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Adsorption Kinetics of Heavy Metal in the catchment soils of Swarna River Basin, Udupi District, Karnataka

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Abstract - *The most fundamental human needs nowadays are for uncontaminated soil and water for fulfilling the food needs, drinking, cooking, and personal hygiene. To meet these needs the quality of both soil and water used, must pose no risk to human health. The quality of the soil for agriculture and the water in nature also impacts the condition of ecosystems that all living organisms depend on. At the same time humans use water bodies and sometimes soil used for agricultural purposes as convenient receptacles for the disposal of domestic, industrial and agricultural wastewaters which of course degrade their quality. Soil and water resource management involves the monitoring and management of soil quality as well as the water quality.*

Key Words: **Atomic Absorption Spectrometry using flame method, agricultural land, catchment soils, environmental contamination, mechanistic surface complexion models, river basin, soil management, trace elements**.

1. INTRODUCTION

For many decades soil scientists and the geologists have sought out the ways of indicating the availability of nutrients to plants, like phosphorus, potassium, magnesium, copper, zinc, cadmium etc. the nutrients that are present in the soil can be both macro and micro nutrients. Soil analysis has been used as an aid in assessing soil fertility and plant nutrient management. Soil audits have been proved to be better approaches to plant nutrient management. Achieving and maintaining appropriate levels of soil fertility is thus of paramount importance if agricultural land is to remain capable of sustaining crop production at an acceptable level. Soil sampling and analysis is the first important step in managing the nutrients required by plants. The second is the interpretation of the analytical data. The third step is the recommendations for nutrient additions, as fertilizers or manures, to optimize crop yields while

minimizing any adverse environmental impact from their application. Currently recommendations for nutrient additions to soil are based on well-tried and tested methods of soil analysis as soil audits, involve additional analyses and recommendations based on different approaches to the interpretation of analytical data are being offered to farmers. The essential feature in crop nutrition and soil fertility is that there must be sufficient amount of macro (N, P, K etc.) and micro (Cu, Zn, Cd etc.) nutrients in the soil solution. This could readily pool to meet both maximum daily demands for each nutrient in the early stages of growth and the maximum uptake to achieve optimum yield. From the studies it was seen that whether it is the adsorption-desorption studies of Macro nutrients such as phosphorous or Micro nutrients such as Cu, Zn etc. mainly batch and leaching column experiments are preferred [1]. Because these experiments have a few disadvantages which hinder the experimental results thus to carry out these experiments Stirred Flow Chambers are used that continuously renew the equilibrium solution where the adsorbate is continuously agitated and circulated through the flow chamber of the experimental setup. This further facilitates the smooth acceleration of the adsorption process as the adsorbate concentration is constantly maintained.

According to some studies it was observed that soil and groundwater contamination pose a serious threat to the health of not only humans but also that of the other living organisms in the close vicinity such as animal species, marine life and the most important plants. The mobility of heavy metals or trace elements in the environment usually occurs by the adsorption of the trace elements on the surface of the solids [2]. However, the adsorption of trace level contaminants on solid surfaces such as soil has been described by two methods that is Mechanistic Surface Complexion Models as well as by empirical isotherms [2]. The contamination of soil is a matter of great concern to the scientists and the researchers and this occurs primarily because of several reasons being: First is the liberal use of chemical fertilizers and pesticides which lead to heavy metal contamination of the soil. Second is the dumping of wastes on the land and in the soil, which is also a potent source of heavy metal accumulation in the soil due to leaching. With the growing concerns regarding the contamination of the soil quality it is essential to analyze, monitor and evaluate the heavy metal concentration in soil thus successfully optimizing the crop yields and reducing any future threat to humans and the environment.

The main objective of the study deals with the determination heavy metal concentration in catchment soils of Swarna River Basin, Swarna River being one of the important west flowing rivers of Karnataka and is a major source of water to the agricultural land in Udupi District in the state of Karnataka. The study will help in bringing certain regulations and mandates that can be useful to minimize the environmental contamination, thus reducing any future threat to the humans as well as the environment. The

concentration of Cu, Co and Ni in the soils of Swarna River has been analyzed using Atomic Absorption Spectrometry using Flame Method.

2. STUDY AREA

The study area comprises Swarna river basin which lies in between latitudes N13^{0}08′58.4″and 13^{0}42′66″and longitudes E74^{0}42′07.8″and 75^{0}04′31.4″ (Fig 1). The area can be approached by road from Udupi. The River Swarna is one of the major west flowing rivers in Dakshina Kannada District of Karnataka State taking its origin in Western Ghats and joining Arabian Sea near Kameshwara village in Udupi taluk.

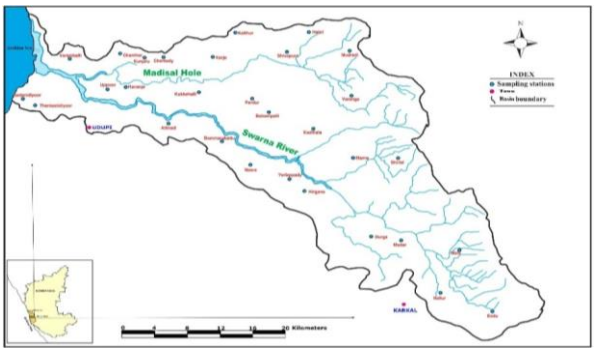

Fig – 1: Study Area, Swarna River Basin

The river flows for a length of 61.05 km up to its confluence with the Arabian Sea at Bengre. Three distinct seasons prevail in this basin, summer season from March to May, monsoon from June to November and winter from December to February. Geo-morphologically, the area consists of narrow stretch of coastal tract, upland area, hilly and valley terrain with thick dense forest. Most of the valley side is cultivation land. About 44 % of this area consists of cropland which is drained mainly by Swarna River. The drainage pattern is rectangular. Most of the rivers in this area are perennial during normal rainfall and dry during summer. Important physiographic feature in this area is lateritic capped Pedi plain.

3. METHODOLOGY

3.1 Experimental Site

The soil samples from the Swarna River basin were collected from 29 locations in three different seasons that is pre-monsoon (March-May), monsoon (June-November) and post-monsoon (December-February).

3.2 Sampling of Soil Samples

For collecting of soil samples, trench of 1-inch depth or 30cm was made in the ground to collect the soil samples. This was done in order to avoid the organic component present in the top layer. Two kilograms of surface soil samples were collected from each sampling point. The soil samples were collected in zip bags or polythene bags. These bags were labelled properly with the sample numbers and location names. Soil samples were then air dried or dried in the oven at 25-degree Celsius.

These samples were then sieved using a mesh of 2mm diameter and then taken to the laboratory for further analysis.

Fig-2: 1-inch deep trench, soil sample collection

3.3 Basic Parameter Analysis

The sieved soil samples were analyzed for basic parameters namely pH, conductivity, resistivity, total dissolved solids (TDS), salinity etc. The pre-requisite requirement was the incubation of the soil samples mixed in double distilled water, which was done on a horizontal shaker for 24 hours. After an incubation time of 24 hours the samples were allowed to settle down. The supernatant of each sample was analyzed for the above mentioned five parameters using *Hach Meter*. The readings were recorded.

3.4 Microwave Digestion

Microwave Digestion is a common technique used to digest the heavy metals in the presence of organic molecules. It is used for the quantitative determination of chemical elements in solids by spectroscopic technologies. Digestion with microwaves was carried out in closed containers made up of chemically inert materials which are transparent to microwaves.

For the same, 0.2g of the soil sample was taken in a vessel. Then the triacid solution of acids HNO_3, HCI and HF (5ml, 3ml, and 2ml respectively) was added to each container. This solution was then allowed to react for one minute prior to the sealing the vessels. The vessels were then placed in the rotor and in the microwave. The vessels then heated to 120^{0}C for about 40 minutes. The digested solutions were then transferred to 30ml bottles and stored for further analysis by atomic absorption spectroscopy using flame method.

3.5 Batch Experiments [3]

Batch experiments are the experiments that allow to execute numerous successive simulation runs. Batch experiments are used to explore or to optimize a set of model parameters.

These experiments are carried out to determine the adsorption behaviors of the different heavy metals Copper, Cobalt, Nickel, Cadmium, Chromium, Lead etc. in natural soil. Through batch experiments the effects of contact time, adsorption isotherms and temperature were investigated. The procedure of the batch tests started by weighing 2gm of the soil samples in conical flasks. Then the soil samples were mixed with the heavy metal solutions in concentrations of 30mg/L, 40mg/L and 50mg/L respectively. These mixtures were the shaken in the horizontal shaker for a period of 24 hours. After a certain period of time the soil percolated with heavy metal were passed through Whatman Filter paper of 0.41µm pore size. The filtered solutions were diluted by adding 1% nitric acid. All the steps were carried out at a temperature of 30^0C. Finally, the diluted solution concentrations were analyzed using atomic adsorption spectrometer with the flame method.

3.6 Absorption Atomic Spectroscopy – Flame Method

Atomic absorption spectroscopy is an analytical technique used to measure the concentrations of elements. It a highly sensitive technique.

The samples digested in the microwave digestor were later analyzed by atomic absorption spectroscopy using flame method. The samples were analyzed for metals Copper (Cu), Cobalt (Co) and Nickel (Ni). The digested sample gets aspirated through the tube when the nitrogen gas is provided. This tube carries the solution to the flame. As the solution reaches the flame, the flame changes into the color that is characteristic to the metal that is being analyzed.

3.7 Spatial Distribution of Copper (Cu) and Nickel (Ni) using Arc GIS [5]

The concentrations of Copper (Cu) and Nickel (Ni) in the catchment soils of Swarna River basin were analyzed for the abundance of heavy metal concentrations. The order for the same was found to be Cu >Ni [4]. It has been observed that the concentrations of Cu and Ni vary inside the river basin and at some locations exhibit higher concentrations than average value. The heavy metals with enrichment levels exceeding the normally expected distribution in soil give rise to concern over the suitability of soil for growing crops. Although, the values are much lower than threshold limit, slightly above average values at some locations may be a cause for concern in the future.

4. RESULTS

4.1 Basic Parameter Analysis

The soil samples collected from the catchment area of Swarna River Basin were subjected to basic parameter analysis in which the soil samples were tested for pH, Conductivity, Resistivity, Salinity and Total Dissolved Solids. For the same the results obtained for the samples of all the three seasons that is Pre-Monsoon, Monsoon as well as Post-Monsoon is shown in the tables 1, 2 and 3 respectively.

From the study of basic parameters, we can see that the soil in both the monsoon and post-monsoon seasons is acidic in nature with pH ranging from 2 to 4. The reason behind the soil being acidic is the excessive rainfall in the coastal state of Karnataka. Because of excessive rainfall the calcium ions (Ca^{2+}) magnesium ions (Mg^{2+}) present in the soil naturally or incorporated in the soil through the chemical fertilizers get leached out rendering the soil acidic in nature. The pH in the pre-monsoon season soil is also found to be acidic to a certain extent with pH ranging from 3 to 4. The conductivity (measured in micro-siemens per cms) and the total dissolved solids (measured in mg/L) are elated as –

CONDUCTIVITY = 4 × TOTAL DISSOLVED SOLIDS

Thus, the conductivity and the total dissolved solids stand correctly in the relation in all the three seasons. The resistivity and salinity were also measured using Hach Meter. Resistivity was measured in kilo-ohms per cms and salinity is measured in percent (%). Both the parameters were found to be within the permissible limits. The maximum permissible limit for salinity in soil is 0.05%.

4.2 Batch Experiments [3]

The soil samples that were collected had to be tested for their adsorption behaviors to various heavy metals such as Copper, Nickel and Cobalt taking three different soil sample location namely Eedu, Perdur and Thenkanidiyoor. One location each from the Ghat section, Hinterland and the Coastal section were taken as shown in the map in Fig 1.

Through these studies the contact time, temperature etc. could be easily identified for each soil sample. The soil samples that were taken were mixed with the heavy metal solution is the concentrations of 30mg/L, 40mg/L and 50mg/L respectively. The samples were allowed an incubation time of 24 hours on the horizontal shaker. Later the samples were analyzed for the heavy metal concentration that is being adsorbed after 24 hours using atomic adsorption spectrometer using flame method. The batch experiment results can be deduced from the charts 1, 2 and 3 respectively.

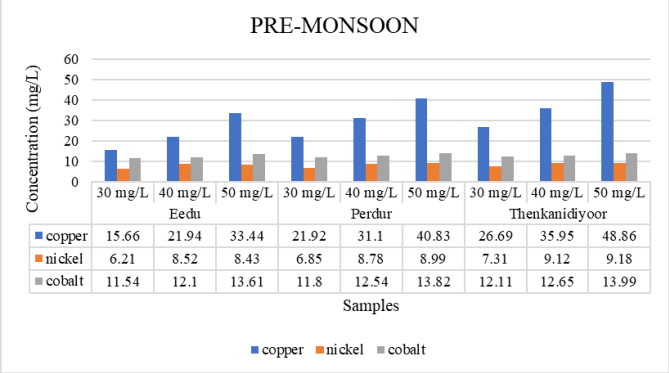

Chart – 1: Adsorption values of heavy metals in the soil in Pre-monsoon season

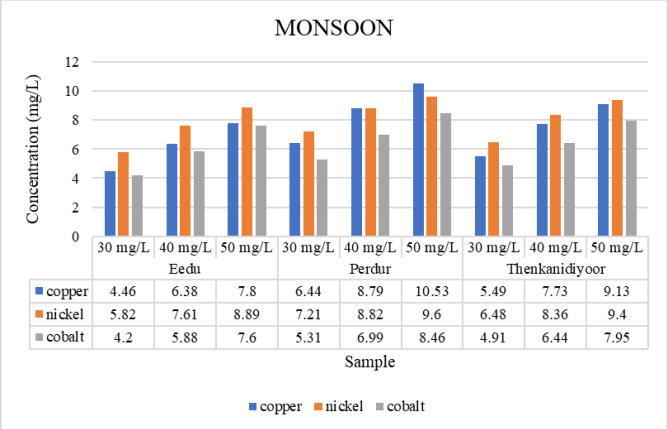

Chart – 2: Adsorption values of heavy metals in the soil in Monsoon season

The absorption that has taken place in the soil samples of monsoon season clearly shows that the absorption has decreased to a certain extent as compared to the absorption that took place in the soil samples of pre-monsoon season. This is because of the fact that during monsoon season, the vacant spaces within the soil become occupied by the rain water thus, leaving only a few vacant sites to absorb the heavy metal solution to which the soil is subjected to.

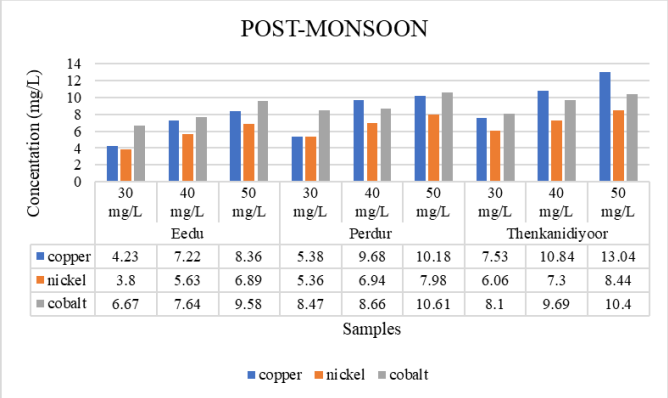

Chart – 3: Adsorption values of heavy metals in the soil in Post-monsoon season

Similarly, the absorption that has taken place in the soil samples of post-monsoon season shows very little absorption as compared to that of pre-monsoon season, reason being the same that after monsoon rains the vacant spaces within the soil are left occupied by the rain water and hence leave only a few vacant sites to absorb the heavy metal solution.

4.3 Spatial Distribution of Copper (Cu) and Nickel (Ni) using Arc GIS [5]

4.3.1 Spatial Distribution of Copper (Cu)

The copper is the most abundant heavy metal found in the study area. The copper concentration in the area varies from 0.04 to 0.30 mg/L (average = 0.16 mg/L). The spatial distribution of Cu in the Swarna river basin is displayed in Fig – 3

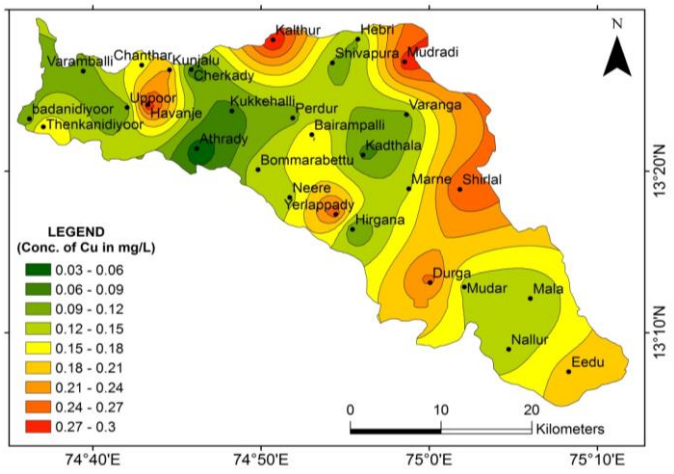

Fig – 3: Spatial Distribution of Copper (Cu)

Copper is associated with organic matter, oxides of iron and manganese, silicate clays, and few other minerals. Copper is specifically fixed or adsorbed in soils and is one of the least mobile heavy metals at any pH [7]. Copper content in the soils largely depends upon the nature of the parent rock, weathering of biotite, orthoclase and plagioclase feldspars and soil characteristics [7]. From the map, it is evident that the soils of Eedu and Thenkanidiyoor have moderate amounts of Copper in it ranging from 0.15mg/L-0.21mg/L whereas Perdur has low amounts of Copper ranging from 0.06mg/L-0.09mg/L.

4.3.2 Spatial Distribution of Nickel (Ni)

The Nickel concentration in the area varies from 0-0.68mg/L (average = 0.07 mg/L). The spatial distribution of Ni in the Swarna river basin is displayed in Fig – 4.

The concentration of Nickel is well within the threshold value.

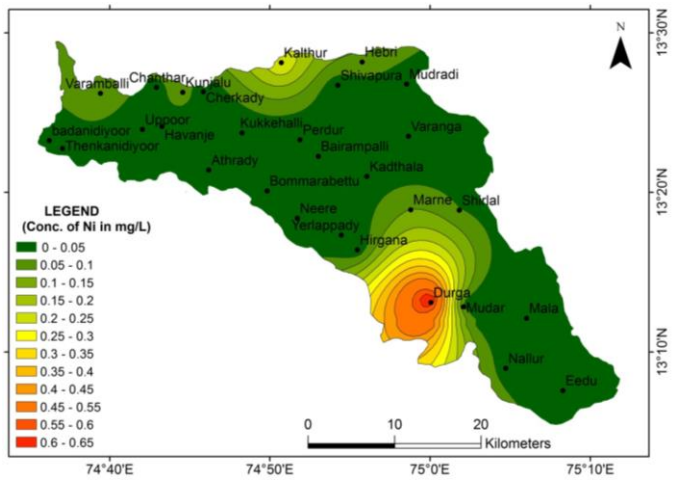

Fig – 4: Spatial Distribution of Nickel (Ni)

From the map, it is clear that the soils of Eedu, Perdur and Thenkanidiyoor all have low amounts of Nickel ranging from 0mg/L-0.05mg/L which is way within the standards.

5. CONCLUSION

The investigation on agricultural soils samples of the catchment area of Swarna River basin was carried out to assess the on heavy metal concentrations (Cu, Ni, Co) and their contamination level in natural as well as agricultural soils. The study provides baseline data on the existing levels of heavy metal concentration in the agricultural soils of the area. The abundance order of heavy metal concentrations is Cu > Co> Ni. The concentrations of Cu, Co and Ni vary inside the river basin and at some locations exhibit higher concentrations.

As from the Spatial Distribution maps, we concluded that the concentration for Copper is usually seen in moderate or low levels with the concentration ranging from 0.15-0.21 mg/L and 0.06mg/L-0.09mg/L respectively. Similarly, in case of Nickel the concentration is below the toxic level in more than 90% of the Swarna River Basin. For Nickel most of the Swarna River Basin has less accumulation of Nickel in the soil that is of the range 0-0.05 mg/L.

Overall the heavy metal accumulation in the soils of Swarna River Basin are less or within the threshold limit thus posing no threat to humans as well as to the environment.

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