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# **Nutrient X-Ray Energy Shift Studies in Wheat Plants and Soils**

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## **Authors' contributions**

This work was carried out in collaboration between both authors. Author PR performed the pot experiment on wheat and EDXRF measurements on wheat plant / soil samples. She processed the measured data and prepared first draft of manuscript after reviewing the concerned literature. All the work is done under the supervision and guidance of author RM. She concluded the interpretation of results and finalized the manuscript.

## **Article Information**

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**Original Research Article** 

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## **ABSTRACT**

**Aims:** To check the effect of soil environment on chemistry of potassium and calcium nutrients in wheat plants with varying soil conditions.

**Study Design:** Energy Dispersive X-ray Fluorescence (EDXRF) measurements on plant/soil samples. Study of fluorescent X-ray spectra and data processing to calculate shift in photo peak energies of nutrients.

**Place and Duration of Study:** XRF laboratory, Nuclear science laboratories, Physics Department, Punjabi University, Patiala during December 2013-March 2014.

**Methodology:** A pot experiment was performed on wheat plants grown on soils collected from different sites of six cities / town / village in Punjab, India. Low power X-ray tube set up for Energy Dispersive X-ray Fluorescence (EDXRF) measurements has been used to record the fluorescent X-ray spectra of wheat plants and soils for macro nutrient studies. SOLVER a powerful program included in Microsoft Excel for Windows was applied to predict nutrient X-ray energies with precision  $10^{-4}$  of channel width. The shifts in peak energies were evaluated with reference to that of plant/soil from an environmentally protected ground site.

\_ **Results:** The shift in calcium photo peak energies was found higher than that of potassium photo

peaks. In case of soils, the shifts are related to level of contamination of soils from sewage system, factory sites and road sides. The changes in soil nutrients' chemical state lead to these shifts and accordingly from studied shifts, the height of the contamination level  $-$ is approximated and correlated with the population life style of localities and environment of occupations on the soils like industries, farming and gardening etc. The shifts in nutrient photo peak energies in plants, generally, in opposite direction to that for soils signify the -wheat plants' quality to cope with stress conditions.

**Conclusion:** Shifts in photo peak energies for nutrients can be used as tool to sense the contamination level of soil.

Keywords: Energy dispersive X-ray fluorescence (EDXRF); shift in X-ray peak energy; SOLVER program; nutrients; plants and soils.

## **1. INTRODUCTION**

Generally, soil is the foremost medium for existence and growth of plants. It is an anchor for roots and by holding water provides a domain in which soil nutrients change into ions, to be up taken by plants. Basic components of soil are minerals, organic matter, water and air. Soils differ regionally because of numerous factors; parent material, climate and terrain of the region, type of plant/vegetation and human influences like industrial activity, agricultural activities, waste disposal, accidental oil spills and acid rain etc. [1].

Cation exchange capacity and pH properties of soil depend on clay and organic matter of the soil as both clay and organic matter have high cation exchange capacity with negatively charged sites that attract and hold positively charged particles. Clay particles with large surface area increase soil activity by forming compounds with external materials. Organic carbon results in many complex types of structures with other molecules including smaller organic molecules introduced from pesticides, insecticides, fertilizers etc. and provide negative sites in soil that attract large amount of positive charge [2]. Heavy-metal cations get introduced into soils by fertilization, sewage, other industrial and urban waste materials cause adsorption reactions and compete with nutrients for adsorption sites in soil and disturbs the chemistry of nutrients [3]. Components of soils like organic matter, clay and contamination vary with environment, as soil environment is prime factor which further directs nutrient status in terms of concentration and their mutual chemistry.

Soil–plant interrelations are dynamic and subject to both inputs (fertilizers, pollutants and soil properties) and losses (erosion, leaching and harvesting etc.). Ions are available for plants if picked up by their root system. Along with the

ions in soil solution, ions adsorbed onto exchange sites can be available or influence available fraction for plants. This is because of dynamic equilibrium between the soil solution ions and ions from other pools. It means chemical environment of elements in soil affects greatly their availability to the plants. Thus, ion capacity of soil in terms of ion intensity and rate of replenishment of soil solution ion pool from the other pools (solid soil particles, organic compounds or other readily soluble compounds) affects ion supply to plant roots. Capacity factor determines a buffer power for a particular nutrient. The relationship between capacity and intensity factors for each nutrient is dependent on soil pH [4]. There exist a number of mechanisms for genotypic variations in plant nutrient requirements and its efficiency in nutrient use under deficiency conditions [5]. So, same plant grown on soils taken from different environments may differ in growth/yield/nutrient status/chemistry of nutrients in plants.

Study of nutrient characteristic fluorescent X-rays in plants and their soils provides a mean to track its status from soil to plant. Under Energy Dispersive X-ray Fluorescence (EDXRF), the difference in K-shell and outer shell electron binding energies comes as K X-ray energy. Presence of an electron acceptor / donor / both functional groups in the vicinity of an element of interest (whose X-rays are being measured) can affect the emitted X-ray energies according to their net strength. Hence, the shifts in nutrient Xray energy both in plants and soils are expected. Understanding of the shifts is valuable as the chemical environment of a particular nutrient in soil/plant is unknown and the particular status of nutrient element can provide information about the soil's ability to serve plants with nutrient like potassium and calcium, essential for plants. Potassium and calcium are consumed in larger quantities in plant tissue in concentrations 0.2- 5% (on dry matter weight basis). Potassium is

primary macro-nutrient whereas calcium is the secondary. Potassium in plants performs a number of important functions related to enzyme activation, neutralization of negative charges, maintenance of cell turgor, plant growth and organ movement  $[6]$ .  $Ca^{2+}$  is intracellular messenger molecule involved in many signal transduction pathways in plant. It is needed as a counter-cation for inorganic and organic anions in the vacuole and as an intracellular messenger in the cytosol. Calcium is a critical constituent of the plant cell wall [7].

Since, chemical environment of an atom can affect the availability of ion in soil and its uptake by plants along with its effect on emitted fluorescent X-ray pattern of the ion like shift in photo peak energy, variation in line width and change in index of asymmetry etc. The measured change in X-ray energy provides information on chemical bonding, structure of molecules/complexes and their activity in the changed environment. Thus, chemical shift in botanical samples with unknown (dark) matrix like plants, fruits, vegetables etc. along with their soils may be influenced by chemical environment of nutrients.

Wheat, an essential commodity for human, is the second most important cereal crop in India [8] and Punjab state is leading state contributing to the central pool of India [9]. Under these considerations, pot experiment on wheat was performed in lab for varying soil conditions and EDXRF analysis of samples collected was done. In our lab, already a methodology based on EDXRF technique for determination of nutrients and a powerful program SOLVER included in Microsoft Excel for Windows to predict X-ray peak energies with precision 10 $^4$  of channel width have been employed on mint, maize and fenugreek plants and soils [10-12]. Present work is extension of same, potassium and calcium K X-ray measurements and peak energy evaluations, for wheat plants grown on pot soils and for soils. The details are given in the following sections.

## **2. MATERIALS AND METHODS**

## **2.1 Experimental Details**

Pot experiment during December to March was performed on seventeen different soils, collected from selected six cities / town / village in Punjab, India (Table 1).

After removing the thin upper layer containing grass, pebbles etc. from each site about 4-6 inch thick layer of the soil was removed with help of wooden tool. The wooden tool was used to avoid additional metal contamination. Pot soils were uniform mixture of equal amounts of collected soil, sand and clay in 1:1:1 proportion in 17 pots. About 40 equal sized and healthy wheat seeds of variety HD 2967, popular in Punjab State (http://archive.indianexpress.com/news/newwheat-variety-storms-punjab/1195080) were germinated in each pot. The whole experiment was performed in a spacious airy laboratory room of dimensions  $\sim$  24 ft. X 21 ft. X 12 ft. with

S. no.	City / Town / Village in	<b>Site</b>	<b>Pot Identity</b>	
	Punjab, India			
1.	Sangrur City	<b>Runnel site</b> a)	$S_{\text{runnel}}$	
		Pesticides & insecticides Factory b)	$S_{\text{chem fac}}$	
		Kitchen Garden C)	$S_{\text{kit gdn}}$	
		Banasar Garden d)	$S_{\text{Ban gdn}}$	
		Civil Hospital biomedical Waste dump e)	$S_{\text{civil hosp}}$	
2.	Nabha City	Farm a)	$N_{\text{frm}}$	
		<b>Mechanical Factory</b> b)	$N_{\text{mech fac}}$	
		Sewage site C)	$\mathsf{N}_{\mathsf{sew}}$	
3.	Ajrawar Village	Pond site a)	$A_{pnd}$	
		Road Side b)	$A_{\rm rd sd}$	
4.	Patiala City	Runnel site a)	$P_{\text{runnel}}$	
		River (Badi Nadi) site b)	$P_{\text{riv}}$	
5.	Moonak Town	<b>Chemical Factory</b> a)	M <sub>chem fac</sub>	
		<b>Ghaggar River site</b> b)	M <sub>ahaqqar riv</sub>	
6.	<b>Punjabi University Campus</b>	<b>Botanical Garden</b> a)	PUP <sub>botany</sub> <sub>gdn</sub>	
		Sewage site b)	PUP <sub>sew</sub>	
		Ground C)	$PUP_{qnd}$	

**Table 1. List of places and sites of collected soil samples**

proper natural day light (day time luminance of 150-200 lx) and no artificial luminance at night. The pots were watered with 200 ml distilled water when required. Physical characters of plants like colour texture and health were monitored regularly during the experiment.

#### **2.1.1 Sample preparation**

On full growth, plants were cut above the soil surface, washed thoroughly under running water, dried at room temperature for two days and in oven at 60-80℃ for 5-6 h for consecutive two days and then ground. About 5 cm thick upper layer of soils were taken from each pot using wooden tool to avoid any metallic contamination. The soil samples were properly dried in oven, sieved using sieve with 300 mesh size to get very fine powder. The thick pellets of 2.5 cm diameter of each fine powder sample of plant and soil were prepared [13]. proper natural day light (day time luminance of and of dimensions 6 mm<sup>2</sup><br>The pots were watered with 200 ml distilled water voltage was 8 kV, above<br>then required. Physical characters of plants like it of sole with ray down

## **2.1.2 Experimental setup**

Photon induced emitted X-ray spectrum of each pellet targets was obtained in a single reflection geometrical set up (Fig. 1) using 100 watts, Neptune X-ray tube with Rhodium anode as photon source and Amptek X123 spectrometer having Si(PIN) detector with 0.5 mil. Be window and of dimensions 6 mm<sup>2</sup>/500  $\mu$ m with resolution 145 eV at 5.959 keV Mn X-rays. Tube anode voltage was 8 kV, above the potassium/calcium K edge energy and filament current was at 0.03 145 eV at 5.959 keV Mn X-rays. Tu<br>voltage was 8 kV, above the potassiu<br>K edge energy and filament current w<br>mA to keep the dead time losses <1%.



#### **Fig. 1. Schematic arrangement of X-ray tube, sample target and Si(PIN) detector in single sample target and reflection geometrical set up**

Spectrum of each sample was recorded for sufficient time so that error in counting statistics is less than 1%. Typical emitted X-ray spectra of wheat plant and soil samples are shown in Fig. 2.



Fig. 2. K X-ray spectra of S<sub>runnel</sub> Wheat/Soil samples at 8kV/0.03mA

In the spectra, peaks were found at energies corresponding to K X-rays of aluminium + silicon, In the spectra, peaks were found at energies<br>corresponding to K X-rays of aluminium + silicon,<br>K X-rays of chlorine + L X-rays of rhodium, K Xrays of potassium + calcium, titanium and iron. Due to limited resolution of detector photo peaks Due to limited resolution of detector photo peaks<br>of aluminium - silicon, chlorine - rhodium, potassium  $K_8$  - calcium  $K_\alpha$  are merged. The spectra show silicon and iron in greater amounts in soil than in plants, but the soil lacks in potassium that show plant with good extracted amount of potassium from the soil. Titanium and calcium are in comparable amounts in plants and in soil than in plants, but the soil lacks in potassium that show plant with good extracted amount of potassium from the soil. Titanium and calcium are in comparable amounts in plants and soils. In present studies, resolv and calcium  $K_8$  peaks for both plants and soils were considered for analysing the peak positions using SOLVER, a powerful program included in EXCEL [10].

#### **2.2 Methodology for Peak Energy Evaluations**

SOLVER program exploits the excellent normal distribution representation of X-ray peaks by applying it on X-ray peaks in the collected energy dispersive detector data. The problem of existence of low energy tail is handled by performing fitting of peak in ± 2*σ* standard deviations from both sides of the peak centroid) which includes 95% of the peak events. Gaussian function for peak data is  $K_{\beta}$  peaks for both plants and soils<br>red for analysing the peak positions<br>i.R, a powerful program included in<br>**blogy** for **Peak Energy**<br>**ons**<br>gram exploits the excellent normal<br>epresentation of X-ray peaks by<br>X-ray pea th sides of the peak<br>6 of the peak events.<br>lata is<br>(1)

$$
C = H * e^{-(x-m)^2/2\sigma^2}
$$
 (1)

where  $C =$  calculated counts,  $H =$  maximum peak height,  $x =$  channel number,  $m =$  peak centroid and  $\sigma$  = standard deviation.

In peak point evaluations, maximum peak height (H), the maximum counts in 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 parameters from the recorded spectra and are used in

equation (1) to compute the counts at the channels (x) covering the peak region up to  $\pm 2\sigma$ channels. The sum of squared residuals between computed and experimental counts are minimized by SOLVER program generating fresh parameters H, m and *σ*. The m value obtained with precision up to  $10<sup>-4</sup>$  of a channel width is the peak position. The solver fitting applied on  $\mathsf{K}_{\alpha}$ peak of potassium in the obtained spectrum of S<sub>runnel</sub> soil sample is illustrated in Fig. 3.



**Fig. 3. Experimental and SOLVER fitted K Experimental and α peak in a spectrum of Srunnel soil sampl sample** 

## **3. RESULTS AND DISCUSSION SSION**

The obtained centroid positions from SOLVER fitting for K photo peaks of potassium and calcium were in the form of channel numbers and were converted into energies using energy calibration of the detector. To check the reliability fitting for K photo peaks of potassium and calcium were in the form of channel numbers and were converted into energies using energy calibration of the detector. To check the reliability of the computations, 8 scattered da 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 0.03-0.04 for all the cases comes out just 0.0011% of the mean value. Variance evaluation in a typical case of wheat sample is given in Table 2. one for SOLVER fittings and p<br>are determined. The variance in p<br>of the order of 0.03-0.04 for all<br>mes out just 0.0011% of the m

**Table 2. The variance evaluation in K(K** $_{\alpha}$ **) peak energy values evaluated for typical case of Srunnel soil sample**

Channel	966/400	967/463	968/448	965/440	964/432	963/382	969/394	962/411
number/								
Counts								
Fitted				3169.565 3169.844 3169.957 3169.470	3169.539		3169.642 3169.924	3169.596
energy								
value								
(eV)								
mean=3169.692; variance=0.0353844								

Pot identity	pH of soils	<b>Physical condition of plants</b>		Peak Energy Shift (eV) with errors ± 0.001 eV			
				Wheat plants		Pot soils	
		<b>Colour/Texture</b>	Yield	$K(K_{\alpha})$	$Ca(K_6)$	$K(K_{\alpha})$	$Ca(K_\beta)$
$S_{\text{runnel}}$	8	Y/D	Average	8.273	0.133	-17.148	$-10.063$
$S_{\text{chem fac}}$	8	Y/D	Average	22.293	17.943	$-14.619$	$-8.529$
$S_{\text{kit gdn}}$	7	Y/D	Poor	2.97	3.966	$-1.392$	3.345
$S_{\text{Ban gdn}}$	7	G/LD	Good	$-0.77$	$-2.262$	$-0.003$	9.57
$S_{\text{civil hosp}}$	$\overline{7}$	Y/D	Average	$-5.405$	$-7.416$	2.081	6.612
$N_{\text{frm}}$	$6 - 7$	Y/D	Average	$-11.373$	$-16.737$	4.377	13.739
$N_{\text{mech fac}}$	6	Y/D	Good	$-10.194$	$-13.029$	9.011	16.971
$N_{\text{sew}}$	7	Y/D	Poor	$-8.319$	$-14.313$	8.654	21.082
$A_{pnd}$	$\overline{7}$	G/LD	Good	$-3.386$	$-7.721$	6.474	13.411
$A_{\rm rd sd}$	$6 - 7$	G/LD	<b>Better</b>	-6.594	$-10.815$	5.645	12.453
$P_{\text{runnel}}$	$6 - 7$	G/LD	Good	$-11.207$	$-13.311$	4.158	13.842
$P_{\text{riv}}$	$\overline{7}$	Y/D	Good	-18.338	$-20.905$	4.381	8.24
$M_{\text{chem fac}}$	7	Y/D	Good	$-6.931$	$-9.008$	7.902	14.647
M <sub>ghaggar riv</sub>	$\overline{7}$	Y/D	Good	$-1.247$	$-10.091$	0.651	1.51
PUP <sub>botany</sub> gdn	$6 - 7$	G/LD	<b>Better</b>	2.032	$-6.88$	$-0.562$	1.941
$PUP_{\text{sew}}$	7-8	G/LD	Good	1.464	$-2.407$	5.404	13.622
$PUP_{and}$	7	G/LD	Good	0	0	0	0

**Table 3. List of soil pH, physical condition (Colour/texture/yield) of wheat plants on the last day of pot experiment and K(Kα) and Ca(Kβ) X-ray energy shifts for plant and soil samples** 

\*Y/D-> Yellow and dried, G/LD-> Green and lesser dried

Punjabi University, Patiala campus ground site PUP<sub>and</sub> protected from additional / external organic and inorganic material contaminants as well as pollution is taken as reference for soil/plant samples. Peak energy shifts for  $K(K_{\alpha})$ and  $Ca(K_6)$  in recorded spectra of wheat plants/soils with reference to PUP<sub>and</sub> plant/soil are listed in Table 3. To establish the with pH values of soils, the measured pH of soils along with the final day noted physical parameters; colour/texture and yield of the wheat plants of pots are also listed in Table 3.

Since, the measured shifts for wheat 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 / nonstatistical fluctuations due to noise or some other external factors.

Observations from Table 3:

Plants in most of the pots got dried and were yellowish with varying yields depending upon the soils' ability to germinate the seeds. Plant health depends upon the soil's potential to sustain the plant growth as only healthy soil gives healthy plants. In case of pots  $S_{Ban\ gdn}$ ,  $A_{pnd}$ ,  $A_{rd\ sd}$ , PUP<sub>botany gdn</sub>, PUP<sub>sew</sub>, PUP<sub>and</sub>, plant health was found better than the others along with comparative smaller peak energy shifts in  $K(K_{\alpha})$  and  $Ca(K_{\beta})$  photo peaks. It looks that shift measurements can be used as one of the indicators to estimate the soil condition for the plant health and yield. But, in  $S_{\text{kit adn}}$ and M<sub>ghaggar riv</sub> pots in spite of lesser peak energy shifts the plant health was not so good whereas, in pot P<sub>runnel</sub> plant health was good even with large shift values.

- The sign of shift in energies are opposite to each other for plants and soils except in some cases. The observed pattern supports our earlier studies on mint plant and its soils to assess the effect of fertilizer on plant growth by Kaur et al.in 2012 [10].
- Peak energy shift for  $Ca(K_\beta)$  are larger than that for  $K(K_{\alpha})$  for both plants and soils. The results support the fact that calcium being in double positive ionic state  $Ca^{2+}$ has the capability to get tightly held on negatively charged sites than the single ionic state potassium K<sup>+</sup> .

For minute analysis of experimental results with soil conditions, the data is grouped in four categories (Figs. 4a-d): soils affected by waste

fluids  $\mathsf{S}_{\mathsf{runnel}}$ ,  $\mathsf{N}_{\mathsf{sew}}$ ,  $\mathsf{A}_{\mathsf{pnd}}$ ,  $\mathsf{P}_{\mathsf{runnel}}$  and  $\mathsf{PUP}_{\mathsf{sew}}$ ; Soils affected with by-products of industry, hospital and transport  $S_{chem \, fac}$ ,  $S_{civil \, hosp}$ ,  $N_{mech \, fac}$ ,  $A_{rd \, sd}$ 

↓

↓

and  $M_{chem\ fac}$ ; garden and farm soils  $S_{kit\ galn}$ ,  $S_{Ban}$ <sub>gdn</sub>, PUP<sub>botany gdn</sub> and N<sub>frm</sub> and seasonal river soils  $P_{\text{riv}}$  and  $M_{\text{ghagger}}$  riv.





4(b)

7



↑

**Fig. 4. Plot for KKα and CaKβ energy shifts in soils/plants from pots with soils (a) affected by waste fluids; Srunnel, Nsew, Apnd, Prunnel and PUPsew, (b) affected by industrial, hospital and transport by products; Schem fac, Scivil hosp, Nmech fac, Ard sd and Mchem fac. (c) from garden and farm soils; Skit gdn, SBan gdn, PUPbotany gdn and Nfrm. (d) from seasonal river soils; Priv and Mghaggar riv (Black up arrows point positive energy shifts and red down arrows point negative shifts)** 

Illustrations in Fig. 4a show

- Potassium/calcium shifts are with negative pattern for plants and positive for soils except S<sub>runnel</sub> products. Moreover, for S<sub>runnel</sub> K shifts > Ca shifts and is complementary to the shift pattern in other samples.
- The similarity in shift signs of  $A<sub>ond</sub>$  samples as that of  $N_{\text{sew}}$ ,  $P_{\text{runnel}}$  and  $PUP_{\text{sew}}$ , containing organic matter and appreciable amounts of major and micronutrients and variable amounts of heavy metals [14] regulated by the scenario e.g. life style and population of the localities using the runnel for waste water drainage, represents that pond soil is just like sewage and runnel soils. It provides very much relevant explanation to the environment of Ajrawar village's pond soil as sewage water of whole village (approximate population 4000) gets deposited into the pond along with the rain water. Jellinek in 1974 [2] has pointed that organic matter reacts in the soil with a large amount of negative charge that leads to complexation, chelation and produce long chain polymeric materials. In comparison to A<sub>pnd</sub> soil, because of less K shift in PUP<sub>sew</sub> soil predicts it towards the normal as the population level and hence sources of its contamination are less.  $N<sub>sew</sub>$ and P<sub>runnel</sub> soils from comparatively highly populated areas with good existence of industries around are more contaminated.

The reason behind unusual features of  $S_{\text{runnel}}$ samples is alkalinity with 8 pH value (Table 3) and calcareous and phosphorus deficient nature of the soil along with its organic matter [15]. Since, higher pH of soil gives negative charged sites (excess of OH) which attract the cations  $Ca<sup>2+</sup>$  and K<sup>+</sup> and affect the binding energies of the atomic shell electrons. All these result in reduction of energy gap between the bound and outer electrons. It seems surrounding OH ion's whole push on  $K^+$  ion is pointed on single site while for  $Ca^{2+}$  it is dispersed on two sites. This caused the lesser effect of same pull force for calcium electrons than potassium electrons. So, the shifts observed for calcium in S<sub>runnel</sub> soil is lesser than that for potassium.

Illustrations in Fig. 4b shows;

• Potassium/calcium shift pattern in varying magnitudes for S<sub>civil hosp</sub>, N<sub>mech fac</sub>, A<sub>rd sd</sub> and M<sub>chem fac</sub> samples is similar to the illustrations in Fig. 4a.

Like  $S_{\text{runnel}}$  in  $S_{\text{chem}}$  <sub>fac</sub> samples, potassium/calcium shifts are positive for plants and negative for soils and potassium shifts are greater in magnitude than calcium shifts but the shift values are higher for plants that show less ability of plants to survive under  $S_{chem}$  fac soil condition.

Pot  $A_{rd, sd}$  soil is road side soil and according to Christoforidis and Stamatis (2009) & Aslam et al. (2013) [16-17] heavy metals like Cd, Pb, Cu, Ni, Fe, Mn and Zn metals released during different operations combustion, component wear, fluid leakage and corrosion of metals of the road transport make the soil contaminated. Soils in Pots  $N_{mech}$  fac and  $M_{chem}$  fac are from factory site contaminated with heavy metals. The shifts in these cases are direct indication of extra foreign material (chemical) present in the soils that disturb the soil chemistry and, in turn, the type and magnitude of the shift.  $S_{\text{civil\; hosp}}$  pot soil is contaminated with dumped bio-medical waste of civil hospital. As per WHO report (Yadav 2002) [18], around 85% of the hospital wastes are actually non-hazardous, 10% are infective (hence, hazardous), and the remaining 5% are non-infectious but hazardous (chemical, pharmaceutical and radioactive). Thus, hospital site soil is not rich in heavy metal contaminants as other soils in this category, hence the shifts in soil and plant are less.

Pot  $S_{chem\,fac}$  soil is from the site of National Agro Chemicals Limited factory, Sangrur where a gas leak had occurred on October 3, 1998 [http://www.tribuneindia.com/1998/98oct04/punja b.htm#6]. Thus, the site is contaminated with pesticides and insecticides. Pesticide products include ingredients used to kill, control or repel/attract the pest. The products generally contain organic compounds along with some specific chemicals. Like S<sub>runnel soil</sub>, S<sub>chem fac</sub> soil of Sangrur region is also with high pH value and show the same pattern of shifts in two soils. But the presence of additional contaminants (constituents of Pesticides and insecticides) in  $S<sub>chem fac</sub>$  soil has made the soil tough for plants and the plants are acquiring greater shift values.

From Fig. 4c it is clear that;

- The shifts values are very small without any specific pattern for the soils of garden origin in contrast to that of  $N_{\text{frm}}$  soil.
- Calcium shift in  $S_{Ban}$   $_{qdn}$  plants and  $PUP<sub>botany adn</sub>$  soil is considerably higher.

The common property of  $S_{\text{kit qdn}}$ ,  $S_{\text{Ban qdn}}$  and PUP<sub>botany gdn</sub> soils is that the areas are protected from pollutants, traffic and waste dump and fed by organic matter in form of plant residue. The Banasar garden on Sangrur soil rich in calcium content (Table 3) is place with long trees away from pollution sources. As explained earlier organic matter's behavior as well as higher calcium contents in Sangrur area soil leads to higher CaK<sub>β</sub> peak shift. In PUP botanical garden, regular research activities are going on that may be the cause of remarkable Ca $K_8$  peak shift in plants. Apart from this the soil structures from these sites are natural and show comparatively lesser values of peak energy shifts.

Farm soil from Nabha  $N_{\text{frm}}$ , with shifts in intermediate range proves different from garden soils that are natural soil medium in the shadow of plants whereas farm soil has crops with applied fertilizers and pesticides that change the whole chemical configuration of soils. Organic/inorganic compound fertilizers applied to the plants promote growth while the pesticides safeguard the plants against pests. So, a major shift in X-ray peak energies in farm soil clearly points to a major chemical structure effect and difference in electron bindings of farm and garden soils.

 $P_{riv}$  and  $M_{ghagger}$ <sub>riv</sub> soils are from two different seasonal rivers' side i.e Patiala River site (Badi Nadi) and Moonak River site (Ghaggar). According to findings of Shailza, 2011 [19] Patiala River soil carries the waste water from industrial area of Patiala which contains organic matter along with heavy metals like cadmium, chromium and nickel etc. Heavy metals  $Cd^{2+}$ ,  $Cu<sup>2+</sup>$  and Ni<sup>2+</sup> are commonly present in the effluents of electroplating, leather and dye industries. Ghaggar, inspite of its deterioration with industrial and domestic wastewater discharges from the towns located along it or its tributaries

[http://www.cpcb.nic.in/upload/NewItems/NewIte m\_173\_GhaggarReportF.pdf] has a 70-80 km long and clean run before it reaches Moonak (the site from were soil was collected). That is why lesser shifts are measured in Ghaggar pot samples than Patiala River pot samples.

The peak energy shifts in plants mostly negative are opposite in sign to that in soil samples. The basic constituents of plants and soils seem responsible for the observed sign of shifts. Organic material comprising carbon, hydrogen, oxygen and nitrogen etc. along with the traces of nutrients P, K, S, Mg, Ca, Fe, B, Mn, Zn, Mo, and Cu constitute the plants while soils are composed of comparatively heavy elements like Si, Fe, Ca along with various amounts of approximately 90 elements. Negative shifts in plants indicate that a nutrient cation pulls its low Z surroundings towards itself and in soils the high Z surroundings push the nutrient cation. It looks soil contamination of  $S_{\text{runnel}}$  and  $S_{\text{chem fac}}$ has transferred some high Z elements from soil to plants. The organic constituents and growing character of plants make them capable to intake and utilize the calcium and potassium nutrients from soil and signify the wheat plants' quality to cope with stress conditions.

All the interpretation justifies that magnitude / sign of peak energy shifts have correlation with soil contamination and constituents of samples. But, plant soil relationship is complicate and not any single phenomenon could help completely to choose suited soil conditions for selected seeds. Thus, more considerations should be undertaken in future studies of this kind to get a better understanding regarding soil conditions and related plant's health.

## **4. CONCLUSIONS**

Level of contamination of soils correlated with the population life style of localities and environment of occupations like industries, farming and gardening etc. change the soil nutrients' chemical state that lead to these energy shifts. The shifts in nutrient photo peak energies in plants, generally, in opposite direction to that for soils signify the wheat plants' quality to cope with stress conditions. Thus, shifts in photo peak energies for nutrients can be used as tool to sense the contamination level of soil.

## **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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