and in their soils has been done. The experiment involved the pot treatments with different nutrient fertilizers keeping all other environment factors; soil, light, temperature and watering same. Fertilization affects the relative concentration of nutrients in plants and soils. The measurements have been done in an energy dispersive X-ray fluorescence (EDXRF) set-up comprising low power Neptune X-ray tube and Si (PIN) detector. The energies of peaks in the spectra were evaluated with the SOLVER fitting program that gives a precision up to 10^{-4} of channel width. The results show shift in peak energies with fertilizations relative to those of untreated pot. The calcium fertilization produced more shift as compared to that produced by potassium fertilization. The shift pattern in maize samples is different from that of corresponding soil samples; moreover, it is in contrast to our earlier findings in mint plants. All the outcomes point to chemical changes in plants with fertilization.

Keywords: Pot experiment**,** Energy dispersive XRF, peak energies, Energy shifts, chemical changes

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INTRODUCTION

Potassium and calcium are among the essential macronutrients of plants and play an important role in soil-plant relationships. These elements are not only essential to the biochemistry of plant growth, but their presence in the soil in adequate amounts and in suitable proportions is necessary where soil is a suitable medium for plant-root development [http://gsr.lib.msu.edu/1970s/1972/721101.pdf]. Thorough understanding of plant nutrition is difficult, partially because of the variation between different plants and even for species or individuals of a given clone, the variations do exist (http://en.wikipedia.org/wiki/Plant_nutrition). Between the potassium and calcium, potassium is primary and calcium is secondary macronutrient. Potassium is an essential element for plant growth and is an extremely dynamic ion in plant and soil system. Potassium cation is highly mobile in the plant system but only moderately mobile in the soil [1]. It is unique in its diverse roles in plant chemical processes. So, its uptake and utilization often get affected with the availability and uptake of other nutrients e.g. calcium and magnesium etc. (www.ipni.net/bettercrops). Therefore, it is an attractive area to investigate whether these effects cause some chemical, structural and bonding changes in plants and soils.

Chemical environment of an atom may affect the X-ray peaks in its fluorescent X-ray emission spectrum in the form of shift in its peak energies, distortion of lines shape and change in X-ray intensities [2]. The findings of Obert and Bearden [3] and Ichikawa et al. [4] predicted that changes occur in line width and index of asymmetry with the change in percentage composition of an element in a compound. In the context of XRF studies of macro/micro nutrients in plants and their soils, Qi et al. [5] has done chemical state analysis of sulfur and phosphorus in biological samples of leaves and bones using double-crystal high-resolution X-ray fluorescence spectroscopy. Speciation of Cu in a contaminated agricultural soil has been measured by XAFS, μ-XAFS, and μ-XRF by Strawn and Baker [6]. However, studies on the molecular characterization of elements in soils are difficult because multiple species may exist in a single soil.

Energy dispersive systems do simultaneous multi-element detection and are highly efficient in detecting the Gaussian peaks with excellent energy and resolution stability. Our earlier work on mint saplings and their soils treated with calcium and potassium fertilizers [7] that involves the SOLVER fitting on peak data and gives a precision up to 10^{-4} of channel width for peak positions has been applied on EDXRF measurements to search the shift in energy of potassium K X-ray peaks in maize plants from the soils treated with different amounts of potassium chloride (KCl) and calcium sulphate ($CaSO_4$) fertilizations as well as in their soils. The details of the measurements and findings are given in the following sections.

MATERIALS AND METHODS

Pot experiment and preparation of samples

A pot experiment [8] similar to that for mint plants [7] was performed on maize plants with potassium and calcium fertilizations. Twelve pots with a mixture of soil and sand in 1:1 ratio were used to germinate 35-40 seeds of maize in each pot. The pots were watered with 200 ml water on alternate day. On ninth and eleventh day after the germination of seeds, pots were fertilized with $CaSO_4$ and KCl; five pots with KCl solutions (50,100,150, 200, 250 mg of KCl per 200ml of water), other five pots with $CaSO_4$ solutions (50, 100, 150, 200, 250 mg of $CaSO_4$ per 200ml of water), one pot with both calcium and potassium fertilizers in equal amounts (150 mg each) and one pot was left untreated.

The maize saplings cut from above the soil surface and the soils around the maize roots from the pots were collected. The saplings were washed, dried at room temperature and in oven at 100-120º C and sampled as pellets from grinded powder of the saplings. The soils were dried, grounded and passed through standard sieves and sampled as pellets. Since in the processing soils, seeds and environmental conditions such as light, water and air were kept same as far as possible for all the pots except fertilization, therefore the observed variations of characters of macronutrients would be due to fertilization.

Experimental Set-up

The pellet targets of plants and soils from different pots irradiated with photons from 100 Watts Neptune X-ray tube with rhodium anode produced fluorescent X-rays and were detected at 90º to the source in a single reflection geometry with a Si (PIN) detector (AMPTEK model XR-100CR) (Fig. 1) [9]. The tube and the detector were at symmetrical positions to the target.

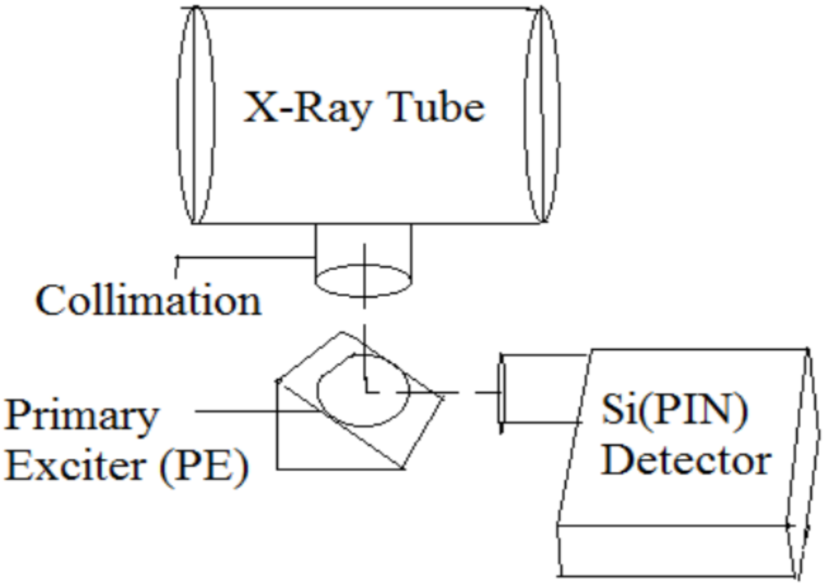


Fig. 1 Schematic arrangement of X-ray tube, single reflection geometry and Si(PIN) detector

For selective excitations of potassium in K-shell, the anode voltage was set at 4 kV [9] that was above the potassium K edge energy and filament current at 1 mA to keep the dead time losses < 1 %. Spectrum of each sample was recorded for sufficient time so that error in counting statistics was less than 10%. A typical emitted X-ray spectrum of maize sample is shown in fig. 2.

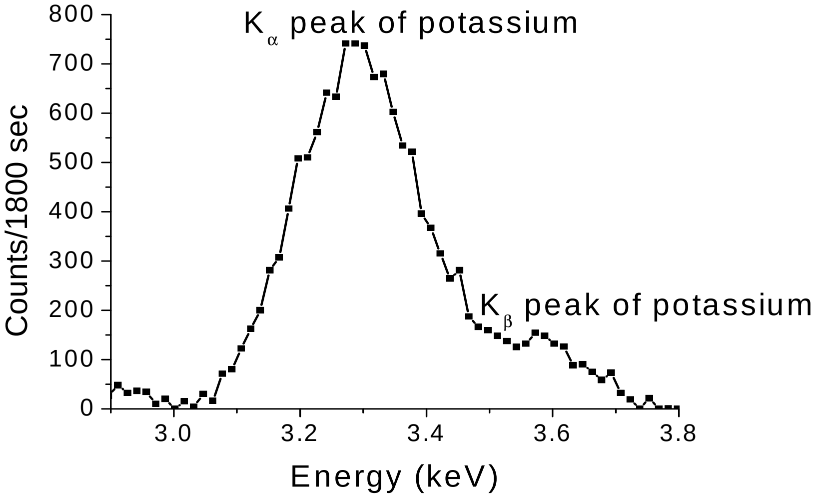


Fig. 2 Typical spectra of one of maize samples

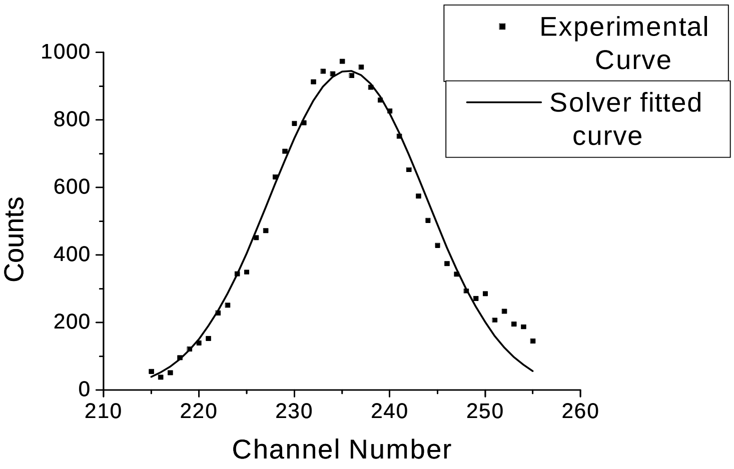


Fig. 3 Experimental and solver fitted peak in one of the spectra of maize samples

Peak Energy Evaluations

For evaluation of potassium K peak positions, X-ray peak fittings are done using SOLVER program included in EXCEL. It is an ideal tool for mathematical modeling of experimental data because of easier user interface, dynamic display of iterative search process and universal availability of EXCEL [10]. The advantage of Solver fittings for X-ray peaks in an energy dispersive X-ray spectrum is because of excellent representation of peaks by a normal distribution. The problem may arise due to existence of low energy tail that is rectified by performing fitting of peak in ±2σ or ±3σ region i.e. two or three standard deviations from both sides of the peak centroid which includes 95% or 99% of the peak events, where the effect of tail becomes negligible.

SOLVER computations involve representation of X-ray peak by Gaussian function, ------- (1),

where C = calculated counts at channel number x, H = maximum peak height, m = peak centroid and σ = standard deviation.

Maximum peak height (H), the maximum counts at the peak in spectra obtained by ORTEC-MCA software; peak centroid (m), channel number of maximum counts and standard deviation, $\sigma = FWHM / 2\sqrt{2\ln 2}$ where FWHM is full width at half maximum are known from the recorded spectra and are used in equation (1) to compute C at different channels x covering the peak region up to ± 3σ channels. The sum of squared residuals between computed and experimental counts are minimized by SOLVER program and fresh parameters H, m and σ are produced. The produced m values are precise up to 10^{-4} decimal position in terms of channel width. The solver fitting applied on K potassium peak of recorded spectra of one of the maize samples is shown in figure 3 along with the experimental peak.

RESULTS AND DISCUSSION

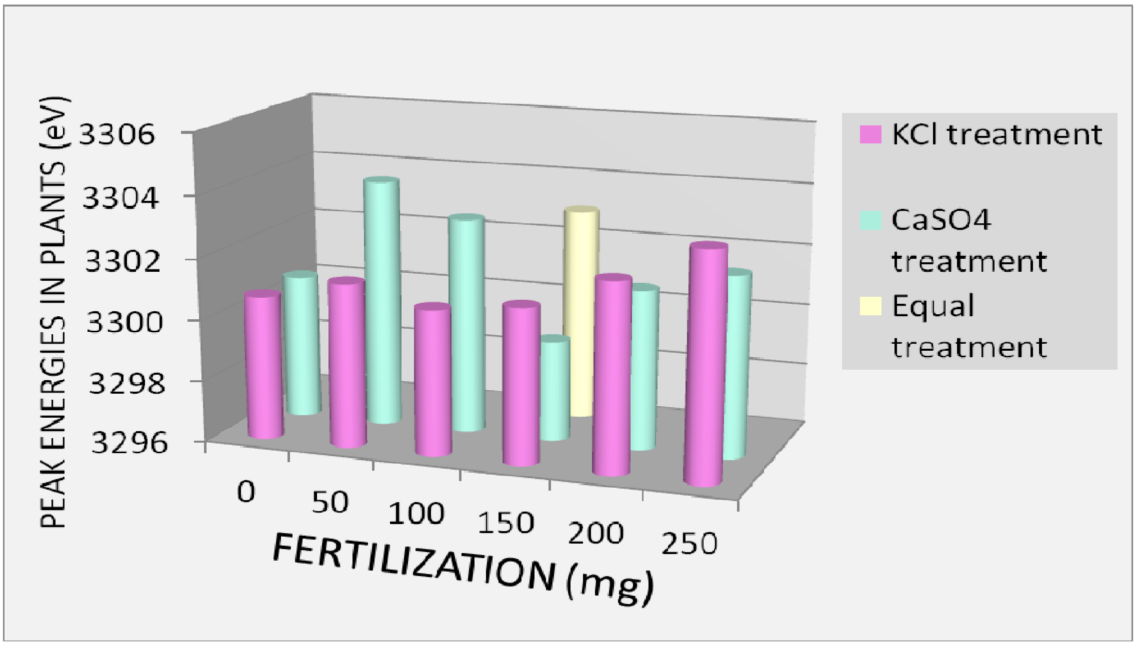
In the stated methodology, the obtained centroid positions are in the form of channel numbers and are converted into energies with energy calibration of the detector. K peak energy shifts obtained in maize plants and soils for different amounts of KCl and $CaSO_4$ fertilizations with respect to unfertilized sample are given in table l. The potassium K peak energy values plotted for various amounts of KCl and $CaSO_4$ fertilizations in maize plants and soils are shown in fig. 4.

Table 1 K_α peak energy shift in maize plants and soils for different amounts of KCl and $CaSO_4$ fertilizations w. r. t. unfertilized sample

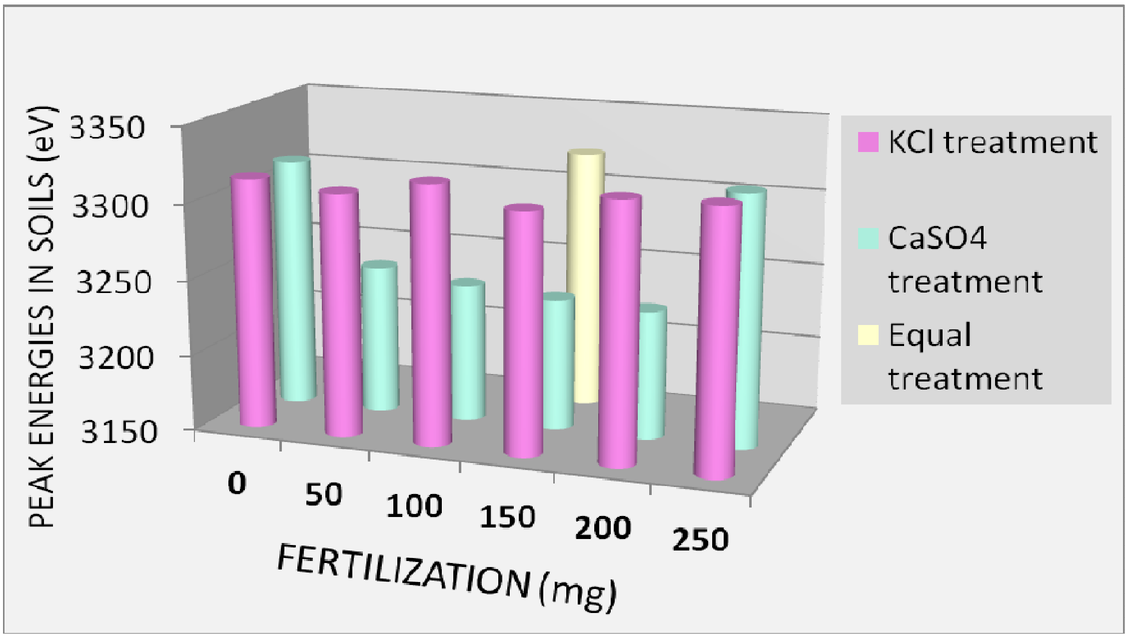
Fertilization (mg/200ml of water)	Peak energy shift (eV) in maize plants	Peak energy shift (eV) in maize soils
Unfertilized	0	0
KCl fertilization		
50	+0.65	-5.10
100	+0.06	+5.55
150	+0.37	-7.28
200	+1.44	+4.50
250	+2.64	+4.97
$CaSO_4$ fertilization		
50	+3.36	-66.95
100	+2.34	-74.12
150	-1.42	-78.06
200	+0.50	-80.09
250	+1.21	+0.85
Equal amount (150 mg) of each KCl and $CaSO_4$	+2.25	+5.98

\- *sign means shift is towards lower energy side with respect to unfertilized sample*

\+ *sign means shift is towards higher energy side with respect to unfertilized sample*



(a)



(b)

Fig. 4 Peak energy variation with various KCl and $CaSO_4$ fertilizations in (a) maize plant and (b) soil samples

To check the reliability of the computations, 4 to 7 scattered data points at the peak in some cases are individually selected one by one for SOLVER fittings and peak energies are determined. The variance in peak energies of the order of 0.10 for all the cases comes out just 0.003% of the mean value. The variance evaluation in a typical case of maize sample is given in table 2. Since, the measured shifts for maize plants and soils are much higher than the calculated variance in almost all the cases, it supports the fact that the observed shifts are the genuine energy shifts and not the statistical/ non-statistical fluctuations due to noise or some other external factors.

Table 2.Variance evaluation for a typical case of maize

Channel number/Counts	Solver fitted energy value (eV)
232/618	3300.059
233/603	3300.341
234/644	3300.5795
235/651	3300.749
236/626	3300.8405
237/513	3300.869
238/562	3300.9125
	Variance 0.1011675
	Mean 3300.6215
	Percentage variance w. r. t. mean 0.0030651

Some exploring points of results are
(1) Potassium K peak energy shifts in maize plants with fertilizer treatments, KCl or $CaSO_4$ treatment (fig. 4(a) and table 1) indicate that the overall chemical surroundings of potassium in maize plants are affected on adding fertilizers. Peak shift in range 0.06-2.64 eV with KCl treatment and 0.50-3.36 eV with $CaSO_4$ treatment openly predicts larger effect on potassium surroundings that may be in terms of the structural changes, variations in complex ion formations or alterations in number of attached ligands etc. of maize plant with $CaSO_4$ treatment than KCl treatment.
(2) Potassium K peak energies in soils shift towards both higher and lower energy sides with KCl treatments, ranging 4.50-7.28 eV (fig. 4(b) and table 1). Peaks show a drastic shift to lower energy side with $CaSO_4$ treatment, ranging 66.95-80.09 eV. However, in case of 250 mg $CaSO_4$ treatment shift noticed is too small (0.85 eV) towards higher energy side. Again, $CaSO_4$ treatment has much larger influence on peak positions in soils than KCl treatment.
The observations that calcium treatment influences more than the potassium treatment the potassium peak positions in maize saplings and particularly on maize soils may be justified by the hierarchy in the process of cation exchange on colloids, the cation differ in the strength of adsorption by the colloid and hence their ability to replace one another. If one cation is added in large amounts, it may replace the others by the sheer force of its numbers (mass action). This is largely what occurs with the addition of fertilizer (http://en.wikipedia.org/wiki/Soil).

The reciprocal relationship between calcium and potassium has been widely attributed to antagonism between the two ions [11]. There is competition between calcium and potassium because of their similar sizes and addition of any one of them reduces the uptake rate of the other [1]. Moreover, there are interactions between ions with similar chemical properties to compete for sites of adsorption, absorption, transport and function. In competitive binding, the amount of any ion bound will be related to the concentration of that ion relative to its competitors and the affinity constants for the ion-ligand pairs [12]. However, the optimal levels of calcium improve uptake of potassium [1]. That may be the reason for potassium peak energies showing minimal shift at 250 mg $CaSO_4$ fertilizer application.

Potassium K peak results in soils show more variations as compared to those of plants with KCl treatment. The difference is much more prominent with $CaSO_4$ treatment. As pointed out by Ujwala Ranade-Malvi [1] that there is a highly controlled selectivity process involved in uptake of nutrients by plants may be the reason why the plant does not contain the same ratio of nutrients inside the plant as found in the soil. Plant uptake is only one of the possible fates of potassium and calcium in soil solution. Potassium and calcium both are mobile nutrients in soil and may be lost to leaching, retained by soil particles or precipitated as secondary minerals. Secondly, there is difference in the methods by which calcium and potassium uptake takes place in plants. An appreciable amount of calcium uptake is done by root interception and mass flow. On the other hand, potassium uptake by plants takes place through diffusion. Uptake of calcium by plants is not as efficient as for other plant nutrients. It occurs just behind the root tip, in contrast with potassium where uptake occurs along most of the length of the root. In addition to this difference of plant uptake, calcium and potassium differ in mobility within plant and soil. Potassium is a mobile nutrient within plant whereas calcium is not very mobile in the soil or in plant tissue. Also, mobility of a nutrient within soil is closely related to chemical properties of soil e.g. the nutrients which are easily leached are usually those that are less strongly held by soil particles. Potassium will leach more strongly than calcium since calcium is more strongly held to soil particles than potassium (www.ctahr.hawaii.edu/mauisoil). Therefore, there are mutual interactions and exchange of minerals and elements in plants and soils.

The obtained results are found controversial on their comparison with previous outcomes for mint saplings and their soils [7]. Peak shift of potassium K peak was more with potassium fertilization than calcium fertilization in case of mint plants. Also, peak shift in corresponding soil samples was far less than in maize soils. The controversial behavior got support from the findings of Marschner [13]. The uptake of nutrients by higher plants is characterized by selectivity of transport and accumulation in specific tissues, cells or sub cellular compartments. These characteristics are genetically determined and can differ both between and within plant species. Selective ion uptake is also a typical feature of higher plants. Moreover, maize and mint differ in their structural and morphological characters as maize is a monocot and mint is a dicot. Maize is an annual grain crop often 2.5 m in height; some natural strains can grow 12 m whereas mints are aromatic perennial herbs having wide-spread underground and over ground growth with branched stems and grow 10–120 cm tall. That is why the uptake rates, especially for potassium and calcium can differ between plant species, maize and mint.

So, although these interactions are complicated, they provide interesting results and increase our curiosity to further explore in this direction.

CONCLUSION

Fertilization certainly cause some changes in the maize plants and soils as is shown by the shift of K peak energy of potassium in fertilized maize saplings as compared to unfertilized sample. Calcium treatment of maize saplings is having much more variations in potassium peak as compared to potassium treatment because of mutual competition between potassium and calcium cations. Also, the changes occurring in plants and soils are varied with larger peak shift observed in maize soils than maize plants. So, changes in peak energies in maize plants and soils treated with fertilizers indicate chemical environment changes with fertilization which may include changes in bonding types, coordination numbers, types and number of ligands etc.

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