Trace Metal Accumulation in Water, Soil and Crop Plants along the Basin of Ujjani Reservoir, India

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Abstract The excessive application of fertilizers and of polluted irrigation water increases the trace metal level in an agricultural ecosystem. This study aimed to assess the concentrations of trace metals (Fe, Cu, Mn, and Zn) in irrigation water, field soil and crop plants. The contents of metals were analyzed by Atomic Absorption Spectroscopy. The range and hierarchy of trace metals concentration (µg/ml) in irrigation water are as follows, Fe (2.16 - 1.53) > Zn (0.30 - 0.17) > Cu (0.18 - 0.11) > Mn (0.11-0.09). The concentration (µg/g) range in field soil showed in an order as Fe (9000- 6961.5) > Mn (984.6 -408.9) > Cu (698.5-26.3) > Zn (145.3- 22.9). Moreover, crop plant parts showed maximum concentration (µg/g.dry weight) range for metal Fe (516.3 - 126.7) followed by Mn (169.7- 0.4), Zn (78.8 - 50) and least for metal Cu (70.5 - 4.1). It was noticed that the Fe concentration in irrigation water is higher than the water quality standards proposed by the Food and Agriculture Organization. Furthermore, the field soil exhibited more Cu, and crops have accumulated excess Fe and Cu than the Indian and European Union guidelines. Further, we reported that among the all plant part, leaves are more prone to accumulate trace metals. The value of the transfer factor indicates that plant has low bioaccumulation potential for studied trace metals. Whereas the accumulation index shows that there is a significant Cu contamination in the field soil. So we suggest that farmers should avoid the application of copper-rich fertilizers.

Keywords Trace Metals, Irrigation Water, Bioaccumulation, Ujjani Reservoir, Atomic Absorption Spectroscopy

1. Introduction

The environmental pollution with trace metals has become a worldwide problem during recent years. Among the environmental pollutants, trace metals are of particular concern, because of their bioaccumulation potential in ecosystems [1,2]. Trace metal pollution in aquatic ecosystems is usually studied by measuring their concentrations in water, sediments and biota. It was noticed that their concentrations generally exist low levels in water and attain substantial concentration in sediments as well as biota. Trace metals such as Fe, Cu, Ni, and Cr are essential metals since they play a central role in biological systems, whereas Pb and Cd considered as non-essential metals, they are toxic, yet in trace amounts. These essential metals can also create toxic effects when the metal ingestion is excessively high [3-5].

Agricultural soil and crops contaminated by trace metals becoming serious environmental problem. Their non-biodegradable nature and long biological half-life leads to their potential accumulation in different plants and animals' body parts. Trace metals such as Zn, Pb, Cd and Cu are generally found as contaminants in vegetables grown using polluted water. These trace metals enter into plants, animals, and humans through air and water. Trace
metals exhibit bioaccumulation at the higher tropic level of the food chain [6-8]. Agricultural soils are mainly contaminated through irrigation water cause threats to resident’s lives, due to consumption of crops and vegetables grown in contaminated areas [9]. There is a potential risk to human health due to the accumulation of trace metals in plants [10,11]. Trace metals such as Pb and Cd have shown carcinogenic effects on animals [12]. Elements such as Zn and Cu at higher concentrations cause toxic effects on living organisms. The higher dose of Zn can reduce immune function and levels of high-density lipoproteins [13,14]. Copper cause acute stomach and intestine aches and also liver damage [15].

Soil is a supporting layer for all organisms and acts as a medium for plant growth. Soil can absorb trace metals in the polluted river as well as groundwater and cause side effects on plant growth and metabolism [16]. Trace metals present in soil water and soil particles are absorbed by plant roots and accumulated in vegetables [17]. The natural concentration of trace metals in soil depends mainly on the composition of geological parent material, but it can also originate from anthropogenic activities [18]. Applications of compounds to soils and crops have become a common practice in crop cultivation. The purposes of the use of chemicals are the improvement of the nutrient supply in the soil or crop protection. These practices might cause chemical deprivation of soil, which result of accumulation of compounds at undesirable levels. Due to economic reasons, most fertilizers are generally not sufficiently purified at the time of the manufacturing process [19]. Extensive use of agrochemicals and inorganic fertilizers for higher crop yield are responsible for agricultural pollution and leads to degradation of the ecosystem and the environment [20]. Similarly, land application of sewage sludge, organic waste manure industrial by-products, and irrigation through highly polluted water are the main sources of trace metals into agricultural ecosystems [21]. Trace metal contamination of agricultural lands poses a latent threat to safe crop production globally, and to a great extent has been spent to identify its sources of pollution [22].

In this study, we have assessed the bioaccumulation of trace metals (Fe, Cu, Mn and Zn) in irrigation water, field soil and crop plant cultivated along the basin of Ujjani reservoir, spread in the Pune district of Maharashtra, India. Also, metal Transfer coefficient and Geoaccumulation index were calculated.

2. Materials and Methods

2.1. Study Area

The Ujjani reservoir (Topo sheet No. 47 N/4; Latitude 180 04’ 24” N and Longitude 750 07’ 15” E) is located in the district Solapur of Maharashtra. Its catchment area is about 14856 Sq. Km [23]. This reservoir receives water from several rivers such as Mula, Mutha and Bhima which passes through metropolitan and industrialized cities namely Pune, Pimpri Chinchwad and Chakan. Finally, the river water is cached in Ujjani reservoir. The Ujjani reservoir water and sediment quality are declining day by day [24]. The study was carried during the spring season of 2019, in the village Malvadi, located 2 Km apart from the basin of Ujjani reservoir. The Basin of the reservoir has intensive agricultural practices and variety of crop patterning such as sugarcane, banana, pomegranates, wheat, maize, and leafy vegetables. The water source used for irrigation is mainly from Ujjani reservoir and to some extent from Bore wells and Wells. Extensive applications of fertilizers, pesticides and long-term continuous irrigation to field soil cause degradation of soil fertility.

2.2. Collection of Water, Soil, Plant Materials

The water samples used for irrigation of field crops (banana, sugarcane and pomegranate) were collected from different sources such as Bore wells, Wells and Ujjani reservoir, separately in pre-cleaned bottles. Similarly, banana field soil (field A1, A2, A3), sugarcane field soil (field B1, B2, B3) and pomegranate field soil (field C1, C2, C3) were collected from 0 to 15 cm depth with the help of a plastic knife and transferred into polythene bags. The fresh plant parts such as fruits, leaves, and stem of banana, young leaves, mature leaves and stem of sugarcane and fruits and leaves of pomegranate were harvested separately at the mature stage of the crops. The irrigation water, field soil and harvested plant parts collected in triplicates and brought to the laboratory and processed further for acid digestion to analyze the content of trace metals.

2.3. Preparation of Water, Soil and Plant Samples

In order to determine the trace metal contents in irrigation water, initially water samples were treated with 3 ml of 70% concentrated HNO3. Later, to concentrate sample, 500 ml of the water sample was evaporated separately for 3 hours on a hot plate. Next, samples were digested using 3-5ml of 70% concentrated HNO3 at 140°C on a hot plate until the volume reduced to 25-30 ml. Similarly, the field soil samples collected were initially oven-dried at 105°C, for 10- 20 hours then ground and sieved through plastic mesh having a pore size 0.5 mm afterward weighed 0.5 g and digested with a mixture of concentrated HNO3 and HClO4 (3:1), initially at 40°C for 1 hour, followed by 140 - 160°C for 2 hours on a hot plate. Plant parts harvested were washed with tap water, followed by deionized water, oven-dried at 85°C, for 10-12 hours. Furthermore, powdered samples were meshed through 0.5 mm plastic mesh, weighted 0.5g each and digested separately using a mixture of concentrated HNO3 and HCl (3:1), initially at 40°C for 1 hour, followed by 120°C to 140
by calculating geoaccumulation index \( I_{\text{geo}} \). The level of pollution in sediment and soil were characterized as contaminated, and \( 2 \leq I_{\text{geo}} \leq 3 \) moderately to heavily contaminated, \( 3 \leq I_{\text{geo}} \leq 4 \) moderately to heavily contaminated, \( 4 \leq I_{\text{geo}} \leq 5 \) heavily to extremely contaminated. Geochemical background values (in µg/g) for metal Fe, Cu, Mn and Zn were assessed in various irrigation water sources such as Bore wells, Wells and Ujjani reservoir. (Figure 1). The results indicate that the concentration of metal Fe was observed uppermost than other studied metals. The maximum concentration of Fe observed in Wells water followed by bore wells and Ujjani reservoir water. The concentration of Fe in Bore wells and Ujjani reservoir water did not show a significant difference. Also, the concentration of Cu detected more in Wells water and least in Bore well water. Whereas Mn content showed a reverse trend, Mn content was observed highest in Bore well and lowest in Well water. It was detected that the Ujjani reservoir has the highest Zn concentration than the other two water sources studied. The concentration of trace metals in all water sources used for irrigation showed descending order such as Fe > Zn > Cu > Mn (Figure 1). We observed that except Fe, other studied metals in water samples are below the standards proposed by the Food and Agriculture Organization [37] (Table 1).

2.5. Transfer Coefficient

The transfer coefficient of trace metals from soil to plant body was calculated by dividing the mean concentration of trace metals in the respective soil field by the mean trace metals concentration in the respective soil field [25].

\[
TF = \frac{C_{\text{plant}}}{C_{\text{soil}}}
\]

Where, \( C_{\text{plant}} \) = mean trace metal concentration in plant body (µg/g) and \( C_{\text{soil}} \) = mean trace metal concentration in soil (µg/g). The concentration of trace metals in the extracts of the field soils and plants were calculated on the basis of dry weight. If the ratios >1, the plants have accumulated trace metals, the ratios around 1 indicate that the plants are not influenced by the trace metals, and ratios <1 indicate that plants eliminate the elements from the uptake [26].

2.6. Geoaccumulation Index \( (I_{\text{geo}}) \)

The transfer coefficient of trace metals from soil to plant body was calculated by dividing the mean concentration of trace metals in the respective soil field by the mean trace metals concentration in the respective soil field [25].

\[
I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5 \times Bn} \right)
\]

Where, \( C_n \) is the concentration(µg/g) of metal in the soil and \( Bn \) is the geochemical background value (element) in the background sample [28]. Geochemical background values (in µg/g) for metal Fe, Cu, Mn and Zn are 35000, 25, 600, 71 respectively. The factor 1.5 is introduced to decrease the possible variations in the background values which may be ascribed to lithogenic effects. Geoaccumulation \( I_{\text{geo}} \) index values interpreted as, \( I_{\text{geo}} \leq 0 \), uncontaminated, \( 0 \leq I_{\text{geo}} \leq 1 \) uncontaminated to moderately contaminated, \( 1 \leq I_{\text{geo}} \leq 2 \) moderately contaminated, \( 2 \leq I_{\text{geo}} \leq 3 \) moderately to heavily contaminated, and \( 3 \leq I_{\text{geo}} \leq 4 \) heavily contaminated and \( 4 \leq I_{\text{geo}} \leq 5 \) extremely contaminated.

3. Results

3.1. Trace Metals in Irrigation Water

In this study, the content of trace metals such as Fe, Cu, Mn and Zn were assessed in various irrigation water sources such as Bore wells, Wells and Ujjani reservoir. (Figure 1). The results indicate that the concentration of metal Fe was observed uppermost than other studied metals. The maximum concentration of Fe observed in Wells water followed by bore wells and Ujjani reservoir water. The concentration of Fe in Bore wells and Ujjani reservoir water did not show a significant difference. Also, the concentration of Cu detected more in Wells water and least in Bore well water. Whereas Mn content showed a reverse trend, Mn content was observed highest in Bore well and lowest in Well water. It was detected that the Ujjani reservoir has the highest Zn concentration than the other two water sources studied. The concentration of trace metals in all water sources used for irrigation showed descending order such as Fe > Zn > Cu > Mn (Figure 1). We observed that except Fe, other studied metals in water samples are below the standards proposed by the Food and Agriculture Organization [37] (Table 1).

3.2. Trace Metals in Soil

The trace metal (Fe, Cu, Mn and Zn) concentrations were analyzed from different field soil. The field soil samples were collected from banana (field A1, A2, A3), sugarcane (B1, B2, B3) and pomegranate (field C1, C2, C3) field respectively. (Figure 1.) The content of Fe in banana, sugarcane and pomegranate field soil were observed in the descending order such as A1 > A3 > A2, B3 > B2 > B1 and C1 > C2 > C3 respectively. It was found that the concentration of Fe in banana field soil was more than the sugarcane and pomegranate field soil. Similarly, the Cu content in banana, sugarcane and pomegranate field soil was observed in the descending order such as A1 > A2 > A3, B3 > B2 > B1, C2 > C1 > C3 respectively. The field soil under cultivation of banana showed a drastic decrease in the Cu content than pomegranate and sugarcane field soil. Moreover, the Mn concentration in banana, sugarcane and pomegranate field soil showed the hierarchical order such as A3 > A2 > A1, B2 > B3 > B1 and C2 > C1 > C3 respectively. It was detected that there, is no significant variation in Mn content among the banana and sugarcane field soil. The mean content of Zn was observed highest in the banana field soil followed by pomegranate and least in sugarcane field soil. In the banana, sugarcane and pomegranate field, Zn accumulation exhibited order such as A3 > A2 > A1, B3 > B2 > B1 and C3 > C2 > C1 respectively (Figure 1). Among the trace metals under study, Fe content was more in all studied field soil followed by Mn, Cu, and Zn. Accumulation of metal Cu in field soil was observed more than the permissible limit proposed by the European Union [30] and Indian standards [29].
Table 1. Indian, European Union and FAO standards for trace metal contents in water, field soil and plant parts

| Sample type   | Fe    | Cu    | Mn    | Zn    |
|---------------|-------|-------|-------|-------|
| **Water**     |       |       |       |       |
| - Indian standards [29] | 0.05  | 0.1   | 5     | 0.3   |
| - FAO (1985)  | 0.2   | 0.2   | 2     | 0.5   |
| **Soil**      |       |       |       |       |
| - Indian standard [29] | 50,000 | 135-270 | 100-4000 | 300-600 |
| - E. U. Standards [30] |      | 100   | 2000  | 300   |
| **Plant Parts** |       |       |       |       |
| - Indian standard [29] | 20    | 30    |       | 50    |
| - E. U. standards [31] | 20    | 500   |       | 50    |

Description: Standard values for trace metal contents in irrigation water (µg/ml), field soil (µg/g), and plant parts (µg/g dry weight). EU European Union, FAO Food and Agriculture Organization.

**3.3. Trace Metals in Crops**

The highest Fe concentration was detected in stem followed by leaves and least in fruits of banana, whereas in case of sugarcane plant parts mature leaves showed maximum Fe followed by young leaves and lesser in the stem. Moreover in pomegranate, the maximum concentration of Fe was detected in leaves followed by fruits. Among the plant parts under study metal Fe was detected more than Cu, Mn and Zn. The metal Cu contents in banana was more in leaves afterward in fruits and less in the stem, whereas sugarcane young leaves accumulate more Cu than mature leaves and stem. Among the plant parts understudy, Cu concentration in pomegranate leaves and fruits were significantly high. Also, significant
variation in the Mn level was noticed within the leaves and fruits of banana. The order of Mn contents in banana showed leaves > stem followed by fruits. In the case of sugarcane Mn showed concentration order such as young leaves > mature leaves and least in the stem. Also, pomegranate leaves accumulate higher Mn than fruits. Accumulation of metal Zn in banana plant parts did not show significant variation. However, sugarcane parts under study detected higher Zn contents in young leaves than mature leaves and stem. Similarly, Zn contents in pomegranate leaves were detected highest among all plant parts under study. It was generally noticed that among all plant parts understudy leaves accumulate more trace metals.

3.4. Transfer Factor

The transfer factor (TF) for banana field soil A1 (Mn > Zn > Cu > Fe), A2 and A3 (Cu > Mn > Zn > Fe) showed the lowest value for metal Fe. However, in the sugarcane field soil B1, B2 and B3 (Zn > Mn > Fe > Cu.) exhibited minimum TF for metal Cu and highest for Zn, whereas in pomegranate field soil C1, C2, C3 (Zn>> Cu > Fe > Mn) lowest TF was observed for metal Mn (Figure 2).

It was noticed that the transfer of Zn was higher in sugarcane and pomegranate, However metal Mn and Cu transfer more easily in banana plant. All values of studied TF were below the 1, indicating that studied plants are not contaminated by trace metals [28].

3.5. Geoaccumulation Index

The values geoaccumulation index detected for metal Fe, Mn and Zn were below the 1 indicating field soil is not contaminated by Fe, Mn and Zn, whereas field soil A1 and A2, (≥ 1geo>1) is moderately contaminated. Field soil B1 and B2 (3 < Igeo>4) is heavily contaminated, and field soil C1 and C4 (Igeo> 4) is heavy to extremely contaminated.

4. Discussion

In this study we have investigated metal contamination and its distribution pattern in irrigation water, field soil and crop plants along the basin of Ujjani reservoir. Generally, micronutrients are beneficial to plant growth in adequate quantity, but its abundance causes deleterious effects. In general, among the metals, Fe content is observed more than other metals in irrigation water, and plant parts. Iron (Fe) is an essential micronutrient in a plant but excess iron is highly toxic to plants. The excess Fe retards primary and lateral growth of roots [32,33]. It is reported that Fe toxicity in rice cropping system minimizes grain size and also yield. Also, chronic exposure of Fe through food in humans causes constipation, nausea, diarrhea and chronic ulcerations. Here, in our work, the concentration of Fe in irrigation water and plant parts observed more than the limit prescribed by the Food and Agriculture Organization [34 European Union [30] and Indian standards [29].

To acquire further insight into the other metal content we determined Cu level and it was drastically higher in field soil and plant parts under study. Copper is essential for plant nutrients, but concentration more than 270 µg/g considered as toxic to soil health. The toxic effects of Cu are studied in several crop species. Soil’s Cu level more than 300 µg/g cause decrease in 50 percent yield of rice grains [35]. Accumulation of Cu could be occurring due to applications excess essential elements for plant growth as remedies for deficiency in the soil. Application of biosoilid sands, fertilizers and manure to field soil causes accumulation of metals such as Cu, Zn, Fe, Pb and Mn in the soil [13].

The degree of contamination in soil is studied by total trace metal concentration [7]. The accumulation of trace metals in field soil depends on a range of factors, such as soil pH, the chemical form of element, texture, cation exchange capacity of the soil and its organic matter contents [36].

The higher level of soil trace metals may pose health problems in residential [37]. The Mn phytotoxicity is manifested in a reduction of biomass and photosynthesis, and biochemical disorders such as oxidative stress [38]. The Mn concentration observed in this study was found lower than previously detected in polluted soil [39]. It representing that the Mn has no significant contamination in the studied field soil samples. Also, irrigation water and plant parts show a lower accumulation of Mn than the permissible limit prescribed by the standards proposed by the European Union [30] and India [29].

The contents of Zn observed in all samples collected were bellowing the permissible limit. Although Zn is an essential element for plant metabolism, excess level of Zn causes browning of leaves and reduction in chlorophyll contents and photosynthesis. We noticed that Ujjani reservoir water contains more Zn levels than other sources. Soil Zn level more than 500 µg/g cause a drastic reduction in photosynthetic activity of plant [40].

The uptake and release of metals in the plant depend on soil composition, plant species, and plant growth stage. The trace metals concentrations in plant organs are generally lower than field soil. Demirezen and Aksoy[37] reported the trace metal concentrations are lower in vegetables than soil. It was reported that Cu contents in urban soil (63.39–110.3 µg/g) ranges higher than the vegetables (22.19–76.5 µg/g) grown on those soil. Similarly, metal Zn in urban soil ranges from 44.3-294.4 µg/g, and in vegetables between 3.56–259.2 µg/g [37]. The vegetable grown on trace metal contaminated soil accumulates elevated concentration of metals in their edible parts. The high level of trace metals in the soil does not always indicate high concentrations in plant parts. Accumulation of trace metals in the plant depends on
environmental factors and plant species [41]. The level of all studied elements was observed higher in leaves than in other parts. Accumulation of particular metals in plant leaves, stem and fruits depend on the type and species of plant. It was noticed that pomegranate leaves accumulate more Fe (355.4 µg/g), Cu (60.3 µg/g), and Zn (72.3 µg/g), than the leaves of other plants. Similarly leaves of banana showed more Mn (153.3 µg/g) than the other plant parts studied. The concentration of metal Fe (8976.4 µg/g) in the banana field soil was observed higher, whereas, Cu (628.4) and Zn (122.9 µg/g) were observed more in pomegranate field. Further, Mn (943 µg/g) was detected more in sugarcane cultivated filed soil. Moreover, the level of metal contents obtained in this study were compared with international standards and noticed that Cu contents in field soil was found more, whereas other metals were within the safe limit. Also the level of metal Fe, and Cu in some plants parts detected more than the international standards (Table 1). Variations in the level of trace metal composition in the field soil may be due to applications of crop specific fertilizers, pesticides and frequency of water irrigation. The results of our study showed that accumulation of trace metals mainly depends on type of crop species. Even higher contents of metals in the field soil, accumulation in the plants parts did not showed peak concentration value.

In order to study contamination of trace metals in plant and field soil is estimated using transfer factor (TF) and Geoaccumulation Index (Igeo). These factors are influenced by an excess of metal levels in soil and plant. The concentration range of trace metals in the field soil varies with the type of metal and crop plant patterning. It may be occurred by the application of crop-specific fertilizers [42]. The concentrations of studied metals in field soil showed the order such as Fe > Mn > Cu > Zn. The concentration of metals in the soil also depends on their concentration in the upper continental crust [43]. The transfer coefficient of studied metals from soil to plant is species-specific. The metal Zn transfers more efficiently in Pomegranate and Sugarcane, whereas metal Cu and Mn transfer more efficiently in banana. However, the transfer coefficient is less than 1 in all studied plants. It may be due to the unique metabolic activity of particular plant species. We observed that Igeo values for Fe, Mn and Cu were lesser than unity indicating field soil is not contaminated. Whereas Igeo of metal Cu reached up to 5 indicating that field soil is extremely contaminated with copper.

5. Conclusions

Present study was conducted to evaluate the impact of modern agriculture activities on the environmental quality and food safety. Excessive use of fertilizers and pesticides to increase crop yield are responsible for increasing concentrations of some toxic metals into the soil and crops cultivated on those soil. Moreover, trace metals are essential for normal growth and development but excessive accumulation of these metals causes adverse effects on plant. This metal enters into the human and other animals through food chain and causes toxicity. Ujjani reservoir is main irrigation water source in the study area. Industrializations, urbanizations and agriculture development are responsible for addition of elements into the agriculture ecosystem. Different irrigation water sources assessed indicate that except metal Fe, the content of trace metals found are below the environmental standards. Water from Wells and Ujjani reservoir contains higher Fe and Zn respectively. Whereas Cu and Mn were found more in bore well water samples. Similarly, the concentrations of trace metals in studied field soil vary with crop plant cultivation pattern. It was noticed that Cu, Mn and Zn were detected more in pomegranate field soil. It indicated that the application of crop-specific fertilizer and pesticides may affect the level of a contaminant in the field soil. The concentrations of trace metals in studied plant parts indicate that there is a higher accumulation in leaves. It may be due to the unique metabolic activity of leaves. Also, the accumulation of trace metals depends on plant species and types of organs and not always on their soil contents. Even more metal contents in the soil do not always give higher accumulations in plant parts. Transfer factors calculated is bellowing the unity, indicating that studied crop plant has lower phytoremediation potential. It is also noticed that Igeo value of metal Cu is more than 4; indicating soil is highly contaminated by copper. Further we suggest that farmers should analyze soil and water trace metal profile before application of fertilizers to crops. Also, government environment agency needs to monitor soil and water qualities periodically for safe food production and environmental sustainability.

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Declaration of Interest Statement

The authors declared that they have no conflicts of interest in this work. We do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.
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