HEAVY METAL CONTAMINATION IN IRRIGATION WATER AND ITS EFFECTS ON PLANTS

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Abstract - *Reclaimed water is an important resource for irrigation, and exploration in making full use of it is an important way to alleviate water shortage. This paper analyzes the effects of irrigation with reclaimed water through field trials on the content and distribution of heavy metals in both okra and the soil. By exploring the effects of reclaimed water after secondary treatment on the content and distribution characteristics of heavy metals in okra and the heavy metal balance in the soil-crop system under different conditions, the study shows that there are no significant differences in the heavy metal content when the quantity of reclaimed water for irrigation varies. Reclaimed water for short-term irrigation does not cause pollution to either the soil environment or the crops. Nor will it cause the accumulation of heavy metals, and the index for the heavy metal content is far below the critical value of the national standard, which indicates that the vegetables irrigated with reclaimed water during their growth turn out to be free of pollutants. The heavy metals brought into the soil by reclaimed water are less than that taken away by the crops. The input and output quantities have only small effects on the heavy metal balance in the soil. This paper provides a reference for the evaluation and safety control of irrigation with reclaimed water. Scattered literature is harnessed to critically review the possible sources, chemistry, potential biohazards and best available remedial strategies for a number of heavy metals (lead, chromium, arsenic, zinc, cadmium, copper, mercury and nickel) commonly found in contaminated soils. The principles, advantages and disadvantages of immobilization, soil washing and phytoremediation techniques which are frequently listed among the best demonstrated available technologies for cleaning up heavy metal contaminated sites are presented. Remediation of heavy metal contaminated soils is necessary to reduce the associated risks, make the land resource available for agricultural production, enhance food security and scale down land tenure problems arising from changes in the land use pattern.*

***Key Words*: Heavy Metals, Contamination, Irrigation Water, Effects on Plants, Remedies**

1. INTRODUCTION

Pollution of heavy metals directly and indirectly affects the human health. These substances adversely affect the productivity of soils, plants, animals and the entire environment if exceed certain limits [1] Since quantity of good quality of water for agriculture is decreasing so, peoples are using raw city effluent for the production of different crops especially for vegetables. This raw city effluent contains lot of carcinogenic constituents like heavy metals, organic pollutants, salts and pathogens. Even in low concentration in soil-water system heavy metals persist for longer time in soil from where these enter into food chain through plant uptake. Sources of heavy metals pollution in environment are mainly derived from anthropogenic in nature. Which include vehicle exhaust, tire wearing, weathering street surfaces, power plants, coal combustion, metallurgical industry, auto repair shop, chemicals plant, domestic emission, weathering of building and pavement surface and atmospheric deposits.

However, the anthropogenic sources of heavy metals in agricultural soils include mining, smelting, waste disposal, urban effluent, vehicle exhausts, sewage sludge, pesticides and fertilizers application. Among all the heavy metals cadmium (Cd) is a highly toxic for both the plants and animals as well as for human beings. Cadmium enters into soil-plant environment mainly through anthropogenic activities. Compounds of Cd are more soluble than other heavy metals rendering it more available for plant absorption where these could accumulate in edible plant parts.

1.1 Scope of The Project

As one of the consequences of heavy metal pollution in soil, water and air, plants are contaminated by heavy metals in some parts of China. To understand the effects of heavy metals upon plants and the resistance mechanisms, would make it possible to use plants for cleaning and remediating heavy metal-polluted sites.

2. MATERIALS AND METHODS

2.1 Study Area

This study includes sampling of soil, plant and water. For the collection of soil, plant and water samples Mannuthi Town of Thrissur city was selected. The samples were taken in the month of June 2017. Samples were collected from every grid 4-Km apart for soil, plant and water. Samples from each grid was collected and prepared according to the prescribed method and then analyzed on Atomic Absorption Spectrophotometer (Model Thermo electron S-Series) for the heavy metals determination. Detailed methods for collection, preparation and analysis of soil, plant and water samples are given below.

2.2 Collection and Preparation of Soil Samples

Soil samples were collected from different urban and peri urban area of Mannuthi Town, after every 4-Km from 0-15 cm and 15-30 cm. soil samples were taken from 3 points at each grid and mixed thoroughly in a plastic bucket. Samples are taken to laboratory air dried, ground with wooden roller and sieved through 2 mm stainless steel sieve.

2.3 Collection and Preparation of Plant Samples

Plant samples were also collected from the above-mentioned places as the soil samples taken. Two Plant samples of vegetables, crops, trees and ornamental plants depending upon the availability of vegetation were taken. Samples were taken to laboratory washed with tap water, diluted HCl water and distilled water to remove the external contamination. Samples were air dried and then placed in Oven at 65°C for drying of samples. After oven drying samples were ground and stored in plastic zipper.

2.4 Collection and Preparation of Water Samples

Water samples were collected from the above-mentioned sites. For water samples groundwater (tube well, hand pump and motor pumps), surface water (canal) and waste water (sewerage, industries effluent) were taken depending upon the availability in the area but ground water was taken from each site.

3. METHODOLOGY

3.1 Ph

The pH value plays an important role in the complexation of GBHA with metals which form chelate complexes. The influence of pH on the solid phase extraction of trace metal ions was studied in the range of 2-12 using acetic acid (2M)/ sodium acetate (2M) and ammonia (1M)/ Nitric acid (1M) for pH adjustment respectively.

Each pH value was tested more than three times. The results have shown the most of the studied metals are largely formed/retained at pH=8. Quantitative recoveries were obtained in the pH of (8) for Pb and 12 for Cd.

Fig-1: pH determination using turbidity meter

3.2 Electrical Conductivity (EC)

These free ions in the water conduct electricity, so the water electrical conductivity depends on the concentration of ions. Salinity and total dissolved solids (TDS) are used to calculate the EC of water, which helps to indicate the water's purity. The purer the water the lower the conductivity.

EC or Electrical Conductivity of water is its ability to conduct an electric current. Salts or other chemicals that dissolve in water can break down into positively and negatively charged ions. These free ions in the water conduct electricity, so the water electrical conductivity depends on the concentration of ions. Salinity and total dissolved solids (TDS) are used to calculate the EC of water, which helps to indicate the water's purity. The purer the water the lower the conductivity. To give a real-life example, distilled water is almost an insulator, but saltwater is a very efficient electrical conductor.

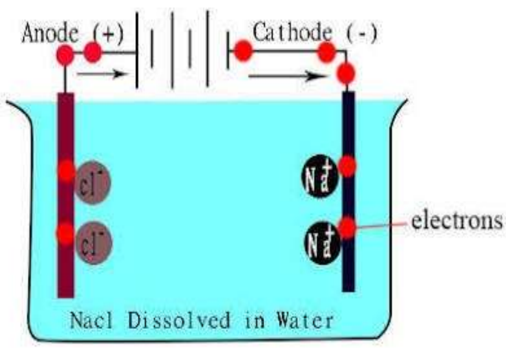

Fig-2: Photographic view of EC

3.3 Effect of Sample Volume

In order to explore the possibility of enriching low concentration of the metal ions from large volumes, the influences of the sample volume on the recoveries of the investigated metal ions were examined and maximum applicable sample volume was determined.

The recoveries of the metal ions from different volumes of aqueous model solution containing the same amounts of the metal ions were tested in the range of 50-800ml. The recoveries were found to be stable up to 500 ml of sample volume for Pb and 700ml for Cd. The result presents in Table1.

Table 1- Effect of the sample volume on heavy metals (%) of the investigated metal ions (n=5)

Volume of sample (ml)	Pb	Cd
150	88.5	79.4
200	89.5	91
300	75.0	97.0
400	71.8	95.2
500	67.0	98.4
600	65.7	83.5

3.4 Effect of Ligand Concentration

The influence of the GBHA concentration on the recovery of the metals was investigated in the range of 10-200 µl of 0.01mol l-1 GBHA solution using the aforementioned model solution. The quantitative values were obtained after 25 µl of GBHA. After this point the recoveries were quantitative in all working range of GBHA.

3.5 Determination of COD

- The sulphuric acid (0.2ml) was added in reflux flask.
- The sample of (20ml) was taken in the flask.
- The potassium dichromate (10ml) silver sulphate, sulphuric acid, H_2SO_4, $AgSO_4$ (30ml) was added to it.
- The flask was connected to condenser and reflux for 2 hours.
- The sample was made up with 150ml distilled water.
- 3 drops of ferroin indicator added to it.
- It was titrated against ferrous ammonium sulphate solution till the colour change to green to wine red.
- Note down the reading and calculated the COD.

3.6 Determination of BOD

- Pure water was taken in a glass container and bubble compressed air for 2 days to attain saturation.
- The Manganese Sulphate (1ml), Phosphate buffer, Ferric chloride and Calcium chloride solution were added to each liter of distilled water.
- If the water is not expected to certain sufficient bacteria population, it was seeded.
- It was neutralized to pH7.0.
- The dilution of the sample was made such that about 50% depletion of DO.
- Take place and residual DO after incubation for 5 days is not done 1mg per liter.
- 0.1% - 1% of strong waste, 1% - 5% of raw sewage and 5% - 25% treated effluent.
- The two bottles were prepared as blank for determination of initial DO.
- The four bottles were kept in incubation at 20ºC for five days.
- One blank bottle and one sample bottle were taken to determine its initial DO contents by adding 1ml of Manganese sulphate, Calcium chloride, Ferric chloride, and Phosphate buffer concentrated H_2SO_4.
- Then it was titrated with 0.025N Sodium thiosulphate solution using starch as an indicator.
- Then the burette reading was noted and calculates initial DO.
- After 5 days, the DO was determined in the similar way.
- DO - DO of the sample on 0th day and D1 – D.O of sample on 5th day.

Fig - 3: Experimental setup for BOD

3.7 Determination of Hardness

- 50ml of hard water sample is taken.
- 2ml of buffer solution, 3ml of Erichrome Black-t indicator were added.
- EDTA solution was taken in the burette.
- IT was titrated till the color changes from pink to blue colour.

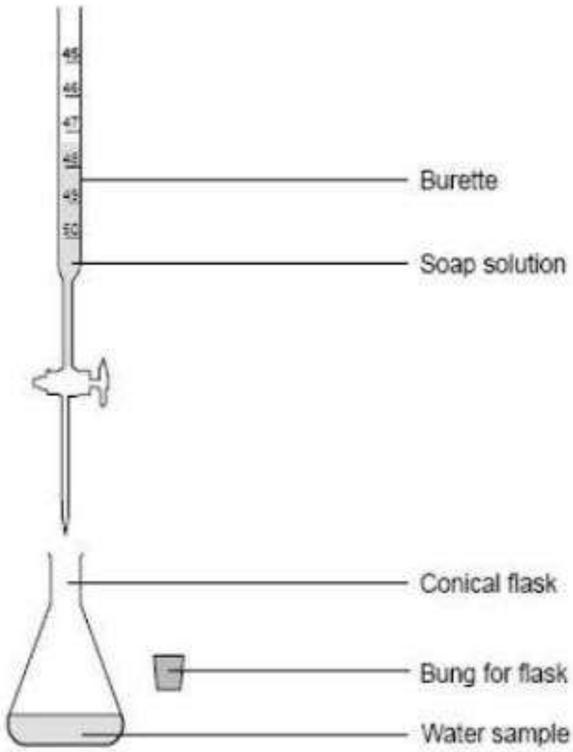

Fig-4: Hardness test

3.8 Field Experiments

3.8.1 Experimental Design

The Okra vegetable field crop experiments were conducted at the Agricultural Research Station of mannuthi. The station is located in Trissur. Beside okra, several vegetable crops were studied for different purposes. However, in this research only okra was selected for detailed investigations due to its importance in the daily human diet and its nutritional value. A strip plot design (Split block) was used for each studied crop. The main plot treatments contain six wastewater qualities, whereas the irrigation systems were arranged in strips as subplot treatments. The crop was cultivated under each waste water quality treatment for each irrigation system. The subplot area was 2×3 m with 4 replicates.

Fig-5: Okra vegetable (Ladies finger)

3.8.2 Water Quality

The sigma waste water treatment plant was the primary source of irrigation water. The water was conveyed to the field site by trucks and stored in two large reservoirs, one for each irrigation system. Each reservoir was connected to six different storage tanks constituting six different water qualities; the dilution process occurs within these storage tanks based on the desirable ratio of waste water and local ground water. The waste water was diluted with the local ground water source to four different percentages. A water quality of 100% waste water in addition to the local ground water and the four dilutions of waste water provide six irrigation water qualities, as shown in Table 3. Irrigation water qualities were given codes according to the dilution percentages. The six water qualities are as follows: local ground water source, 100% treated waste water, and four different dilution percentages as shown in the table above. For example, the code 40 T indicates 40% treated waste water mixed with 60% local ground water of known quality. Hence, the six storage tanks were used to supply the experimental plots, each with its assigned water quality.

4. EXPERIMENTAL RESULT

Effects of heavy metals on plants result in growth inhibition, structure damage, a decline of physiological and biochemical activities as well as of the function of plants. The effects and bioavailability of heavy metals depend on many factors, such as environmental conditions, pH, species of element, organic substances of the media and fertilization, plant species. But, there are also studies on plant resistance mechanisms to protect plants against the toxic effects of heavy metals such as combining heavy metals by proteins and expressing of detoxifying enzyme and nucleic acid, these mechanisms are integrated to protect the plants against injury by heavy metals.

Fig-6: Picture shows damage of leaves due to effect of heavy metals

4.1 Effect of Heavy Metals on Seeds

4.1.1 Nickel (Ni)

Ni is reported to be toxic to most plant species affecting amylase, protease and ribonuclease enzyme activity thus retarding seed germination and growth of many crops. It has been reported to affect the digestion and mobilization of food reserves like proteins and carbohydrates in germinating seeds, reducing plant height, root length, fresh and dry weight, chlorophyll content and enzyme carbonic anhydrase activity, and increasing malondialdehyde content and electrolyte leakage. Ni stress has been reported to affect photosynthetic pigments, lessen yield and cause accumulation of $Na+$, $K+$ and $Ca2+$ in mung bean. The combination of Ni and NaCl in germinating seeds of Brassica Ingra causes significant decline in growth, leaf water potential, pigments and photosynthetic machinery by increased electrolyte leakage, lipid peroxidation, H2O2 content, activity of anti-oxidative enzymes and the level of proline. It is also reported to decrease membrane stability and nitrate reductase and carbonic anhydrase activity.

4.1.2 Copper (Cu)

Cu has been reported to be toxic to sunflower seedlings inducing oxidative stress via generation of reactive oxygen species and by decreased catalase activity via oxidation of protein structure. Cu stress leads to reduced germination rate and induces biomass mobilization by release of glucose and fructose thereby inhibiting the breakdown of starch and sucrose in reserve tissue by inhibition in the activities of alpha-amylase and invertase isoenzymes

4.1.3 Cadmium (Cd)

Cadmium is a naturally occurring toxic heavy metal with common exposure in industrial workplaces, plant soils, and from smoking. The primary use of cadmium is in the manufacturing of NiCd rechargeable batteries. The primary source for cadmium is as a byproduct of refining zinc metal. Stomatal opening, transpiration, and photosynthesis have been reported to be affected by cadmium in nutrient solutions, but the metal is taken up into plants more readily from nutrient solutions than from soil. ... Chlorosis, leaf rolls and stunting are the main and easily visible symptoms of cadmium toxicity in plants.

4.1.4 Lead (Pb)

Lead toxicity causes inhibition of ATP production, lipid peroxidation, and DNA damage by over production of ROS. In addition, lead strongly inhibits seed germination, root elongation, seedling development, plant growth, transpiration, chlorophyll production, and water and protein content. It is one of the most widespread heavy metal contaminants in soils. It is highly toxic to living organisms. Pb has no biological function but can cause morphological, physiological, and biochemical dysfunctions in plants. Plants have developed a wide range of tolerance mechanisms that that are activated in response to Pb exposure. Pb affects plants primarily through their root systems. Plant roots rapidly respond either (i) by the synthesis and deposition of calluses, creating a barrier that stops Pb entering (ii) through the uptake of large amounts of Pb and its sequestration in the vacuole accompanied by changes in root growth and branching pattern or (iii) by its translocation to the aboveground parts of plant in the case of hyperaccumulators plants.

4.1.5 Arsenic (As)

It is a chemical element with symbol As atomic number 33. Arsenic occurs in many minerals, usually in combination with sulfur and metals, but also as a pure elemental crystal. Arsenic is a metalloid. It has various allotropes, but only the gray form is important to industry. The two forms of inorganic arsenic, arsenate (AsV) and arenite (AsIII), are easily taken up by the cells of the plant root. Once in the cell, AsV can be readily converted to AsIII, the more toxic of the two forms. AsV and AsIII both disrupt plant metabolism, but through distinct mechanisms. AsV is a chemical analog of phosphate that can disrupt at least some phosphate-dependent aspects of metabolism. AsV can be translocated across cellular membranes by phosphate transport proteins, leading to imbalances in phosphate supply. It can compete with phosphate during phosphorylation reactions, leading to the formation of AsV adducts that are often unstable and short-lived. As an example, the formation and rapid autohydrolysis of AsV-ADP sets in place a futile cycle that uncouples photophosphorylation and oxidative phosphorylation, decreasing the ability of cells to produce ATP and carry out normal metabolism. AsIII is a dithiol reactive compound that binds to and potentially inactivates enzymes containing closely spaced cysteine residues or dithiol co-factors. Arsenic exposure generally induces the production of reactive oxygen species that can lead to the production of antioxidant metabolites and numerous enzymes involved in antioxidant defense. Oxidative carbon metabolism, amino acid and protein relationships, and nitrogen and sulfur assimilation pathways are also impacted by As exposure. Readjustment of several metabolic pathways, such as glutathione production, has been shown to lead to increased arsenic tolerance in plants. Species- and cultivar-dependent variation in arsenic sensitivity and the remodeling of metabolite pools that occurs in response to As exposure gives hope that additional metabolic pathways associated with As tolerance will be identified.

4.1.6 Mercury (Hg)

The three most common forms of mercury (elemental, inorganic and methylmercury) can all produce adverse health effects at sufficiently high doses. ... Mercury can damage human health because it is toxic to the nervous system — the brain and spinal cord — particularly the developing nervous system of a fetus or young child. Mercury poisoning has become a problem of current interest as a result of environmental pollution on a global scale. Natural emissions of mercury form two-thirds of the input; manmade releases form about one-third. Considerable amounts of mercury may be added to agricultural land with sludge, fertilizers, lime, and manures.

The most important sources of contaminating agricultural soil have been the use of organic mercurial as a seed-coat dressing to prevent fungal diseases in seeds. In general, the effect of treatment on germination is favorable when recommended dosages are used. Injury to the seed increases in direct proportion to increasing rates of application. The availability of soil mercury to plants is low, and there is a tendency for mercury to accumulate in roots, indicating that the roots serve as a barrier to mercury uptake. Mercury concentration in aboveground parts of plants appears to depend largely on foliar uptake of Hg^0 volatilized from the soil. Uptake of mercury has been found to be plant specific in bryophytes, lichens, wetland plants, woody plants, and crop plants. Factors affecting plant uptake include soil or sediment organic content, carbon exchange capacity, oxide and carbonate content, redox potential, formulation used, and total metal content.

5. RESULTS AND DISCUSSIONS

Several heavy metal elements are essential for biological and physiological functions of plants, including biosynthesis of proteins, nucleic acids, growth substances, synthesis of chlorophyll and secondary metabolites, stress tolerance, structural and functional integrity of various membranes and other cellular compounds. However, beyond permissible limits, these metal elements become toxic depending upon the nature and species of metal and plants. Metal toxicity may inhibit electron transport, reduce CO_2 fixation, and cause chloroplast disorganization. It may also affect plant growth through the generation of free radicals and ROS, which pose a threat for constant oxidative damage by degenerating important cellular components. Visible symptoms of metal toxicity include drying of older leaves, chlorosis, necrosis of young leaves, stunting, wilting, and yield reduction. In addition, heavy metal stress can induce a series of events in plants leading to decrease in number and size of leaves, enhancement of leaf rolling and leaf abscission changes in stomatal size and resistance, and higher degree of root suberization. However, plants use complex processes (perception, transduction, and transmission of stress stimuli) and several no enzymatic and enzymatic mechanisms such as, SOD, POD, CAT and APX which activate the cell to adapt their metabolism to metal stress.

6. SUMMARY AND CONCLUSIONS

There are two aspects on the interaction of plants and heavy metals. On one hand, heavy metals show negative effects on plants. On the other hand, plants have their own resistance mechanisms against toxic effects and for detoxifying heavy metal pollution. Heavy metals still represent a group of dangerous pollutants, to which close attention is paid. Many heavy metals are essential as important constituents of pigments and enzymes, mainly zinc, nickel and copper. The influence of plants and their metabolic activities affects the geological and biological redistribution of heavy metals through pollution of the air, water and soil. Various physiological and biochemical processes in plants are affected by metals. The contemporary investigations into toxicity and tolerance in metal-stressed plants are prompted by the growing metal pollution in the environment.

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