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Research Paper

Studies on the Assessment of Toxic Metals Present in Biological Samples (Part-1)

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Abstract - *Development in the 20th century has brought social and economic benefits to us but the changes have also caused a wide range of environmental problems at both local and global level. Increased industrial activities has increased the incidence of percolation of toxic metal ions to the soil and water bodies and presently their presence in ecosystem, have reached to an alarming level that whole planet and entire humanity is at stake. The toxic metals have a great tendency of bioaccumulation through which they enter the food chain system and ultimately affect adversely the life in various ways. Further, due to contamination of irrigation system by the harmful and deleterious Chemicals and toxic metals, the toxic metals have found their ways through the aquatic systems and soil to the farm products, food grains, vegetables, fruits, and even milk. In continuation of our efforts to find out the toxic metals in the ecosystem, this communication describes the estimation of the metal contents in various samples of summer vegetables and fruits collected from the agriculture fields near the bank of the River Ganges from Rishikesh onwards to Garhmukteshwer. For the sake of comparison, the samples of soil and water used by villagers for irrigation purpose were also analyzed for these metals.*

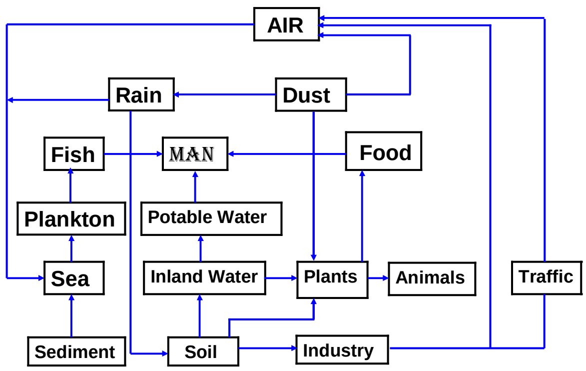
Key words: Toxic Metals, Summer Vegetables and Fruits, Soil, Irrigation Water.

Introduction

A number of metals are key factors for health and body function, and are required for protein structure, and to produce hormones. These act as co-factors, catalysts or inhibitors of all enzymes in the body. Many metals play critical role in maintaining life and some are important for the bio-mineralization to give supporting hard structure, some stabilizes protein in unique conformation. Some are essential for electron transport system–cellular energy production, metabolism and degradation of bio-molecules. Few metals act as charge carriers for very fast information transfer. Some are involved in transport, storage and conversion and generation of paramagnetic oxygen molecule, fixation of molecular nitrogen and its conversion to ammonia and are also essential for blood coagulation, fluid balance, osmotic regulation, and are important constituents of certain bio-macromolecules essential for survival of the life [1-3].

Toxic metals have always been present in the ecosystem, but since the industrial revolution there has been a massive redistribution of metals on the surface of the earth. Many metals in certain very small quantities are needed to play their roles to sustain life, and it is when the concentrations are too high that they contaminate soil and water and exert toxic effect [4, 5]. Development in the 20th century has brought social and economic benefits to us but the changes have also caused a wide range of environmental problems at both local and global level. Industrial activities, rapid urban growth, agricultural intensification and other domestic activities have increased the percolation of toxic metals to the soil and water bodies, to an alarming level. The ground water which was very clean and safe, few decades back is charging continuously with deleterious materials. Human activities and large number of small and big industrial units are increasingly discharging deleterious metals present in the effluents and wastes, to the environment and aquatic systems including ground water have contaminated heavily [6,7].The contamination of irrigation system has multiplying effect[8-10] and the harmful Chemicals and toxic metals have found their ways through water and soil to the farm products, food grains, vegetables and fruits.

The heavy metals have a great tendency of bioaccumulation through which they enter the food chain and bring about adverse effects on human beings and other living organisms and plants. The key factor for metals is that no metal is degradable, as they stay for a long time, this stability lets them be carried long distances through air and water. Irrigation water transports the dissolved heavy metals to agri-fields when metals such as Cd, Hg, Pb, As etc are incorporated to plant tissues [5]. Toxic metals are now everywhere and affect everyone on this planet Earth. The human body is unable to process and disperse of the metals, therefore they get deposited in various sites of internal organs. Large deposits may cause series of damage in the body and have become a major cause of illness, ageing and even genetic defects. Heavy metals may form carcinogenic compounds in the body even at very low levels, which not only affect the first generation, but theirs affect can be passed onto the coming generations in the form of genetic abnormalities and birth defects[1].



General Pathways of Toxic Metals[6]

The intake of mining waste, washings of blast furnaces, finishing of metal and metal products, electroplating, leather tanneries, battery manufacturing, coal- fields, power plants, foundries- refectories, steel-cement-tile industries, manufacture and use of fertilizers, insecticides and pesticides, hospitals-laboratory effluents, etc have contaminated largely our ecosystem. Toxic metals travel to soil and surface water mainly as a result of weathering of metalleferous rocks, industrial effluents, direct use of domestic waste and sewage from urban and rural habitations and agricultural runoff. During rainfall events, outflow from agri-fields carries significant quantities of nutrients, pesticides, herbicides and other pollutants to nearby streams and rivers.

The present investigation describes the estimation of Toxic Metals in the samples of irrigation water, soil, summer vegetables and fruits grown by farmers of villages from Shyampur to Jagjeetpur. In this presentation results of samples of summer vegetables and fruits collected from only first ten sites falling in the Uttarakhand state from Shyampur to Jagjeetpur are included.

Material and Methods

Sampling Sites: Samples of soil, Irrigation water, summer vegetables and fruits were collected from various agri-fields near the bank of the River Ganges from Rishikesh onward.

Vegetables and Fruits Samples: The samples of water melon, musk melon, peach, tomato, Beet root, squash melon, Bitter gourd, Spinach, Sponge gourd and bottle gourd grown by the farmers of the study area, were collected from March to June 2010.

Soil and Water Samples: The samples of water (being used for irrigation purpose) and soil (20 cm depth) were collected from 28 different sites from Rishikesh to Garhmukteshwar in pre-monsoon season.

Reagents and Chemicals: Borosil glass containers were used for collection of the samples of vegetables, fruits and soil. Water Samples were collected in the brand new, transparent polythene cans pre-rinsed with dilute HNO_3- double distilled water.

The collection of samples and evaluation of metal ions were done in accordance to Standard Methods for the Examination of Water and Wastewater, APHA, 2005 [9] .Various A.A.S. standard stock solutions of metal ions used were from *Sigma-Aldrich, which were diluted to required concentrations to prepare working standards. O*ther reagents, chemicals, and solvents used were of Analytical grade. Double distilled water is used for all purposes.

Estimation of Metal ions: The samples of vegetables and fruits were washed with double distilled water, cut into pieces and grinded and 100 gm of the material were digested with $HClO_4$: HNO_3 (1:5 mixture) for several hours till transparent light colored liquid is obtained, which was filtered and diluted to a volume of 100ml with double distilled water. Soil samples collected from the agricultural fields were air dried, mechanically ground and the fine material thus obtained were digested with $HClO_4$: HNO_3 (1:5 mixture) for several hours to get the transparent extracts used for analysis of the heavy metals. The quantitative estimation of toxic metals was performed on Atomic Absorption Spectrometer (PerkinElmer, US).

Results and Discussion

The analytical results of toxic metal contents in samples of water melon, musk melon, peach, tomato, Beet root , squash melon, Bitter gourd , Spinach, Sponge gourd and bottle gourd grown by the farmers of the study area were collected from March to June 2010 are presented in Table 1. The analytical results of toxic metal contents in samples of water used for irrigation purpose and agricultural soils are not included here.

The entire study area right from Rishikesh onwards is subjected to human activities, directly or indirectly affecting the water and soil quality. The most of the urban area with large settlements without sewage system, the urban solid waste and medical wastes from hospitals and pathology labs and effluents from chemistry laboratories of educational institutions is discharging directly to the water bodies and agricultural fields. Further some of the agricultural crops are being irrigated by industrial waste water. A large number of nalahs carrying domestic waste water and effluents from small and big industrial units are releasing variety of pollutants to the agriculture land and water bodies including the river Ganges.

Industrial units like Rice Mills, Oil Extraction plants, Paper and pulp, surgical instruments, Steel and Alloys, Gur-Khand-sugar, ceramics, distilleries, brick kilns, stone crushers, handloom, dyes-paints-distempers-pharmaceuticals- chemicals- drugs- detergents, cement-tiles, electroplating and metal products finishing etc are the main source of toxic metal contamination in the study area. The waste water and industrial effluents disposed by these industrial establishments containing hazardous metals in more than maximum limit as prescribed by APHA[9] has contaminates surface water and ground water and agricultural land.

The data presented here reveal that toxic metal ion concentrations in almost all the samples were near or above the permissible limit. The vegetables and fruits grown in the river Ganges basin were found to contain significant amount of toxic metals due to percolation of untreated sewage, urban wastes, industrial waste water, vehicular exhaust and smokes from brick and other industrial units. Fruits and vegetables, especially leafy vegetables like spinach were found to contain elevated levels of metals (Figure 1-3). Toxic metals from waste water are transported to the soil and ultimately to the vegetables and fruits, pausing serious threat to humanity. Most of the metals from industrial effluents gradually move down the soil-solid profile. The rate depends on the chemical characteristics of soils and the value of intrinsic properties of metal.

In almost all the samples cadmium contents were much above the admissible limits[9,10] The cadmium contents found in water melon, spinach, musk melon, squash melon, tomato, sponge guard and peach were 0.106, 0.094, 0.092, 0.086, 0.084, 0.064 and 0.046 mg / kg. Cd which is toxic to human being even at low level causes nausea, vomiting, diarrhea, sensory disturbances, convulsions, liver and renal failure[6,8]. Vegetables grown in soils with high levels of cadmium may be the source of cadmium accumulation in living beings [12]. Other sources of Cadmium are aluminum solders, storage batteries, dental amalgams, and cigarette smokes [13].

Cobalt was also found to be between 0.082 to 0.328 mg/ kg in vegetable samples. It exerts toxic effects to plants and animals when intake is high[14].The high concentration of Co in soil than water indicates high accumulation in to soil from water[15].

In all the samples Cr was also above the safe limit. It was found to be between 0.092 and 0.342 mg / kg in vegetables and fruits. Chromium reaches to the ecosystem due to Chrome platting, steel fabrication, paint and pigment manufacturing, leather tanning [16]. etc. Occupational exposure causes dermatitis, perforation of nasal septum, ulcer on hands, forearms and inflation of larynx and liver. The hexa-valent Cr compounds are most harmful [17]. Fe was found between 5.40 to 18.26 mg/kg in vegetable samples with high accumulation in beet root, spinach, peach, tomato, bitter gourd and sponge guard. The concentration of Ni was also in higher range. Ni is responsible for lungs and nose cancer and liver intestine and respiratory tract damage [18].

Zinc which is non-toxic below 5.0 mg/l was found quite above the permissible limits in almost all the samples of water, soil and vegetables. In all the vegetable samples under observation Manganese was found to be either at toxic or alert level i.e. between 0.094 to 0.336 mg/kg. The Mn above 0.15 ppm produces undesirable taste of water[19].

The concentration of copper was found to be from 0.624 to 1.86 mg/kg in vegetable and fruits samples.

Lead which is non-essential for plants and animals was also found to be above permissible limit in many samples.

Thus the release of untreated effluents containing toxic metals to nearby soil, water bodies and irrigating system has multiplier effect [19,20] and toxic metals and harmful chemicals have found their ways through water and soil to the farm products, pausing serious threat to the consumers health[21].

Conclusion

Thus the release of untreated effluents containing toxic metals to nearby soil and water bodies is posing health hazards to animals and human beings. Further, the contamination of irrigating system has multiplier effect and toxic metals and harmful chemicals have found their ways through water and soil to the farm products, pausing serious threat to the consumers health. Proper management of water resources and waste water disposal, released by industrial establishments should be cared effectively to save humanity from sufferings.

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Table 1: Concentration (mg/kg) of Toxic Metal ions in the Samples of Summer Vegetables and Fruits

Metal	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Cd	0.106	0.092	0.046	0.084	0.012	0.086	0.034	0.094	0.064	0.034
Co	0.246	0.118	0.102	0.224	0.326	0.286	0.124	0.082	0.328	0.316
Cr	0.106	0.092	0.226	0.148	0.204	0.342	0.136	0.260	0.208	0.112
Fe	6.68	10.46	14.24	13.48	18.26	10.46	12.92	15.38	14.18	5.40
Ni	0.614	1.21	0.864	0.816	2.12	0.602	0.428	0.508	0.346	0.782
Zn	4.32	8.24	10.42	7.26	5.24	9.24	7.62	9.34	7.08	4.78
Mn	0.116	0.098	0.236	0.128	0.264	0.182	0.336	0.094	0.146	0.234
Cu	1.27	1.16	1.86	1.84	0.684	1.46	1.26	0.964	0.624	0.928
Pb	0.164	0.228	0.096	0.312	0.264	0.068	0.348	0.062	0.196	0.086
Vege tables	**Water melon**	**Musk melon**	**Peach**	**Tomato**	**Beet root**	**Squash melon**	**Bitter gourd**	**Spin ach**	**Sponge Gourd**	**Bottle gourd**

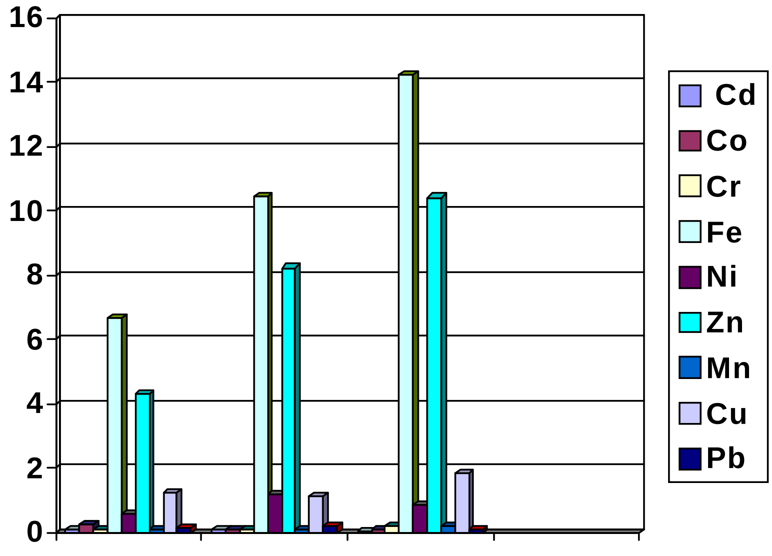

Figure 1: Metal Ions (mg / kg) in Water melon, Musk melon and Peach

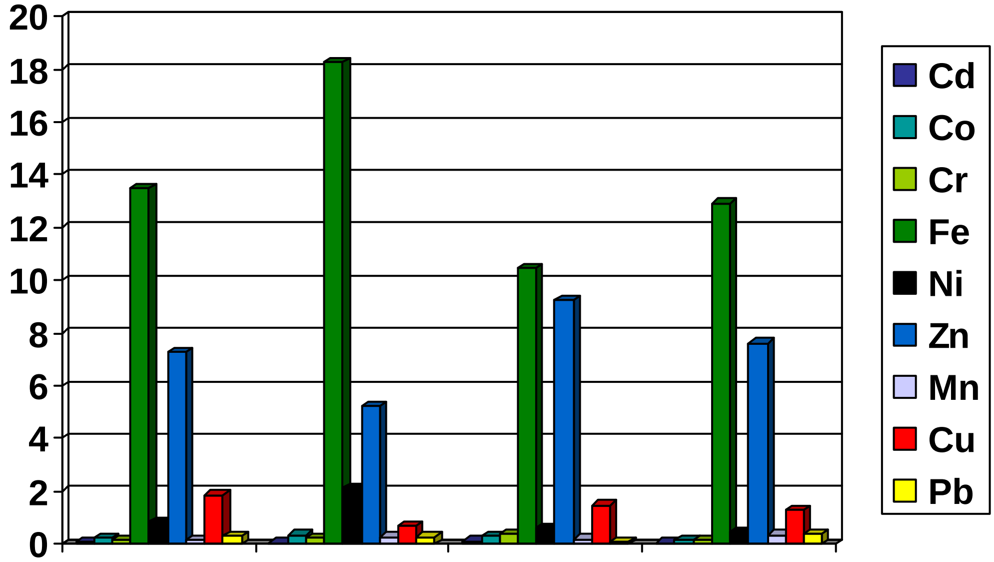

Figure 2: Metal Ions (mg / kg) in Tomato, Beet root, Squash melon and Bitter gourd

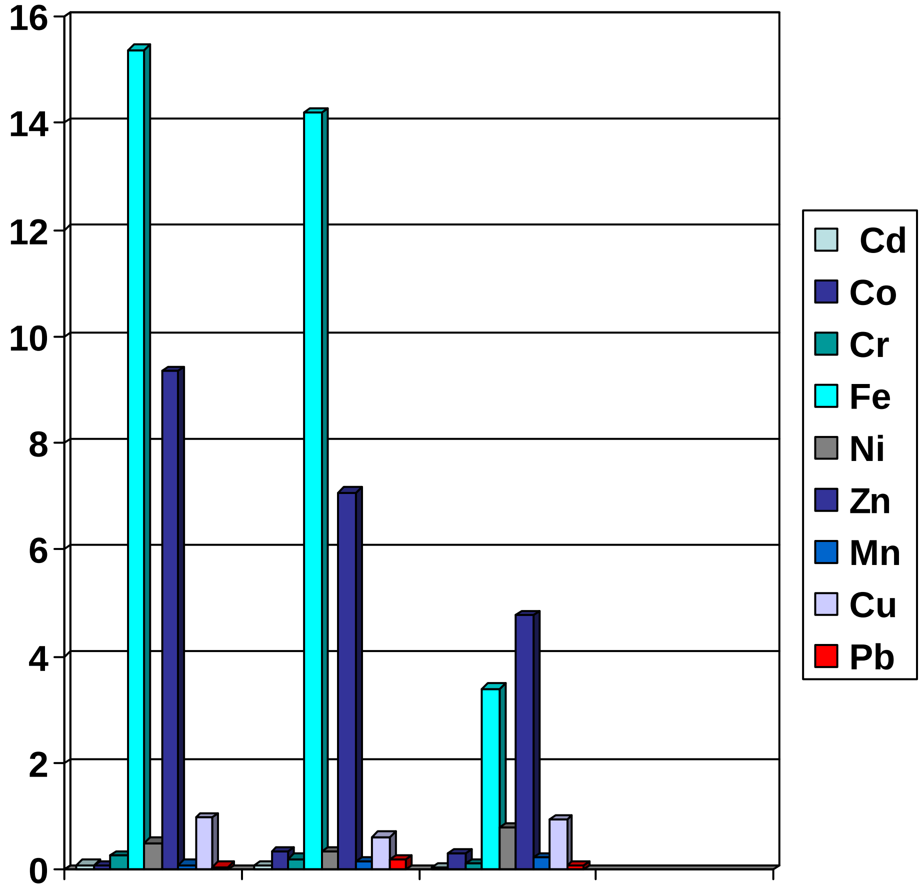

Figure 3: Metal Ions (mg / kg) in Spinach, Sponge gourd and Bottle gourd