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EDXRF Analysis of Soil Samples to Study the Role of Trace Elements in Optimizing the Yield

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Abstract : The crops always demand the best composition of soils for them to grow well and so the multielemental study of soil is essential for the betterment of crop production. The EDXRF technique has been used for multielemental analysis of the soil, under study. The soil samples investigated here were treated already with macro, micro and biofertilizers. The concentrations of eight trace elements namely V, Cr, Mn, Fe, Co, Ni, Cu and Zn have been determined in soil samples. The grain yields of wheat and rice crops were obtained and it has been found that the yields depend strongly on the given treatments and the concentrations of the trace elements in the soil. Some of the micronutrients like Zn, Cu, Fe and Mn have shown the major role in the productive yields.

The concentration equations of the eight trace elements as a function of atomic number were fitted using the cubic spline method. The equations may be useful for database purpose and the cross validation can be done in subsequent years to obtained more accurate empirical relation for the studied soil.

Keywords – Cubic Spline Method, EDXRF, Fertilizers, Yield

Introduction

The multi-elemental study of soils is much needed in order to study the role of different elements in plant growth. The data on the concentration of trace elements and metals in soil are valuable for predicting the availability of these elements to plants as well as any toxic effect that might have occur on crops and on their biological activities in soils. The concentrations of micronutrients, e.g. Mn, Cu and Zn in soil are minute in comparison to macro nutrients but they are essential, particularly for cereal crops [1], for proper plants growth and functioning. These micronutrients are also indispensable for humans and animals in minute amount and can be in taken through the food chain.

The multielemental analysis of soil samples has been carried out with Energy Dispersive X-Ray Fluorescence (EDXRF) technique. The technique has many advantages over other techniques, like AAS, ICP-MS and chemical methods, that it is multielemental, non-destructive and has better sensitivity and precision. The total concentrations of eight trace elements (V, Cr, Mn, Fe, Co, Ni, Cu and Zn) have been determined in samples which were treated with various fertilizers. In EDXRF, the atoms in the sample material are excited by X-rays, emitted from an X-ray tube. All element specific X-ray fluorescence signals, the intensities of which is proportional to concentration of respective elements, emitted by the atoms after the photoelectric ionization are measured simultaneously by detector.

In case of soil analysis, EDXRF probe has been used in last decade by researchers and scientists for various purposes of study. Multielemental analysis of soil has been done to investigate the uptake mechanism in the herbal drugs [2]. Yu et al. [3] determined the multielemental profile of Hong Kong soils using energy dispersive X-ray fluorescence (EDXRF). The distribution of soil nutrients with depth was studied to understand the importance of plants in structuring the vertical distributions of the nutrients [4].

The empirical relations of elemental concentrations were obtained by fitting the curve using cubic spline method. The concentrations of elements, as a function of atomic number, were given by a set of equations governed by a single function. Every equation is in the form of cubic polynomial and having four parameters.

Experimental Procedures

2.1 Experimental Site & Soil Taxonomy

The soil samples have been collected from an agricultural field of G.B.Pant University of Agriculture and Technology, Pantnagar, lying in tarai region of Uttarakhand, India. The site is in the foothills of Shiwalik range of Himalayas at 29^0 N latitude, $79^0 3'$ E and an altitude of 283.8 m. It is an Agro ecological sub region -14.1. Based on physico-chemical and morphological characteristics, the soils of this particular tarai region have been classified as Mollisols. The soil of experiment has subgroup-Aquic hapludoll, Family- Fine Loamy and series-Silty Clay Loam.

2.2 Treatments

Five treatments were being given to soil under study. The soil samples from control field were also investigated. The treatments code and details are given in TABLE 2.

Fertilizer doses (Kg ha^{-1}) used at optimal level (100 % NPK) were based on initial soil tests in terms of nutrients. Quantitatively the doses are given below:

TABLE 1.

Crop	N (kg ha^{-1})	P(kg ha^{-1})	K(kg ha^{-1})
Rice	120	26	37
Wheat	120	26	33

In the treatments, the nitrogen (N), phosphorus (P) and potassium (K) were given in the form of urea [$(NH_2)_2CO$], phosphorus pentaoxide (P_2O_5) and muriate of potass (KCl) respectively.

2.3 Sample Collection and Preparation

The soil samples have been collected from 0-25 cm depth. The samples were air dried, sieved and crushed homogeneously. A 200 mg sample is used to make the pellet by press pelletizer applying the pressure of 150 Kg /cm^2. A 13 mm die was used to make the pellets.

2.4 Soil Sample Analysis

Jordan Valley EX-3600 EDXRF spectrometer was used to carry out all the measurements under vacuum condition. All the samples were analyzed in three replicates for better results. The inbuilt ExWin software was used for the quantitative analysis.

2.5 Cubic Spline Method

The method was used to fit the curve drawn by data points of concentration vs. Atomic number (Z). The condition for a cubic spline fit is that a set of cubics is passed through the points, using a new cubic in each interval. Briefly the method is discussed here:
The cubic for *i*th interval ,which lies between the points (x_i, y_i) and (x_{i+1} ,y_{i+1}) would be

$$y = a_i(x - x_i)^3 + b_i(x - x_i)^2 + c_i(x - x_i) + d_i \quad (1)$$

Since it fits at the two end points of the interval, then:

$$y_i = a_i(x_i - x_i)^3 + b_i(x_i - x_i)^2 + c_i(x_i - x_i) + d_i = d_i \quad (2)$$

and

$$y_{i+1} = a_i(x_{i+1} - x_i)^3 + b_i(x_{i+1} - x_i)^2 + c_i(x_{i+1} - x_i) + d_i$$

$$= a_i h_i^3 + b_i h_i^2 + c_i h_i + d_i \quad (3)$$

Where $h_i=\Delta x_i$ is the *i*th interval

Let S_i represents the second derivative at the point (x_i, y_i). Differentiating (1) by two times and equating the slopes and curvature of joining polynomials, we get the values of parameters. Substituting the values of *a ,b ,c and d* in terms of *S and y*, finally we got the relation:

$$h_{i-1}S_{i-1} + (2h_{i-1} + 2h_i)S_i + h_iS_{i+1} = 6\left(\frac{y_{i+1}-y_i}{h_i} - \frac{y_i-y_{i-1}}{h_{i-1}}\right) \quad (4)$$

(4) applies at each interval point from *i*=2 to *i*=n-1, n being the total number of points. So we get n-2 equations. Two more equations will be obtained by taking linear extrapolation of S_1 with S_2 and S_3, with analogous linearity of S_n, S_{n-1} and S_{n-2} :

$$\frac{S_2-S_1}{h_1} = \frac{S_3-S_2}{h_2}, \quad h_2S_1 - (h_1 + h_2)S_2 + h_1S_3 = 0 \quad (5)$$

and

$$\frac{S_n-S_{n-1}}{h_{n-1}} = \frac{S_{n-1}-S_{n-2}}{h_{n-2}}, \quad h_{n-1}S_{n-2} - (h_{n-2} + h_{n-1})S_{n-1} + h_{n-2}S_n = 0 \quad (6)$$

Finally, we have a set of data which are fitted throughout by a single cubic.

Results and Discussion

The concentrations of elements, determined by EDXRF technique, are presented in TABLE 3. Arithmetic mean and arithmetic standard deviation (ASD) of concentrations have been calculated also.

The Vanadium was found in bit high amount in the T1 and T2 samples, which were treated with NPK fertilizers. Both V and Cr are poorly soluble and the use of FYM seems to improve the uptake of both of the elements. The usefulness of Cr and V is limited for the plants but these elements were illustrated as essential for the humans [5]. A similar trend was observed for iron and manganese concentration values. Added weedicdes and Zn increased the uptake of Fe and Mn as shown by the decreasing concentrations in T1, T2 and T3. This result was also supported by Singh and Nand Ram [6] who studied the uptake of Fe, Mn, Cu and Zn micronutrients for same soil samples and treatments, and observed the highest uptake for T4 treatment (i.e. 100 % NPK+FYM) with decreasing order as T4 > T3 > T2 > T1 > T5 > C . In all the soil samples, the Fe concentration was found to be high and this humid sub-tropical region was considered to be the Fe rich region. Despite the higher amount of iron in soil, no symptoms of iron toxicity have been monitored in the rice and wheat plants. The reason is that the iron toxicity occurs in soils high in active iron and potential acidity (mostly Ultisols, Oxisols, and acid sulfate soils) and not in Mollisols. Besides that, the application of nutrients such as P, K, and Zn reduce iron toxicity, improve growth, and increase rice yield [7]. A least amount of all trace elements and also the poor crop grain yields was observed in T5, i.e. soil treated with biofertilizers. Application of azolla biofertilizer has been found to improves the properties of soil but these improvements were considerable only for nitrogen , organic matter and other cations (Mg, Ca and Na) released into the soil [8]. Cobalt was in quite high amount in all the samples and that could be due to the high amount of Co in the ground water used for irrigation or/and pesticides used here.

The Ni and Cu concentrations were found in a low amount in all the soil samples; although the role of nickel is not clear in the growth of rice and wheat plants. Cu, Mn, Fe and Zn were considered the most essential trace elements for rice and wheat crop and proper fertilizer should be chosen to prevent the deficiency of these elements [9]. Cu concentration and Cu uptake both were highest for T4 sample; indicated that the Cu is highly associated with OM which is the main content of FYM [10].The second most considerable results were obtained by the addition of Zn concerning the plants growth and yield. The highest and almost same concentration of Zn was obtained for T3 and T4 treatments. It may be concluded by results that along with Cu, significant amount of zinc is also contained with FYM.

The graphs of yields of rice and wheat grain vs. years have been plotted (Fig.1 to Fig.6). The best grain yield of Rice and Wheat is obtained for the treatment T4 (Fig. 4). Addition of FYM with 100% NPK have offered the superior crop production with a higher uptake of micronutrients. FYM is consist of 26.38 % Organic matter which is one of the main soil parameter governing the processes of sorption and desorption of trace elements [11]. The yield of rice and wheat has been increased also in the subsequent years by the adding FYM. Addition of Zn has clearly enhanced the grain yields of both rice and wheat by substantial amount. A slightly better yield was obtained by adding biofertilizers in soil (Fig. 5) compared to control (Fig. 6). The use of biofertilizers with Zn or FYM could be a better option.

The empirical relations, for concentrations values as a function of atomic number, have been obtained.

If the concentration (in μg/g) is denoted by C(Z), the equations of C(Z) as a function of atomic numbers are:

$$C(Z) = 0.7780709925 \times 10^8 - 0.1016150467 \times 10^8 + 442082.2227\, Z^2 - 6406.988733\, Z^3, \quad \text{for } Z = 23$$

$$= -0.4591923012 \times 10^9 + 0.5696341861 \times 10^8\, Z - 0.2354789657 \times 10^7\, Z^2 + 32438.45405\, Z^3, \quad \text{for } Z = 24$$

$$= 0.1102960231 \times 10^{10} - 0.1304948853\ 10^9\, Z + 0.5143542504 \times 10^7\, Z^2 - 67539.30812\, Z^3, \quad \text{for } Z = 25$$

$$= -0.1277355453 \times 10^{10} + 0.1441569241 \times 10^9\, Z - 0.5419988627 \times 10^7\, Z^2 + 67890.57818\, Z^3, \quad \text{for } Z = 26$$

$$= 0.7165788765 \times 10^9 - 0.7739133459\, 10^8\, Z + 0.2785502433 \times 10^7\, Z^2 - 33411.78057\, Z^3, \quad \text{for } Z = 27$$

$$= -0.2099348092 \times 10^9 + 0.2187798883\, 10^8\, Z - 759830.5453\, Z^2 + 8794.564393\, Z^3, \quad \text{for } Z = 28$$

$$= 0.4761506567 \times 10^8 - 0.4765101657 10^7\, Z + 158896.7127\, Z^2 - 1765.519030\, Z^3, \quad \text{for } Z = 29\ \&\ Z = 30 \qquad (7)$$

Generally it is not so easy to fit the data points which have large variations in the values and less in number, as the case here. To fit a smooth curve to such data points, the cubic spline method is a better approach. The method covers all data points and the fitted curve will be discontinuous on intermediate points.

The (7) were fitted well with the experimental values of concentrations of different elements (TABLE 4). More research in later years may be done to obtain the more accurate empirical relations. Moreover, after creating a database of subsequent years, the variation trends of elemental concentrations may also be studied.

Conclusion

Soil composition for trace elements depends strongly on the given fertilizers treatments and fertilizers concentration. EDXRF is competent technique for analyzing the soil like complex material. Application of farmyard manure (FYM) with 100% NPK has the highest effect on the yield of wheat and rice crops. It also improves the concentrations of some essential trace elements like Cu and Zn in the soil, as confirmed by EDXRF results. The study also pronounces that chemical fertilizers can not be substituted by biofertilizers, concerning plant growth of rice and wheat. Zn has proven to be the most important trace element for rice-wheat cropping system and has a significant role in obtaining higher yield. Except Co, the concentrations of all the trace elements, determined here, in the soil were found to be influenced by the treatments of different fertilizers. The empirical relations obtained by cubic spline method are useful for current and future research purposes.

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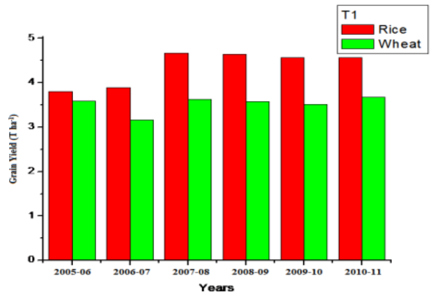

Fig. 1: Grain yield bar graph of rice and wheat crops for the consecutive years and for treatment T1

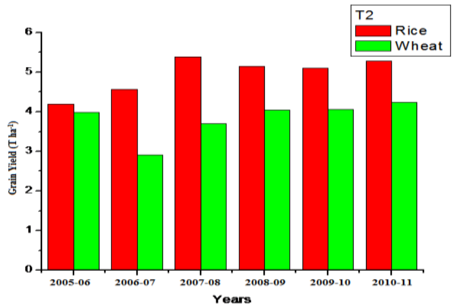

Fig. 2: Grain yield bar graph of rice and wheat crops for the consecutive years and for treatment T1. Addition of Zn alone has substantially enhanced the yields

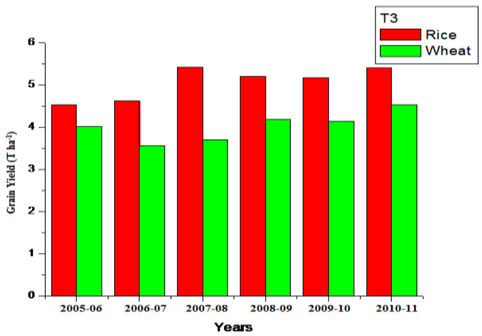

Fig. 3: Grain yield bar graph of rice and wheat crops for the consecutive years and for treatment T3. The grain yields were almost same as for T2.

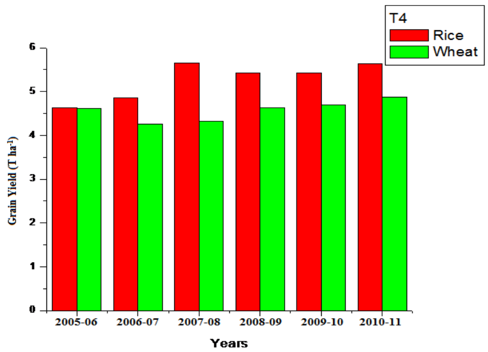

Fig. 4: The highest yield was obtained for the T4 (100% NPK+FYM). FYM has some essential trace elements associated with, for proper plants growth

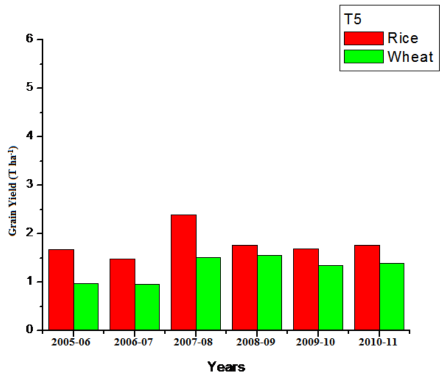

Fig. 5: A slightly greater yield than Control is obtained for T5. The addition of biofertilizers alone in soil is not sufficient for proper plants growth.

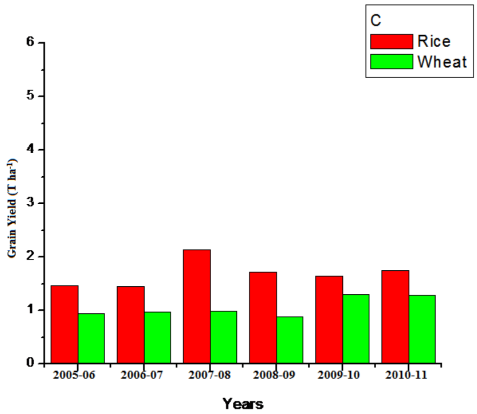

Fig. 6: The lowest yield was obtained for Control.

TABLE 2: The Treatments Given to Soil Prior to Sampling for EDXRF Analysis

Treatments	Treatment Code	Treatment Detail
Treatment 1	T 1	100 % NPK[a] of recommended dose
Treatment 2	T 2	100 % NPK+Hand Weeding+Zinc
Treatment 3	T 3	100 % NPK+ Zinc
Treatment 4	T 4	100 % NPK+ Farmyard Manure (FYM)
Treatment 5	T 5	Biofertilizers
Control	C	Control

TABLE 3: Concentrations of Eight Trace Elements Determined by EDXRF Technique. The Concentrations were Given in the Form of 'Arithmetic Mean± Arithmetic Standard Deviation'.

Treatments	Concentration in µg /g							
	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
T 1	117.48 ±5.17	114.65 ±3.7	497.78 ±25.24	60429.58 ±1620.7	39.09 ±1.75	6.97 ±0.45	8.49 ±0.5	40.78 ±2.81
T 2	128.27 ±8.78	99.57 ±19.14	483.39 ±5.37	58542.35 ±1437.31	35.95 ±1.24	6.84 ±0.72	8.31 ±0.68	48.36 ±4.55
T 3	111.95 ±5.61	98.73 ±12.17	470.05 ±19.95	57760.67 ±4910.49	39.42 ±5.27	7.24 ±0.09	8.23 ±1.38	43.43 ±6.04
T 4	114.3 ±4.82	92.06 ±8.96	473.25 ±26.1	57063.91 ±3688.6	39.12 ±0.37	8.12 ±0.94	9.34 ±0.28	43.53 ±2.43
T 5	106.22 ±1.72	94.69 ±14.78	436.69 ±10.12	53385.35 ±1898.35	37.69 ±1.75	5.91 ±1.09	9.03 ±0.36	36.99 ±2.01
C	118.5 ±5.23	100.05 ±16.41	472.89 ±13.64	57765.63 ±2252.19	36.71 ±4.76	5.96 ±0.71	8.76 ±0.06	40.61 ±0.97

TABLE 4: The Experimentally Obtained Concentration values and the Values Fitted by Cubic Spline Method

Element	Atomic Number (Z)	Experimental Values (in µg/g) (Arithmetic Mean)	Arithmetic Standard Deviation	Fitted Values
Vanadium (V)	23	114.3	4.82	114.33
Chromium (Cr)	24	92.06	8.96	91.8
Manganese (Mn)	25	473.25	26.1	474.12
Iron (Fe)	26	57063.91	3688.6	57063.84
Nickel (Ni)	27	39.12	0.37	39.27
Cobalt (Co)	28	8.12	0.94	8.08
Copper (Cu)	29	9.34	0.28	9.38
Zinc (Zn)	30	43.53	2.43	43.58