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Assessment of Essential and Trace Elements in Soil Profiles of Paddy Fields of Southern District of Kashmir Himalaya

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Abstract: **- The concentrations of micronutrients and rare earth elements in soil profile of paddy fields in Kulgam district (J&K) were assessed in this study. Standard methodology was adopted to analyse the soil samples using WDXRF. The concentrations of various elemets in the paddy soil profile were recorded in the order of Zn(79.3 ppm)> Ni (47 ppm) >Cu (31.5 ppm) >Co (26.33 ppm) > Mo (2 ppm), the Zn being found in maximum concentration and Mo in minimum concentration. Amoung other trace elements, Ba was found in maximum concentration and Sb in minimum concentration and among rare earth elements, the vanadium being found in maximum concentration and uranium in minimum concentration. Deeper layers exhibited higher concentration for all elements except Zn, Cu, Mo and Zr. Among the micronutrients highly significant positive correlation was found between the element pairs of cobalt-nickel (r = 0.97), zinc-copper (r= 0.99) and zinc-molybdenum (r= 0.99), indicates close association of these metals with each other and source. However negative correlation was found in some element pairs like metals (Sb-Sc , Sb-V , Sb-Cr , Sb- Sr, Sb -Rb , Sb- Y,Sb- Sb- Zr,Sb- Nb, Sb- Sn) and no significant relation was found between Ga- Zr, Ga- Sn,Ga- Sb, Ga- Ce and Ga- U. The concentrations of the micronutrients, rare earth metals and other trace metals in the paddy soil profile were significantly within safe limits of polluted and non-polluted standards for agriculture soil.**

Keywords: Micronutrients & Trace metals, paddy soil profiles, Inorganic fertilizers, Waste water

INTRODUCTION:

Contamination of soils by heavy metals can be caused by various factors such as, mining or industrial activities, non point sources of metals, especially atmospheric and automobile emission, application of chemical fertilizers, farmyard manures, sewage sludge, and wastewater irrigation and metal-enriched parent materials (Freedman and Hutchinson, 1981). However, soil contamination by heavy metals and trace elements due to parent materials or point sources often occurs on limited areas and is easy to identify (He et al., 2005). The excessive application of other inorganic fertilizers and organic manures to the Paddy crops can accumulate high levels heavy metals and trace metals. Consequently their consumption by humans and animals can pose serious threat to health. A major pathway of soil containing through atmospheric deposition of heavy metals from point sources such as: metal smelting and industrial activities. Other non point sources of contamination affecting agricultural soils include inputs such as, fertilisers, pesticides, sewage sludge and organic (Singh 2001). Although some trace metal such as Cu, Zn, Mn and Fe are essential in plant nutrition, many of them do not play any significant role in the plant physiology. The uptake of these heavy metals by plants is an avenue of their entry into the human food chain with harmful effects on health (Ihekeronye and Ngoddy 1985). In fact, large amounts of the waste comprise organic material, but there are considerable proportions of plastic, paper, metal rubbish and batteries which are known to be real sources of heavy metals (Lisk, 1988; Zhang et al., 2002; Pasquini and Alexander, 2004). Heavy metals and non bio degradable materials can accumulate in soils to toxic concentrations that affect plant and animal life.

In agricultural systems including paddy agro-ecosystems, soil contamination of heavy metals is mainly related to input and accumulation of these elements through repeated application of metal enriched chemicals such as chemical fertilizers, pesticides including fungicides, farm manures, and biosolids (Webber, 1981). Biosolids and/or municipal waste composts made of biosolids often contain higher concentrations of Cu, Zn, Cd , Cr and Ni (He et al., 2001, Reddy and P attnaik, 2009). The movement of heavy metals down the soil profile is often evident in systems with higher application of fertilizers both chemical and organic nature, sewage sludge, and in soils with low organic matter and clay contents, higher pH conditions, and under high rainfall or irrigation rates. The movement occurs through soil macro pores or cracks which is also referred to as preferential flow (Dowdy and Volk, 1983). Though information on heavy metals and trace elemental distribution in soil profile of crop fields is inadequate, little information is available on such aspects in paddy field soil in India. Therefore, the objective of the present investigation is to assess the distribution of essential metals and other trace metals in the soil profile of the paddy fields at Nillow in the rice bowl (Kulgam) of Kashmir, the Himalayan state of India.

MATERIAL AND METHODS:

Study area description: The sampling site is located at Nillow, an agricultural a picturesque place site along the bank of Veshew stream originated from glacier located east of the Kulgam city(33°40'19''N_to33°40'49'' N ; and $74^0$59'05'' N to $74^0$59'31''N) elevation of 1739 metres above sea level (Fig. 1)in Kulgam district, of Jammu and Kashmir. Nature has gifted this whole area with agroclimatic conditions suited for paddy cultivation in its lower belts and fruit culture in the upper areas of the district. Because of fertile lands with better paddy yield and productivity Kulgam is considered as 'Rice – Bowl' of Kashmir. Upper areas of Kulgam are known for the production of quality apple. Rice is grown only once in a year In Kashmir region because of extreme climatic conditions. In this area of study, sewage sludge and, composite manures (like cow dung and rice husk) and indiscriminate use of inorganic fertilizers are used are used by farmers to improve soil fertility for the growth of paddy.

The Veshew receives plentiful amounts of wastes from residential areas along its course. The contaminated water from these streams is used extensively for the irrigation of the paddy fields. Hence, this poses significant effect on the heavy metal contents of paddy field soil there by exposing consumers due to bioaccumulation of trace metals with time.

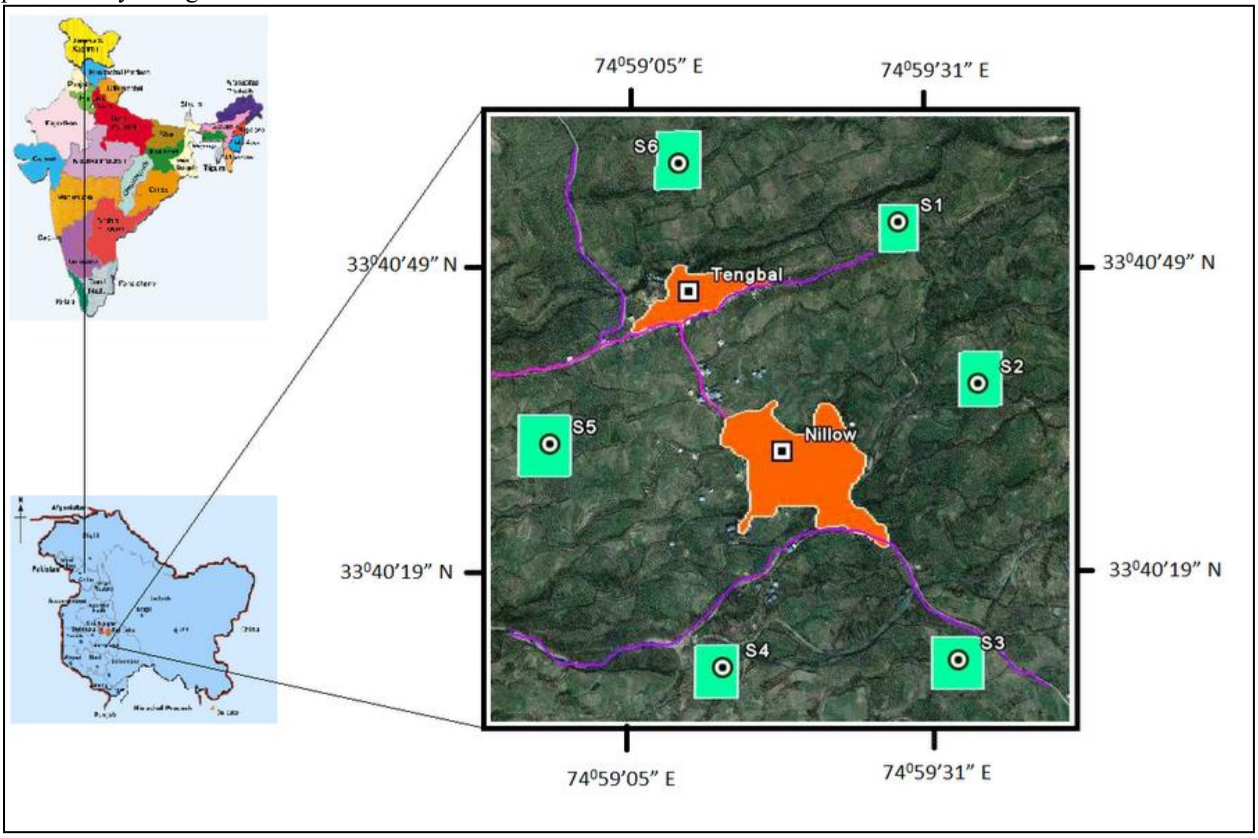

Fig.1. Study area and sampling sites

Soil sample collection, Preparations and analysis: Soil samples were collected from the six randomly selected agricultural fields of Nillow area located nar Kulgam city. Soil samples were collected from three depths (0-5 cm, 20-25 cm and 35-40 cm) of the fields by using spiral auger of 2.5 cm diameter. The soil samples were bulked together soon after collection to form a composite sample. In all cases, soil samples were put in clean plastic bags and transported to the departmental laboratory and then air-dried at room temperature, crushed and passed through 2 mm mesh sieve. The samples were then put in clean plastic bags and sealed. Soil samples were analyzed for the essential elements (micronutrients) and other trace elements.

Determination of Heavy Metals in Soil Sample: Two grams of the soil samples were weighed into acid-washed glass beaker. The samples were digested by the addition of 20 cm^3 of aqua regia mixture of HCl and HNO_3, ratio 3:1) and 10cm^3 of 30% H_2O_2. The H_2O_2 was added in small portions to avoid any possible overflow leading to loss of material from the beaker. The beakers was covered with a watch glass, and heated over a hot plate at 90 ˚C for two hours. The beaker wall and watch glass were washed with distilled water and the samples were filtered out to separate the insoluble solid from the supernatant liquid. The volumes were adjusted to100 cm^3 with distilled water. Blank solutions were handled as detailed for the samples. All samples and blanks were stored in plastic containers. The results were expressed in mg/kg (ppm) dry weight. All statistical analyses were carried out with the program SPSS 12.3for windows.

Trace elemental Analysis: Determination of Ni, Cu, Zn, Mo, Co, Ga, As, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, La, Ce, Pb, Sc, V, Cr, Th and U in soil samples were made directly on each of the final solution using wavelength dispersive x-ray fluorescence spectrometer (WDXRF).

RESULTS AND DISCUSSION:

The concentration of different micronutrients in the soil samples were found to follow the order as: Zn (79.3 ppm)> Ni (47 ppm) >Cu (31.5 ppm) >Co (26.33 ppm) > Mo (2 ppm). The concentration of different rare earth metals in the paddy soils were recorded in the order as: V(199 ppm)> Ce(102.33 ppm) > Y (36.33 ppm) >La(25.16 ppm) >Sc (23 ppm) > Th (11.33 ppm) > U (3.166 ppm). The concentration of other trace metals in the paddy soils of Kulgam were found in the sequence as: Ba (408 ppm > Zr (237 ppm) > Sr(175 ppm) > Cr(135.16 ppm) > Rb(78 ppm) > Pb(25.83 ppm) > Nb (20.83 ppm) > Ga (17.66 ppm) > As (10.33 ppm) > Sn(7 ppm) > Cs (4.66 ppm) > Sb (0.33ppm). Over all concentration of different micronutrients, rare earth metals and other trace metals in the paddy soils of Kulgam were found in the following ranking order: Ba> Zr> V> Sr> Cr> Ce> Rb = Zn > Ni> Y> Cu> Co> Pb> La> Sc> Nb> Ga> Th>As> Sn> Cs> U> Mo> Sb. All the micronutrients, rare earth metals and other trace metals increased significantly ($p < 0.05$) with depth, i.e. from 0-5 cm, 20- 25 and 35-40 cm. But concentration of certain elements like Zn, Cu, Mo and Zr not increases with the depth, however more concentration of these metals were found in the second layer indicates that the metal concentration increases with depth in these metals, but takes time to leach downwards that may be the reason why concentration was found more in the second layer (20-25 cm).The concentration of Zr ranges from 230-237 ppm , The concentration was higher (237.66 ppm) in the second layer (20-25 cm) which was followed by the third layer (35-40 cm) with concentration of 232.32 ppm and first layer (0-5 cm) with concentration 230 ppm respectively. It was found that concentration of Zr was higher in the second layer may be due to higher retention time as moving downwards. The concentrations of the rare earth earth element Uranium and trace metal antimony was 0.33 ppm respectively, which was found to be same in all the depths. The concentrations of different essential micronutrients like Mo and Zn in the paddy soil of Kulgam were found in the range of 1.66 ppm to 79.3 ppm respectively. The concentration of Zn(79.3 ppm) was higher followed by Ni (47 ppm), Cu (31.5 ppm), Co (26.33 ppm) and Mo (2 ppm). The concentrations of other trace metals such as Sb and Ba in the paddy soil was found in the range of 0.33 ppm to 408 ppm. The concentration of Ba(408 ppm) was found to be higher among the trace metals which was followed by Zr (237 ppm), Sr(175 ppm), Cr(135.16 ppm), Rb(78 ppm), Pb(25.83 ppm), Nb (20.83 ppm), Ga (17.66 ppm), As (10.33 ppm), Sn(7 ppm) Cs (4.66 ppm) and Sb (0.33ppm). The concentrations of rare earth metals such as U and V in the paddy soil were found in the range of 3.166 ppm to 199 ppm. The concentration of V was found to be higher among the rare earth metals which was followed by Ce (102.33 ppm), Y (36.33 ppm), La (25.16 ppm) ,Sc (23 ppm), Th (11.33 ppm),and U (3.166 ppm).

With the objective of evaluating significant differences across the different depths of the paddy soil for the micronutrients, rare earth metals and other trace metals , data were analysed using two – way analysis of variance (ANOVA) at 5% level of significance ,correlation matrix. About five sites composite sample of three depths (0-5 cm, 20-25 cm and 35-40 cm) were compared with each other. The concentration of about twenty four metals which includes the essential micronutrients, rare earth metals and other trace metals, showed that the concentration of all metals across the depths were significantly different from each other ($p < 0.01$ & $p<0.05$). Almost the concentrations of metals increased downward except for few metals like Zn, Cu, Mo and Zr. The concentrations of these metals were found to be higher in the second layer means that the concentration in these metals also increase but these metals showed some deviation from other metals i.e. in these metals there is decrease in the concentration in the third layer (35-40 cm) ,but higher than the first layer (0-5 cm) , this may be probably that these metals take more time to move downwards because the concentration is more in the second layer not in the first layer .

ANOVA analysis in the paddy soil proved that mean metallic concentration of the micronutrients, rare earth metals and other trace metals was significantly different from each other across different depths. The correlation analysis carried for the paddy soil that revealed the results as: Among the micronutrients highly significant positive correlation was found between the element pairs of cobalt-nickel (r= 0.972253), zinc –copper (r= 0.995714) and zinc-molybdenum (r= 0.995714) ,suggesting a possible common origin for these metals which probably may be due to excessive use of inorganic fertilizers ,pesticides and domestic waste water.

The highly positive correlation was found in the following element pairs: V-Sc (0.99), Cr-Sc(0.99) ,Rb- Sc (0.99), Sr-Sc (0.97) ,Y-Sc (0.88), Nb-Sc (0.99), Cs-Sc (0.99), Ba-Sc (0.99), Ia-Sc (0.99), Pb-Sc (0.99) , Cr- V (0.99) , Rb-V (0.99),Sr-V(0.99), Cs- V (0.99), Ba-V (0.99) ,La-V (0.99),Pb-V (0.99), Th-V (0.99), Sr-Cr (0.99), Cs-Cr (0.99), Ba-Cr (0.99), Pb-Cr (0.99), Sr –As (0.99) ,Sr-Rb (0.99), Cs-Rb (0.99), Ba-Rb (0.99) Pb-Rb (0.99),Th-Rb (1), Th-Sr (0.99), Cs-Nb (0.99),La-Nb (0.99), Pb-Nb (0.99),Ce-Sn (0.99),Cs-La (0.99), Cs – Ba (0.99), Cs - Pb (0.99), Cs – Th(0.99), Ba-Th (0.99),La-Th (0.99), Pb-Th (0.99), suggesting the possible source of the contamination of the paddy soil mainly due the inorganic fertilizers ,organic fertilizers , polluted sewage water and also may be due to the heavy vehicular transport near to the paddy soil. However highly negative correlation was found in some metals (Sb-Sc , Sb-V , Sb-Cr , Sb- Sr, Sb -Rb , Sb- Y,Sb-Sb- Zr,Sb- Nb, Sb- Sn) and no significant relation was found between Ga- Zr, Ga- Sn,Ga- Sb, Ga- Ce and Ga- U.

The concentrations of micronutrients, rare earth metals and other trace metals showed spatial and temporal variations, which may be described to the variation in heavy metal sources and the quantity of heavy metals in irrigation water

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and sewage sludge. This trend suggests that continuous application of inorganic fertilizers, sewage sludge and municipal wastewater influenced the soil physicochemical properties (Willett *et al.,* 1984).
Evidence that heavy metals may move in the soil profile was provided by Lund *et al.,* (1976), in their field experiment the researchers used sludge with a high content of heavy metals and found that Zn had moved down to 50 cm, Cd to 17 cm while Ni to 75 cm. Davis *et al.*, (1988) measured the metal distribution in the soil profile in a field experiment where sludge had been applied at a rate of 40 t $ha^{-1}$and rainfall rate was around 560 mm per annum over a period of 4 years. They found a significant movement of Cd, Ni, Pb and Zn to a depth of 10 cm. Also Schirado *et al.,* (1986) reported that heavy metals had a uniform distribution in the soil profile to a depth of 1m, due to their movement.

As the rainfall is in adequate quantity in the Kashmir valley and also snow covers the land for 3-4 months ,this favors the statement of the Davis et al ,which may be probably the cause of the increasing the metal concentration with the increase of the depth. The results that have been obtained from the present study, where movement of micronutrients ,rare earth metals and other trace metals almost increases down the soil profile to a depth of 40 cm. The concentrations of different metals in the soil samples obtained during the present study were found within the safe limits (McGarath et al.,(2001).

Table 1. Concentration of micronutrients (Mean ± SD) in the soil profile of paddy fields

Micronutrients	0-5 cm	20-25 cm	35-40 cm	Total
	Mean S.d	Mean S.d	Mean S.d	
Co	19.5 ±0.16	22±0.66	26.33±2.66	67.83
Ni	42.33 ±2.33	45±0.66	47±1	134.33
Zn	76.16 ±6.16	79.3±6.33	78±3.33	233.5
Cu	28.16 ±3.16	31.5±3.16	29.83±1.5	89.5
Mo	1.66 ±0	2±0.33	1.83±0.16	5.5

Table 2 Concentration of trace elements in the soil profile of paddy fields

Trace elements	0-5 cm	20-25 cm	35-40 cm	Total
	Mean S.d	Mean S.d	Mean S.d	
Ga	17.15±0.166	17.50±0.166	17.66±0	52.33
As	7.66 ±1	9.33±0	10.33±1	27.33
Rb	75.33±4.33	76.66 ±7	78 ±5	230
Sr	156.5 ±19.5	167.5 ±10.16	175±5.66	499
Y	35.33 ±1	36.16 ±1.166	36.33±2.66	107.83
Zr	232.32±11.66	237.66±12.33	230 ±19	700
Nb	19.33 ±1.33	19.83 ±1.5	20.83±2.83	60
Sn	5.16±1.166	5.33±1.33	7±0.666	17.5
Sb	0.33 ±0	0.33 ±0	0.33 ±0	0.833
Cs	2.66 ±2.666	3.5 ± 1.166	4.66±1	10.83
Ba	403.83±11.83	405.83 ±4.16	408 ± 3.333	1217.6
La	22.33 ±3	23.33±0.333	25.16±2.16	70.83
Ce	98.66±0.333	98.83±9.5	102.33±0.333	299.83
Pb	23.5 ±2.5	24.5±0.5	25.83 ±1.83	73.83
Sc	21.33 ±0.333	21.83 ±0.833	23 ± 0.66	66.16
V	179.33 ± 8	189 ±8.333	199 ±8	567.33
Cr	131.16 ±1.166	133.16±1.5	135.16±0.833	399.5
Th	10.66±0	11 ±0	11.33 ±0	33
U	3.166 ±0.5	3.166±0.5	3.166±0.166	9.5

Correlation of micronutrient in paddy soil in Kulgam

	Co	Ni	Cu	Zn	Mo
Co	1				
Ni	0.972253	1			
Cu	0.36173	0.569783	1		
Zn	0.446404	0.643347	0.995714	1	
Mo	0.36173	0.569783	1	0.995714	1

ANOVA: Two-Factor without Replication for trace metals of paddy fields of Kulgam.

ANOVA						
Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	613964.9	18	34109.16	4152.842	3E-54	1.898622
Columns	148.6676	2	74.33382	9.050255	0.000654	3.259446
Error	295.6842	36	8.21345			
Total	614409.3	56				

Correlation of micronutrient in paddy soil in Kulgam

	Co	Ni	Cu	Zn	Mo
Co	1				
Ni	0.972253	1			
Cu	0.36173	0.569783	1		
Zn	0.446404	0.643347	0.995714	1	
Mo	0.36173	0.569783	1	0.995714	1

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