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Study of Heavy Metal Accumulation in Wastewater, Soil and Plants

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Abstract:
Irrigation practices using the wastewater causes the severe soil contamination that results contaminated product to the consumer. This study is about the impacts of irrigation practices using wastewater on contamination of metals and vegetables like Radish, Cauliflower, Brinjal and Red Amaranth that is widely cultivated and consumed in Kolkata city. The water, vegetable and soil sample were collected from East Kolkata Wetland from two sites. The soil, water and vegetable were collected from 12,500 hectares of agricultural area which was analysed for various tests of chemical and microbiological. As well as metals accumulation in soil, water and metals accumulation at various positions of plants, leaves and vegetables available in our laboratory including metals like iron, zinc, coper, nickel, chromium, cadmium and arsenic. The data of microbiological and chemical properties of waters samples contamination shows pH, TDS, TSS, BOD, COD, TC, FC, nitrate, nitrite and sulphate all are within the permissible limits of Indian Standards. The different soil physical properties were also analysed such as pH, texture, total nitrogen, available Phosphorus and total organic carbon. Sequence of metals contained in soil, various parts of vegetables and wastewater are as < Cd < Cr < Ni < Pb < Cu < Zn < Fe. This study concludes that usage of wastewater for irrigation increases the contamination of metals Fe, Zn, Cu, Pb, Ni, Cr, Cd and As in the edible portion of all the four plants causes risk to the health potential for long term practices of agriculture. The study that adherence to standard for heavy metals contamination of soil and irrigation water dose not sure safe food. This study concludes that heavy metal contamination of water and soil are not advisable for safety of food.

Keywords: *Agriculture, Wastewater, Contamination, Concentration*

I. INTRODUCTION

Irrigation practices in ¾ of the cities of Asia, Africa and Latin America were done with the wastewater. Sewage coming from highly developed areas like Delhi, Mumbai, Kolkata etc [1, 2]. are using for agricultural purpose without treating. It is an economical and effective process of irrigation. After that water allows to enter streams. Most of the developed places are continuously allowing the waste substance into the natural streams which causes threat to them [3]. Effluents from the industrial areas are causing trouble to purifying mechanisms. Wastewater irrigation is known to be economical, but it is hazardous for the human in nature [4,5]. Effluents released from industrial practices, thermal power plants, pesticides and municipal solid waste are major creators of toxic heavy metals. These metals are toxic and con not degraded biologically it retains in soil [6,7]. If we do agriculture in these areas of soil those heavy metals sustain in plant tissues and tissues of vegetables [8].

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Water containing these heavy metals are polluted and deposited on the fish bodies etc. Heavy metal like lead (Pb), chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn) can cause deleterious health effects in human and other living organisms. this study investigated on the concentrations of lead(Pb), zinc(Zn), chromium(Cr), iron(Fe), cadmium (Cd), copper (Cu), arsenic (As) and nickel (Ni) in irrigation water, soil and vegetables grown in the agricultural land of this area having long term uses of the treated and untreated wastewater for irrigation [9,10]. We considered the area of East Kolkata Wetland (88°20'E to 88°35'E and 20°25'N to 20° 35'N) are a complex of natural and human-made wetland, India. These area people depend mostly on the fish farm and agriculture [11]. The people in this area use the sewage water coming from the Kolkata metropolitan city for agriculture and pisciculture. Some of the vegetables grown in this area are Chinese onion, carrot, radish, Eggplant, red amaranth etc. Available water on the earth for drinking is in less quantity [12]. Only small amount of freshwater is available on the surface. Particularly the fresh potable water is available in very less quantity. These are classifications of wastewater, the water, which is discharged from homes, offices, hotels, institution etc., comprises sewage i.e., human waste and grey water from bathrooms, kitchens, laundries etc., is said to be domestic wastewater [13, 14]. The liquid discharge from manufacturing units, for example soft drink companies, sugar processing; metal processing; finishing, paper mill, distillery, tannery, chemical industry etc., are considered as industrial wastewater [15,16].

II. STUDY AREA

The study area located in East Kolkata Wetland. It contains huge number of water bodies situated in districts of north, south and west Bengal. It consists of an area of 12,500 hectares. It is nearer to the eastern Kolkata and Salt Lake township. Study area having the water bodies of 5852.12 hectares, Agricultural land 4959.86 hectares, Garbage disposal site 602.78-hectare, Urban settlement area 91.53 ha, rural area 1234.99 hectare. Boro and Aman cultivated during monsoon and winter respectively form the major component accounting for 38 % and 45% of the total produce. The third crop Aus, cultivated during the summer contributes 6% to the production. Apart from paddy, mustard and sesame are grown in a limited extent within the region.

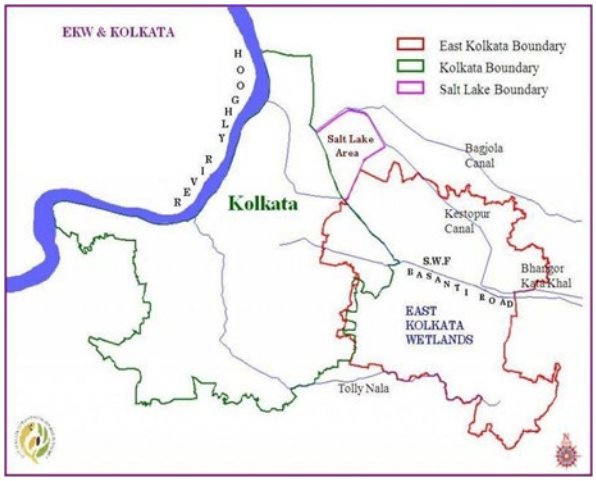

Fig 1: Study area map

A. Topography and Geography:

Study area is situated at 880 20' E - 880 35' E and 200 25' N -200 35' N. It consists of an area of 12,500 hectares. 76 percent of the fish farm are less than 13 ha in area and are located within the southern and eastern portion of the wetland. There is an Agricultural land of 4959.86 hectares and Garbage disposal site of 602.78 hectare. These farms operate with the sewage water made available from the Kolkata Metropolitan area and are the characteristic feature of the wetland. There are 109 villages located within 37 mouzas within East Kolkata Wetland which accounts for 11 % of the land use. The settlements are mostly located within the eastern and southern portion of the wetland and are as disjoint unit of settlement within the landscape.

B. Climate and Rainfall:

It is having the rainfall of 200 cm. It is having max. Temperature of 39 °C and min. temperature of 10 °C. Its average temperature is 30 °C and it changes around 5 °C for midday and mid night. Variation of

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water table in summer varies in between 1m and 2 m. groundwater is concerned, there is hardly any good aquifer up to a depth of 400 feet. Soil is mixed clay and alluvial type.

III. DATA REQUIREMENTS

Wastewater was collected from the dry weather flow (DWF). It was collected from the mid depth of flow with the help of bucket and rope and then measured 250 ml with the help of measuring cylinder and poured it in 2 liter plastic container. This procedure is repeated eight times to fill the 2 liter plastic container. These composite samples of each location are used for quality testing. Soil samples were collected from the vegetables field at 15 cm deep from the top most layer of soil. Use a soil auger to collect to collect a 2.5 cm diameter soil core from sample area. These soil samples were kept in clean plastic bag and Mixed thoroughly by shaking for 2 minutes. Selected vegetable plants samples were uprooted from the roots and washed with irrigation water. Collected samples are kept in polyethylene bags and placed in cool containers. These samples are cleaned with distilled water for further use.

IV. METHODOLOGY

Various tests are done on the collected samples of wastewater and plants. Tests conducted on wastewater are pH, total dissolved solids, Total suspended solids, Biological oxygen demand, Chemical oxygen Demand, micro biological water Quality parameter.

1. pH- It is measured with pH metre. It consists of glass electrode, reference electrode, usually a calomel electrode connected by KCl Bridge to the pH sensitive glass electrode and an indicating unit which indicates the pH corresponding to the electromotive force. pH meter is calibrated before measurement. It is recommended to use hydrated silica gel for glass electrode and electrode should be inside of the water or in a buffer. For accuracy of pH buffer should be in standard temperature which is used for pH meter standardization.

2. Total Dissolved Solids- Pure water is often called as universal solvent. TDS refers dissolved metals, minerals, cations and anions in water. TDS consisting in organic salts are bi carbonates, chlorides, sulphates of Ca, Mg, K and Na. Origin of these TDS are urban sewage, industry wastewater, chemicals from treatment plants and sewage. Cation and anion concentrations combined called as TDS concentration. TDS is an indicator for the quality of water. TDS meter used for calculation of TDS.

Fig 2: TDS meter

3. Total Suspended Solids- These are the solids which can retain on filter. The estimation of suspended solids depends, upon the nature of filter paper and the particle size of solids. Sample is allowed to pass through the standard glass fiber paper, the residue retained on the paper is allowed to dry 103 to 105 degree centigrade to a constant weight. Equation for TSS is

$$\text{TSS} = \frac{W_2 - W_1}{\text{volume of sample filtered}} \times 1000 \text{ mg/L}$$

Here, W_1 = weight of filter paper before passing Sample in gram.

W_2 = weight of filter paper after passing sample In gram.

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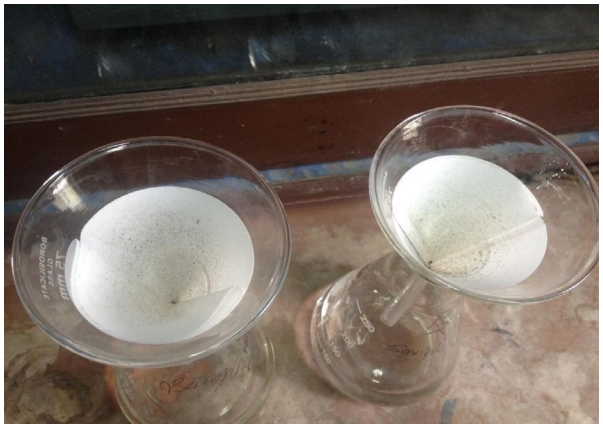

Fig 3: Filtration of Waste water

4. Biological Oxygen Demand- To prepare dilution water for each sample take 1ml phosphate buffer solution, 1ml magnesium sulphate solution, 1ml calcium chloride and 1ml ferric chloride solution was taken in 1000ml of Double Distilled water (D/D) and kept in aeration for 12 hours. Taken sample and dilution water in a 1000ml conical flask and is poured in 3 BOD bottles. 2 BOD bottles were kept for 3 days in BOD incubator at 27 ºC. The rest one was titrated for 0-day DO. Added 2ml manganese sulfate solution and 2ml alkali azide reagent in that BOD bottle and sacked 15 times. The bottles were allowed to form the flock. Then 2ml conc. sulfuric acid is added and it is shacked to dissolve the flock and mustard Color was appeared. Then 203ml is taken in flask and is titrated with sodium thiosulfate solution, when mustered color solution becomes litter lighter add 2ml starch solution to form deep blue color. This was titrated with sodium thiosulfate solution until it becomes colorless. The same procedure was repeated for rest 2 sample after 3 days.

5. Chemical Oxygen Demand- The organic matter present in sample gets oxidized completely by K2Cr2O7, in the presence of H2SO4, AgSO4 and HgSO4 to produce CO2 and water H2O.

$$C_nH_aO_b + cC_{r2}O_{7^-} + 8eH^+ \rightarrow nCO_2 + \frac{a+8e}{2}H_2O + 2cCr^{+3}$$

Here $$c = \frac{2n}{3} + \frac{a}{6} - \frac{b}{3}$$

COD test was carried out in the laboratory on the samples collected from East the study area. 25ml of 0.25N potassium dichromate, 1gm of mercury sulfate, 25ml of D/D, 5ml of conc. sulphuric acid reagent and 25ml sample was mixed in a250ml conical flask with standard joints is taken for each sample and 45 ml of sulphuric acid reagent was added in the flask.

10 pieces of glass beads is added in the flask and conical flask is heated and refluxed in COD digester for 2 hours, at 60ºC for first one hour and at 80ºC for next one hour. To perform standardization, take 10ml of 0.25N potassium dichromate, 10ml of D/D and 20 ml of conc. Sulphur acid reagent and allow it to cool. After cooling add 2 drop of ferrous indicator solution and titrate with 0.25N standard Ferrous Ammonium Sulphate (FAS) solution. After completion of digestion allow the conical flask to cool for 30 minutes and the D/D was added to make the acid solution 250ml and again allowed to cool in room temperature. After cooling at room temperature the solution was taken in a 500ml conical flask and 2 drop of ferrous indicator solution is added. Then it was titrated with FAS solution until the colour changes from deep green to reddish and the Titrated values are noted down.

6. Microbiological water quality parameter- For performing the test Total Coliform we need are 15 test tubes for one sample, 10ml Mac-Conkey Broth (MCB) in 5 test tubes, 10ml MCB + 9ml D/D in 5 test tubes, 10ml MCB + 9.9ml D/D in 5 test tubes. After that 15 Durham's tubes filled with MCB are placed in each tube and plugged tightly with non-absorbent cotton. All test tubes are placed in 2000ml beaker and autoclaved at 15lbs/sq inch for 15 minutes. After that test tubes are cooled at room temperature and 10ml sample is added in 10ml MCB first 5 test tubes. 1ml of sample is added in 10ml MCB + 9ml D/D in 5 test tubes. 0.1ml of sample is added in 10ml MCB + 9.9ml D/D in 5 test tubes.

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Then all the test tubes are placed to incubator at 37ºC ± 2ºC for 48 hours, then positive sample in test tubes show color change in the broth and gas bubble is accumulated in the inverted Durham's tubes.

All positive test tubes are kept for faucal coliform test, In that one number of test tubes has taken for one number of positive test tubes in total coliform test. 4ml BGLB broth in each tube and one inverted dirham's tubes was inserted in each of them. Then all test tubes are plugged and autoclaved in similar way, after autoclaving the test tubes are cooled at room temperature. Inoculation one loop full of sample from each of the positive test tubes in BGLB broth. Then plugged and placed in water bath for 48 hours at 45C temperature. The number of positive test tubes, where formation of gases takes place has been noted. And the result is noted down from the MPN index.

Fig 4. Test tubes containing Mac Conkey Broth for TC

Fig 5. Test tubes containing BGLB broth for FC test.

7. Metal analysis in soil- The soil samples collected from two different plots of farm on the East Kolkata Wetland are mixed and it was dried in the hot air oven at 40 degree centigrade for 24 hours. Using an analytical balance, weight out 10 grams of this oven dried soil sample and is placed into the furnace for ashing at 200° C and also the fumes generated are observed. The sample is left for ashing in the furnace until the color of evolving fumes changed from brown to white. After finding the white fumes being generated, the sample is withdrawn from the furnace and allowed to cool and added concentrated hydrochloric acid and promic acid and the slurry was mixed well with a stirring rod. This slurry of sample is transferred to digesting tubes and placed into the digester for digesting. After that tubes are allowed to cool. The cooled sample is filtered using a glass fibre filter and the filtrated sample is collected. This filtered sample is transferred into 100 ml volumetric flask and added double distilled water in sample to make volume up to 100 ml. To analyze the sample with an Atomic Absorption Spectrometer, the computer and spectrometer are turned on, and the parameters on the instrument are set according to the metal. A hollow – cathode lamp of metals Zn, Pb, Ni and Cr are used for detection of these metal in soil sample. Each sample was atomized and the reading was scaled.

Fig 6. Digester tubes in block digester.

8. Metal analysis of vegetables- The vegetables which are brought from field of East Kolkata Wetland are Eggplant, Radish, Cauliflower and red amaranth. These vegetables are nicely washed with the doubled distilled water.

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The root leaves and fruits are separated and kept in different blows. These samples are dried in the hot air oven at 40 degree centigrade for 24 hours and dried parts of vegetables are grinded. Using an analytical balance, weight out 1 gram of root sample, 1gm leaves sample and 1gm fruits sample make powder. Now powdered samples of roots, leaves and fruits are taken in the digester tubes and Added concentrated hydrochloric acid and promic acid is mixed well with a stirring rod. Placed the digester tubes containing different samples of root, leaves and fruits for digesting of sample. After removing the tubes from digester tubes allowed them to cool. The cooled sample is filtered using a glass fiber filter and the filtrated sample is collected. This filtered sample is transferred into 100 ml volumetric flask and added double distilled water in sample to make volume up to 100 ml. To analyze the sample with an Atomic Absorption Spectrometer, the computer and spectrometer is turned on, and the parameters on the instrument are set according to the metal. A hollow – cathode lamp of metals Zn, Pb, Ni and Cr are used for detection of these metal in these different parts of vegetables sample.

Fig 7. Vegetables Leaves sample.

V. RESULTS AND DISCUSSION

Wastewater properties:

The parameter pH is well within the permissible limits.

Sl. No.	Metals	Units	Concentration
1.	Cadmium (Cd)	mg/L	0.006
2.	Chromium (Cr)	mg/L	0.089
3.	Lead (Pb)	mg/L	0.074
4.	Zinc (Zn)	mg/L	0.134
5.	Copper (Cu)	mg/L	1.56
6.	Nickel (Ni)	mg/L	0.68
7.	Arsenic (As)	mg/L	0.004
8.	Iron (Fe)	mg/L	3.86

Table-1. Different parameters of wastewater

Microbial Biological analysis of the effluent the values of TC and FC of the site do not show any kind of trend. The value of FC does not conform to the guideline for unrestricted irrigation for agriculture use and there are substantial health risks, as the values of FC are high in sewage of DWF channel.

Table-2. Metals concentration in wastewater of DWF channel in EKW

Sl. No	Parameter	Units	Values
1	pH	-	7.95
2	TDS	mg/L	446
3	TC	-	80/100ml
4	FC	-	50/100ml
5	COD	mg/L	74.24
6	BOD	mg/L	2
7	TSS	mg/L	439
8	NITRITE	mg/L	0.037
9	NITRIATE	mg/L	0.3
10	SULPHATE	mg/L	117

The value of nitrate, nitrite and sulphate are also random but it can be said that the values of those

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parameters are well within the permissible limits. The ranges of BOD and COD found on those sites are within the permissible limits. Table 1 Different parameters of wastewater where cauliflower, radish, eggplant and red amaranth were collected during mid period of the crop.

Soil Properties:

The mean highest metals concentration in soil sample were recorded as 2870 mg/kg Fe followed by 784.8 mg/kg Cd > 640.1 Zn > 282.7 mg/kg Cr> 200.4 mg/kg Cu > 160.9 mg/kg Cr > 32.0 mg/kg Ni >12.54 mg/kg As.

Table-3. Physical Parameters of soil

Sl. No	Parameters	Units	Values
1	pH (1:5 Ratio)	-	7.7
2	Texture	-	Sandy Loam
a)	Sand	%	45.8
b)	Silt	%	47.9
c)	Clay	%	6.3
3	Total Nitrogen	mg/kg	1652.6
4	Available Phosphorus	mg/kg	88.1
5	Total Organic Carbon	%	2.0

The mean concentration of Cu, Ni and as in soil of the study area were below the. But the concentration of other elements such as Cd, Pb, Zn, Fe and Cr were above the recommended limits. Metal concentration in soil during the mid-period of crop is shown in table 4.4. The permissible level of soil is according to WHO permissible limits for heavy metals in soil in mg/kg.

Table-4. Metal concentration during mid period of crop

Sl. No.	Metals	Units	Concentration	Maximum Permissible Levels
1.	Cadmium	mg/kg	784.8	0.01
2.	Chromium	mg/kg	160.9	0.05
3.	Lead	mg/kg	282.7	0.1
4.	Zinc	mg/kg	640.1	15.0
5.	Copper	mg/kg	200.4	1.5
6.	Nickel	mg/kg	32.0	5
7.	Arsenic	mg/kg	12.54	0.5
8.	Iron	mg/kg	2870	0.3

Heavy Metals Concentration in Roots of Vegetables:

Accumulation of heavy metals in roots of plants irrigated with the wastewater, the concentrations of heavy metals for eggplant is as followed 1282.3mg/kg Fe > 249.2mg/kg Zn > 85.0mg/kg Cu > 47.8mg/kg Pb >12.5mg/kg Ni > 8.9 mg/kg Cr > 7.67mg/kg As > 1.6mg/kg Cd. For red amaranth the heavy metal concentration is as followed 577.9mg/kg Fe > 115.9mg/kg Zn > 41.6 mg/kg C > 35.1mg/kg Pb > 24.1mg/kg Cr > 21.7mg/kg Ni > 2.9mg/kg Cd and As concentration less than 1 mg/kg. And for cauliflower the concentration were 2232.3 mg/kg Fe > 179.5mg/kg Zn > 116.3mg/kg Cu > 52.1 mg/kg Pb >24.6mg/kg Cr > 14.2mg/kg Ni > 1.9 mg/kg Cd and As concentration less than 1 mg/kg.

Table-5. Metal concentration in roots of plants in mg/kg

Sl. No.	Metals	Roots of Eggplant	Roots of Red Amarah	Roots of Cauli flower
1.	Cadmium	1.6	2.9	1.9
2.	Chromium	8.9	24.1	24.6
3.	Lead	47.8	35.1	52.1
4.	Zinc	249.2	115.9	179.5

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5.	Copper	85.0	41.6	116.3
6.	Nickel	12.5	21.7	14.2
7.	Arsenic	7.67	<1	<1
8.	Iron	1282.3	577.9	2232.3

VI. CONCLUSIONS

This study concludes that the information on metals accumulation in the edible parts as well as non - edible parts of Eggplant, Cauliflower, Radish and red amaranth growing in the soil receiving sewage effluent of the Kolkata City. It is recommended to prepare a baseline using this data as a protocol for the future usage of the city. It is concluded that high concentration of these elements Fe, Zn, Cu, Pb, and Ni are found in the edible parts of the plants and grow alternate crops or vegetables. Overall analysis of the data revealed that the accumulation of toxic metals determined were in sequence Fe > Zn > Cu > Pb > Ni > Cr > Cd > As. For water, soil, roots of different plants, leaves of different plants and vegetables of different plants the heavy metals concentration in wastewater effluent is in the sequence Fe > Cu > Pb > Ni > Zn > Cr > Cd > As. This water sample irrigates the vegetable plants grown in the agricultural land of the study area the metals accumulated in the soil are in sequence of Fe > Cd > Zn > Pb > Cu > Cr > Ni > As. In which the concentration of Cr, Fe, Zn, Cu, Pb, Ni, Cd and as are above the permissible limits according to the WHO guideline. The vegetables grown on this soil absorb the heavy metals. The heavy metals found on eggplant, radish, cauliflower and red amaranth plants in its roots, vegetables and leaves shows that Fe , Zn , Cu , Pb , Ni , Cr , Cd , As were beyond the permissible limits to such an extent which is not at all fit for consumption. The concentration of Cd and as were within the limits that they have less effect on health. The vegetables plants which was grown in these soil have the following concentration Fe, Zn, Cu, Pb, Ni, Cr, Cd and As which have health impact on human against dietary intake of leafy plants i.e. red amaranth, root vegetables i.e. Radish and other vegetables cauliflower and eggplant.

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