SPECTROSCOPIC STUDY OF THE TRACE ELEMENTS ON RICE (ORYZA SATIVA. Linn) IN MEGHALAYA

A THESIS SUBMITTED
IN
PARTIAL FULFILMENT OF THE REQUIREMENT
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By
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SYSTEMS AND BIOPHYSICS

To

NORTH-EASTERN HILL UNIVERSITY
SHILLONG
MAY 1996

Dedicated

to

my Parents

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THIS IS TO CERTIFY THAT THE THESIS ENTITLED "SPECTROSCOPIC STUDY OF THE TRACE ELEMENTS ON RICE (ORYZA SATIVA LINN) IN MEGHALAYA" SUBMITTED TO THE NORTH EASTERN HILL UNIVERSITY BY MR. PAUL SANSAN DKHAR, INSTITUTE OF SELF-ORGANISING SYSTEMS AND BIOPHYSICS, NEHU, FOR THE FULFILMENT OF THE DEGREE OF DOCTOR OF PHILOSOPHY, EMBODIES THE RECORD OF THE ORIGINAL INVESTIGATION CARRIED OUT BY HIM UNDER MY SUPERVISION. HE HAS BEEN DULY REGISTERED, AND THE THESIS SUBMITTED IS WORTHY OF BEING CONSIDERED FOR THE AWARD OF PH.D DEGREE.

THIS THESIS OR ANY PART THEREOF HAS NOT BEEN SUBMITTED FOR ANY OTHER DEGREE TO ANY OTHER UNIVERSITY OR INSTITUTION.

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THIS IS TO CERTIFY THAT MR. PAUL SANSAN DKHAR HAS SATISFACTORILY COMPLETED AND OBTAINED THE FOLLOWING GRADES IN THE PRESCRIBED PRE- PH.D COURSES.

COURSES	GRADES
1. SELF-ORGANISING SYSTEM.	A
2. METHODS OF SCIENCE.	O
3. COMPUTER APPLICATION TO BIOLOGY.	A
4. CONDENSED MATTER PHYSICS.	O

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CHAPTER-I

INTRODUCTION

1.1 TRACE ELEMENTS IN DIFFERENT FIELDS OF SCIENCE

Trace elements are referred to those elements which are present at trace concentration levels of parts per millions (ppm) or parts per billions (ppb) in a variety of matrices. With the development of instrumental systems like Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), the degree of precision in measurement of these elements is enhanced upto the level of parts per trillion (ppt) without much difficulty. Though these elements often seem to be very insignificant, they do have an important role in life. The chronological order of the discovery of the essential requirements for a few trace elements is shown in APPENDIX-I [1]. The characteristic properties of a complex system and many interesting problems that arise in different spheres of science are derived or can be explained from the absence or presence of specific elements at these low levels of concentration. It is now well recognised that the presence of trace elements in various matrices has attained a fundamental importance in many fields of science, such as Agricultural science, Material science, Medical science, Environmental science,

Geological science, Forensic science, Catalyst characterisation and Petroleum products, among others. Consequently, there has been an increasing demand in the detection and assay of these elements. Hence, the study of trace elements has not only evinced the interest of researchers in different fields but also brought together the scientists of many disciplines.

To carry out the trace element analysis, an intensive activity in the investigation of methods of analysis has been evolved. The use of these methods which adopt various analytical techniques for analysis depends on (a) elements of interest (b) chemical characteristics of the sample (c) degree of precision and accuracy necessary for the final analysis and (d) sample availability. A host of techniques varying in degree of success and convenience has emerged. Spectroscopic techniques like Atomic Absorption Spectrophotometry (AAS) and Inductively Coupled Plasma-Optical emission Spectroscopy (ICP-OES) have been widely used for this purpose and have proven to be widely successful. X-Ray Fluoressence (XRF), Neutron Activation Analysis (NAA), Proton Induced X-Ray Emission (PIXE), Charge Particle Activation Analysis (CPAA) are among the other popular techniques being used.

To highlight the wide ranging importance of trace elements,

their role in different fields of science are summarised below:-

MEDICAL SCIENCE:- Analysis of trace elements in various organs under normal and pathological conditions is useful in identification of several diseases. Many therapeutic drugs in Ayurvedic system of medicine are administered to a patient as food supplement to treat various ailments. These drugs contain a large number of trace elements and among them those generally considered to be toxic are Hg, Cd, Pb, and As. Proper standardization of these drugs is essential. Inadequate nutriture of Zn, Cu and Fe lead to the alteration of immuno competence in both human and experimental animals [2]. A person suffering from diabetics is known from the concentration of trace elements like Zn, Cr, Mg and Mo. Their amounts in serum are remarkably lower compared to a normal person while Zn in urine is significantly higher [3].

ENVIRONMENTAL SCIENCE:- The importance of trace element analysis is fully recognised when the general public become concerned about the environment and aware of the serious effects of air and water pollution. Once polluted, it becomes a direct threat to the life of both human beings and other organisms [4]. There is an urgent need to initiate more comprehensive action to combat environmental pollution.

Estimating the concentrations of metals in drinking and ground water is extremely important for proper assessment of the hazards associated with their intake [5, 6]. Air pollution is becoming an increasingly serious problem and is in large part a direct consequence of modern Technology. Some metals like Zn, Fe, Mn, Pb, Cr, Cd, Cu. in the ambient air affect the human beings mainly through the respiratory tract which may lead to some genetic, physiological, behavioral and psychological disorders and even to death. It was reported that exposure to Mn in the atmosphere might be linked with several types of respiratory diseases, heart diseases and cancer [7].

GEOLOGICAL SCIENCE:- Analysis of trace elements in geochemical materials has been reported extensively. The study of trace elements, especially the immobile ones for ancient rocks, has helped the Plate-Tectonic theory which has revolutionised the basic concepts in earth science system to stand the test of time over the years. Chemical composition and trace elements (REE) analysis in the Jiangsu province, China indicated that trace elements enrichment and long term depletion of radiogenic isotopic composition of Sr and Nd were incompatible [8]. The Zawar Pb-Zn deposit of the District of Udaipur, Rajasthan was classified as

carbonate-hosted strata bound deposit. The reported analysis of this deposit for trace elements content was shown to be rich in Ag, Fe, Co, Ni but poor in Cu [9].

MATERIAL SCIENCE:- Extensive research in this field has been made especially in steel industry. The determination of trace and ultra- trace levels of Bi is a critical concern because of the element deleterious effects on certain alloys. The need for highly accurate Boron determinations continues to generate a host of new approaches as observed in the literature. Novel approaches to Boron determination in steel reflect the perceived importance of this field of study. Similarly, trace and Ultratrace determination of lead impurities is another concern in the steel industry [10].

CATALYST CHARACTERISATION:- Analytical characterisation of catalysts, heterogenous and homogenous, occupies the central position in catalysis research, both in academia and in industry. In recent years, emphasis has been stressed in attempting to gain a detailed structural picture of the catalysts themselves. Utilising this information, better understanding as to the function of the catalysts has developed which provides guidance in synthesising new and improved catalyst. It was reported that analysis of oxide preparations for the Co-Mo/alumina catalyst

showed that an apparent Mo coordination decreases as Mo loading increases. Distortion of Octahedral coordination of the Mo was inferred from the edge structure and found to parallel the measurements of Mo coordination number. The study confirmed that the distortion decreased by addition of Co [11].

FORENSIC SCIENCE:- Trace element analysis in Forensic science has become a routine analysis which helps in the investigation of crime committed by individual suspects. The analysis of several trace elements in shot gun pellets is carried out for this purpose. The determination of Sb from a shot gun pellets is consistent with an individual having just fired or handled a firearm. The distribution of Sb around a shot gun hole can be evaluated for firing distance determination. Trace elements like Mn, Ba, Pb and Sb in shot gun residue (SGR) on individual hands are determined to give a better clue [11]. It is reported that Pb concentration in hair determines the age of the person [12, 13].

FOOD ANALYSIS:- Trace elements determination in food is also important to ascertain the presence of toxic elements such as As, Hg, Pb, and Se which may be harmful for human health when consumed. The determination of metals like Pb, Cd, Zn, Cu, Fe. Cr and Ni in foodstuffs is an area of interest to some workers [14].

Trace element concentrations of elements like Fe, Ni, Cu, Zn, Sr and others were reported to have been determined in fish from the Bay of Bengal [15].

PETROLEUM PRODUCTS:- Trace elements in petroleum have received increasing attention in the recent years owing to their importance in understanding problems associated with environmental pollution, petroleum geochemistry, characterisation studies, design and operation of refineries, petroleum migration, and oil spill identification. Petroleum which contains large amounts of hydrocarbons also contains large number of trace elements such as Cu, Co, Cr, V, Ni which significantly influence the performance characteristics of the end product. Other trace elements such as Sb, As, Be, Ni, Cd, Cr, Co, Pb, Mn, Hg, Mo, Se and V are also potential causes of environmental pollution. Ni and V were determined in fuel oil and crude oil by Wood and Keynes [16] and Ni, Zn, Cu, Na, Pb, Cd, and Fe in petroleum crudes by Osibanjo et al [17].

SOIL SCIENCE:- The estimation of trace elements (Micronutrients) in the soils is essential as soil is by far the most important medium that supports plant growth and also plays a key role in crop production. Trace element analysis is extensively used as one

of the diagnostic tools in monitoring nutrient status of the soil for fertility. The study of trace element is important because if a trace element is judiciously applied, it acts as a profitable fertilizer, otherwise it acts as a pollutant. If soil is low in an essential nutrient, plants may suffer from deficiency of this nutrient. Non-availability of the trace elements in the soil may result in the manifestation of specific symptoms on the plant parts. Zinc deficiency in rice plant was first described in India and was found to be wide spread throughout Asia [18].

PLANT SCIENCE:- Plant needs a very small quantity of certain elements ranging from a few grams to a few kilogram per hectare to complete their life cycle. Trace elements occur in plant protoplasm in exceedingly small amounts and each of them plays a specific role for the growth and development of the plant. Several trace elements are involved in the production of chlorophyll, in oxidation-reduction process and in enzymes systems of plant. A deficiency of any of these trace elements cause some abnormal conditions and upsets the growth of the plant. The threshold value of trace elements vary not only with the crops of different species, but also with crops of different varieties of the same species. Lidon and Henriques [19], reported that copper toxicity

in rice plant causes the reduction of root length, which appears to be a direct result of the accumulation of excess copper in the total tissue. Some trace elements function in the enzyme systems of plant and among them, copper acts as cation-forming element which is more likely to serve as coenzymes that activate an enzyme but is not an integral part of the molecules. Hence, the right amount of the nutrient elements must be applied, and it must be uniformly distributed. Plants suffering from trace element deficiency/toxicity need not show any symptoms at all except in so far as growth is not as good as it might be, or they may only display symptoms for a short period in the growing seasons.

Besides the above fields, there are still many other areas [10, 11, 20] in which trace element analysis can be applied to achieve new findings which may finally lead to the improvement and confirmation of the previous results.

1.2 PRESENT STUDY AND ITS IMPORTANCE

The importance of trace elements in different fields of science has motivated us to undertake the present problem. This problem deals with the analysis of trace elements in rice soils and plant of Meghalaya at different growth stages. Spectroscopic techniques were used for the analysis. Samples were collected from

different rice growing areas of varying altitudes. Meghalaya is a hilly state of India. It lies between $25^{o}47'$ N and $26^{o}10'$ N latitude and $89^{o}45'$E and $92^{o}47'$ E longitude. Its main crop is rice and it is also the staple food of the people of this state. Rice is grown in different agro-climatic conditions with altitudes ranging from 80m to 1850m above mean sea level (msl). The production of rice in Meghalaya is only 1.1t/ha which is below the national average production of 1.9 t/ha [21, 22]. In Meghalaya, the area of rice cultivation is 1.04 lakh hectare while the total area of Meghalaya is approximately 22.5 lakh hectare.

There may be many factors which contribute to the low yield of the crop in this state. One of these factors which may be responsible for the growth of the plant and finally its yield is the nutrients which are simple inorganic compounds of a few elements. Among the elements, there are the major elements like N, P, K, Ca, Mg, C, H, O, S which are used in relatively large quantities and they are called Macronutrients. Other elements like Fe, Mn, Cu, Zn, Mo, and B are required by the plant in very small amounts and they are called the Minor elements [23]. The minor elements are also called the Trace-Elements or Micronutrients [24, 25]. All trace elements must be present in optimum amounts and in

forms usable by the plant for its growth and development. At high concentrations, these trace elements are toxic to the plant while at low concentrations, they cause deficiency.

Our study is to determine the status of trace elements in the soil and their concentration in the plant at different growth stages. Some of the important Physico-chemical properties of these soils such as Texture, pH, organic carbon and Cation Exchange Capacity(CEC) will also be studied. Previous workers had tried to analyse few element like Zn, Cu and Mn in the soil but not in the plant [26]. We therefore strongly felt the need of studying the presence of a wider range of trace elements both in rice soils and plants at different growth stages. This will surely help to have a better idea in taking further steps for possibly enhancing the yield. A comparison of the value obtained with the critical values available helps one to have more insight of the problem. The inter-element correlation studies both in the rice soils and plant at different growth stages is also performed.

Trace elements are involved in metabolic processes of plant enzymes which regulate many vital reactions for the growth and development of the plant [25]. It was therefore thought important to study the relationship between the activity of a few

metallo-enzymes and the concentration of the trace elements involved.

In our study, thirteen trace elements have been selected to be analysed both in rice soils and plant at different growth stages. They are B, Al, V, Cr, Mn. Fe, Co, Ni, Cu, Zn, Se, Mo and Cd. The role and effects of these elements either in plant or in man or in both are given in APPENDIX-II.

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