



# Motility of metals in vegetables and Soil irrigated with Yamuna river

Indu Tiwari<sup>1</sup>, Surabhi Yadav<sup>1</sup>, Anjuri Srivastava<sup>1,2</sup>, Abhijit Saha<sup>3</sup>

<sup>1</sup>Bipin Bihari Degree College, Jhansi 284002.

<sup>2</sup>Institute of Engineering and Technology, Lucknow 226021.

<sup>3</sup>Bhabha Atomic Research Centre, Trombay, Mumbai 400085.

## Abstract

Heavy metals can affect public health, but they can also affect the stability of recipients and drug substances. We are hugely empowered with technology. today it doesn't take 6 billion people to destroy this planet, one man can destroy the whole planet. The technology which is supposed to make our life easy and beautiful has become the source of all the problems due to which we are destroying the very basis of our life. Some Heavy metals like Cu, Zn, Mn, Fe, *etc.* act as essential micronutrients but when present above the permissible limit in soil and water along with some other nonessential metals like Pd, Cd, and Gd, they become toxic. As their aggregation increases in soil, the amount of metal in the plant also increases. This study was conducted to itemize the accumulation of heavy metals in spinach, radish, radish leaves, Gourd, Tomato & its growing soil and river water used for irrigation to assess the potential transformation of metals. The contents were measured by IC-PMS. The translocation factor of these metals was calculated by BCTR. Results showed that the concentration of metals in soil (Mg>Gd>Cr>Fe>Zn>Na) and in vegetables (Mg>Mn>Dy>Na>Pd>Cr>Cr>Co>Ni>Ca>Cd>Fe>Zn) is higher than the WHO limits.

**Keywords:** Heavy metal, REEs, LREES, HREEs, reference dose, Bioconcentration transfer ratio

## 1. Introduction

Heavy metal contamination and toxicity are related to each other because they are major environmental issues today and the restoration of the environment i.e., air, water, and soil is also a matter of concern. They can be both beneficial and determinative, which means that at high concentrations, the same element that might be essential for our ecosystem can be toxic and fatal. The major purpose of this continuing research is to solve the Yamuna river's dirty water in Vrindavan (Mathura district).

Although there are no other sources of heavy metal pollution in the research area, the water sample is confirmed to be

contaminated. According to a recent study, the Yamuna river has 100 percent urban metabolism as it flows through Delhi's National Capital Territory (NCT). Thousands of fish have been discovered dead in the Yamuna river in Vrindavan, according to reports.

Fish and other aquatic species die as a result of waste discharge from the Okhla barrage region. Pb, Cd, Cr, Fe, Zn, Ni, Mn, Co, Gd, Dy, Ce, and Eu are heavy metals that can harm human health and other organisms. This study focuses on Pb, Cd, Cr, Fe, Zn, Ni, Mn, Co, Gd, Dy, Ce, and Eu. Water is an essential component of agricultural productivity and is critical for food safety. Phytoavailability of trace elements from

\*Corresponding Author (Email: drsurabhi2020@gmail.com)

water, soil, and plants is a key component that influences and correlates with plant food quality[1]. Heavy metals are typically found in the earth's crust as naturally occurring elements. Because these metals cannot be decomposed or eliminated, they must be ingested by living things through food, water, and inhalation. High Mg dosages from dietary supplements or pharmaceuticals can cause diarrhoea, which can be dangerous. High sodium intake (>2 grammes per day, equivalent to 5 grammes of salt per day) and low potassium intake (3.5 grammes per day) both contribute to high blood pressure and raise the risk of heart disease and stroke[2]. Heavy metals like Fe and Zn are not only beneficial but also necessary for our bodies to function properly. Your RBCs use iron to bind oxygen molecules. Zn is a common and necessary element (WHO). To be taken up by plants, Zn must be in a soluble form. Plants can also absorb Zn that is deposited on the surface of leaves as a result of aerial deposition or fertiliser treatment. Zn replaces iron in the active centre of enzymes in the case of Zn toxicity[3]. Excess zinc has been shown to slow down various physiological processes in plants, including phloem translocation. Zinc deficiency reduces the quantity of chlorophyll as well as the activity of antioxidant enzymes[4]. Plants, animals, and humans can all absorb metals. The oxidation state or speciation of heavy metals is crucial (for example,  $\text{Cr}^{+6}$  is far more hazardous than  $\text{Cr}^{+3}$ ). Cr is soluble in the soil after complexing with organic matter and is tightly bound to humus and clay particles, whereas Cr(VI) is highly soluble and easily passes through plant cells into vacuoles, where it combines with cations to form stable compounds that either accelerate or retard plant growth. Cr is less soluble in soil and water than other potentially hazardous metals. Plants contain between 0.02-1.3 ppm Cr under normal conditions, but concentrations in bogs and lichens can reach 14 ppm[5]. Mn is a poisonous and vital element in the human body. It is a cofactor for a number of critical

enzymes. Manganese is delivered to the liver and kidneys by the blood after absorption in the human body. There is a narrow line between too much Mn and too little Mn, both of which have negative health consequences. Previously, the threshold was 0.4 mg/l, but WHO withdrew those criteria in 2011, and there is currently no standard limit for Mn[6]. Several variables can affect the risk of toxicity from heavy metals, such as toxic metal interactions with essential metals, which is a significant metal effect or share the same homeostatic mechanism as is the case for Pb with calcium and iron. Pb poisoning has been recognized as a significant problem for thousands of years. Pb has no biological function it is not essential and is hardly found in the environment air, water, food, and soil[7]. Symptomatic Pb poisoning is uncommon in children with blood levels <45 Microgram/deciliter and in adults <60 microgram/deciliter. Usually, these metals are soluble under specific environmental conditions when soluble they are fast dispersed in the environment and then they are transported down the gradient leading to the accumulation of the heavy metals. One of the most hazardous metals is Cadmium. Cadmium showing a strong affinity towards sulfhydryl and phosphate groups, it affects the various metabolic processes in a living system[8]. Accumulation of cadmium in river water can be due to weathering of rocks and manufacturing industries. Cadmium present in the soil is taken up by plants, which are taken up by humans and other animals. In humans, cadmium can cause many harmful effects from diarrhoea and stomach pain to psychological disorders, DNA damage, and even cancer[9]. Oral ingestion of cadmium may lead to its accumulation in the kidney and liver and disturb the proper function of an organ system. Some REEs are Ce, Dy, Gd, Eu, and Sm. In which Cr, Sm, Eu are LREEs and Gd, Dy is HREEs. REEs are naturally found in very low concentrations in the environment. Once in the environment, REEs can leach into the soil where their transport is determined by many

factors such as weathering, pH, erosion, groundwater, precipitation, etc. REEs can be absorbed into plants and subsequently consumed by humans and animals, depending on their bioavailability. The use of REE-rich fertilizers and the production of phosphorus fertilizers all contribute to REE contamination[10].

REEs environmental contamination is cerium oxide (CeO<sub>2</sub>) which is produced during the combustion of diesel and is released as an exhaust particulate matter and contributes heavily to soil and water contamination[11]. Gadolinium is a soft, shiny, ductile, silvery metal belonging to the lanthanide group of the periodic chart. Gadolinium reacts slowly with water and dissolves in acids. A major source of Gadolinium Contamination in fresh water and drinking water system is the increasing use of Gadolinium-based contrast agents (GBCAs) for magnetic resonance imaging. There is specific concern regarding UV end-of-pipe water treatments, which may

degrade GBCAs and increase the risk of adverse health effects[12]. Every substitution of Gd<sup>3+</sup> from GBCA complexes by other metal ions, known as transmetallation, can also increase the toxicity of GBCAs by releasing toxic Gd<sup>3+</sup>. Iron (Fe<sup>3+</sup>), zinc (Zn<sup>2+</sup>) and copper (Cu<sup>2+</sup>) in particular, are in focus to be possible substituent because of their similar (or higher) thermodynamic stability and in vivo concentrations[13]. Soil is the major repository of elements obtained not only from close earth crust but also from irrigated water, the element present in the soil is taken by the plants which in turn taken up by humans and another one, so to study the distribution of several selected elements the vegetables, soil and water were analysed by ICPMs to assess the provenance and accumulation of minerals. The study with REEs in soil and their motility in plants are still limited instead of the fact the use of REES in recent years increasing.

**Table 1:Description of analysed vegetable samples**

Common name	Scientific name	Parts
Spinach	Spinaciaoleracea L	Leaf
Radish	RaphanusSativus L	Roots and leaf
Ridge Gourd	Luffaacutangula L	Fruit
Gourd	Lagenariasiceraria L	Fruit
Tomato	Solanumlycopersium L	Fruit

## 2.Materials and Methods



## 2.1 Description of study area

The study site has selected an area called Vrindavan under the Mathura district of U.P., INDIA. Vrindavan area of Mathura District is not treated as an industrial zone but plays a dominant role in the economic growth of the district. It is located approximate 145KM(90 mile) southeast of Delhi about 11KM(6.8mile) from the town of Vrindavan. Water, Soil and vegetable specimens were collected on 28 July.

## 2.2 Extraction of Metals

The water sample was collected from the Yamuna river near the Vrindavan site, about 7-8 liters of water samples were grabbed at approximate 2m depth from the surface of the water and stored in a clean bottle. After collecting the sample the extraction is done as per the method[14]. The soil sample was collected from one side of the Yamuna river from 5-10cm depth. The samples were about 200 gm in weight. The collected samples of vegetables were first dried in sunlight to remove all moisture. The dried samples were then powdered manually in a grinder and stored in polyethene bags. This dried sample of vegetables is now used for the digestion process as per the method given by John, 2003[15].

## 2.3 Method of analysis

A Jordan Valley EX-3600 M EDXRF spectrometer, equipped with an Rh source, an assembly of six filters (Cu, Fe, Mo, Rh, Sn and Ti) and Si(Li) detector with a 12.5  $\mu\text{m}$  thick beryllium window, was used for the analytes determination [Ref: Spectrochim Acta B 63 (2008) 817-819]. The instrument parameters described in the manufacture operation manual to 1500w should be chosen. By the use of shorter or longer integration times on the isotopes, the sensitivity may be influenced to some extent. Generally, three repeated measurements of each solution should be done. The ICPMS should warm up in full running mode for a minimum of 20 to 30min. The mass resolution, mass calibration, sensitivity and stability of the system are checked by the

use of a suitable optimizing solution. Different types of interferences can influence the result obtained by ICPMS measurement.

## 3. Result

The observed concentration of metals in vegetables, soil and water was compared with the recommended limit as established by the WHO/FAO and shown in table 2.

## 4. Discussion

The concentration of Mg and Na in water and soil sample is slightly lower than the permissible limit and the concentration of Mg and Na in vegetable samples comes out is  $>2000$  in Mg and  $>20$  in Na. But we don't have a permissible limit of Mg and Na for vegetables. Too much Mg does not pose a health risk in healthy individuals because the kidneys eliminate excess amounts in urine[16]. The concentration of K is absent in water & soil as well as in vegetable samples. The concentration of iron in water, soil and vegetables is lower than the permissible limit. Iron is a very essential element of our body. The average daily intake of iron in foods and supplements in children, teens, men and women is 13.7–15.1 mg/day, 16.3 mg/day 19.3–20.5 mg/day and 17.0–18.9 mg/day respectively. The concentration of iron is low is may be due to an increase in Mn and Zn concentration. Many studies reveal that a higher concentration of Mn and Zn will decrease the presence of iron. The concentration of Zn in the soil sample and two vegetable samples (Raphanus Sativus L and Luffa acutangula L) is a little higher than the permissible limits while in other samples is within the limit. The concentration of Cr in the water sample is (60mg/l) which is higher than permissible limits and in the vegetable sample Raphanus Sativus L(51mg/kg), luffa acutangula L(28mg/kg) and solanum Lycopersium L seeds (67mg/kg) concentration are higher than permissible limit(1.30mg/kg) recommended by WHO. While in the soil sample the concentration is (11mg/kg) which is lower than the standard

limit. The high concentration of Cr in water causes several adverse effects on vegetables and, in the long run, affects human health. Cr(III) toxicity is unlikely, at least when it is taken up through drinking water. It may even improve health, and cure neuropathy and encephalopathy. Cr(VI) is known for its extreme toxicity. It causes hypersensitive and asthmatic reactions and is 1000 times as

toxic as Cr(III), soil generally contains 2-100 ppm of chromium[17]. Who reports that high Cr(VI) concentration in soil affected shoot growth and it also led to decrease in plant height as reduced root growth, decrease nutrients and water transport to the edible part of the plant which results that Cr

**Table 2: Concentration of Metals in Vegetables, Soil and Water**

Elements	Radish leaves	Radish	Spinach	Ridge guard	Tomato seeds	Guard	WHO limits	Soil	WHO limits	River water	WHO limits
Cr	<10	51±5	<10	28±2	67±3	<10	1.30	11±1	100	60±4	50
Ce	<10	<10	147±7	22±1	167±12	83±5		189±13		50±3	
Dy	<10	244±12	<10	78±3	<10	<10		<10		<10	
Gd	33±2	555±22	<10	44±2	167±12	444±22		300±20		1040±40	
Eu	<10	<10	<10	<10	<10	<10		<10		<10	
Sm	<10	<10	<10	<10	<10	<10		<10		<10	
Mg	2100±120	700±35	144±10	<10	2200±120	67±4		630±25		5400±200	30,000
Ca	22±2	<10	22±1	<10	<10	11±1		11±1		<10	75,000
K	<10	<10	<10	<10	<10	<10		<10		<10	10,000
Na	33±2	17±1	22±2	10±1	128±11	78±3		22±2		220±20	20,000
Fe	<10	13±1	<10	17±1	<10	<10	425	11±1	150	11±1	300
Co	<10	<10	39±2	<10	<10	510±25		<10	-	<10	-
Mn	<10	39±2	600±12	580±25	144±8	220±12	0.2	250±13	20-50	1100±40	100
Zn	<10	33±2	<10	22±2	<10	<10	0.6	66±5	50	167±10	3,000
Ni	133±8	11±1	22±2	17±1	11±1	33±2	10	124±11	35	<10	20
Pb	<10	<10	110±5	17±2	<10	39±3	2	<10	85	<10	10
Cd	55±3	<10	220±14	121±11	67±3	11±1	0.02	<10	0.8	30±2	3

4toxicity present in the growth of edible vegetable seed in Cr polluted soil[18].The concentration of Ni is higher in soil samples (124mg/kg) and vegetables, Spinacia Oleracea L(22mg/kg) and Luffa Acutangula L(17mg/kg), Raphanus Sativus leaves(133mg/kg), Solanum Lycopersicum seeds(33mg/kg) are higher than permissible limits recommended by WHO, while in the water sample Ni is absent. High Nickel concentration may through other heavy metals. the high amount of Ni retard shoot and root growth, affect branching development, deform various plant parts, produce abnormal shape, induce leaf spotting, disturb mitotic root tips, and produce Fe deficiency that leads to chlorosis and foliar necrosis[19].Dietary iron intakes appear to be inversely associated with manganese absorption. Humans absorb only about 1% to 5% of dietary manganese. Mn absorption efficiency increases with low Mn intakes and decreases with higher intakes. it is not only necessary for humans to survive, but it is also toxic when too high a concentrations are present in the human body. The concentration of Mn was recorded between 39mg/kg to 600mg/kg. Mn maximum concentration is 600mg/kg in Spinacia Oleracea L and 580 in Luffa Acutangula L, the concentration of water and soil is also higher. This concentration is much higher than the safe limit as proposed by FAO/ WHO. Manganese may reach toxic levels due to increased solubility of its reduced  $Mn^{2+}$  oxides. Mn is present as Mn(II), Mn(III) and Mn (IV) in which Mn(II) is the dominant form in plants but it can be easily oxidized into Mn(III) and Mn (IV)[20]. Divalent  $Mn^{+2}$  is three times more toxic than trivalent  $Mn^{+3}$ . Pb has no biological function it isn't essential and is harmless and found in the environment, air, water, soil and food. in this study, The concentration of Pb in three vegetables spinach Oleracea L, Luffa Acutangula L and LaGuardia Siceraria L (110mg/kg),(17mg/kg),(39mg/kg) is higher than the permissible limit recommended by

the WHO which is very hazardous. Pb is one of the most toxic heavy metals that have a soil retention time of 150–5000 years and is reported to maintain its concentration high for as long as 150 years[21]. In our study, Pb is not detected in soil and water. The concentration of Cd found in the Water sample (30 mg/l) and some vegetable samples like Raphanus Sativa L(55mg/kg), Spinacia Oleracea L(220mg/kg), Luffa Acutangula L(121mg/kg) are more than permissible limits while in Radish and Guard level the concentration of Cd is absent as well as in soil sample. The concentration of Cadmium mostly occurs in the earth's crust in combination with zinc and some other elements and has no significance in plants; instead higher concentration can be toxic for both plants and animals. Ce, Sm and Eu are light REEs, Ce being the most abundant element found in water, along with other areas. Cerium enhances germination and shoot growth, and alters mineral nutrient concentration[22]. These elements are present in some vegetables but we don't have any reference for their permissible limits. In roots, concentrations of Ca, Fe, Mn, and Zn decreased at higher Ce concentrations, while Mg concentration increased[23]. Ce can also interfere with the absorption of K, Mg, Ca, Na, Fe, Mn, Zn, Cu and Mn in roots and shoots[22]. While Gd and Dy are HREEs, The concentration of Gadolinium is present in vegetable samples to a large extent; no study reveals the presence of Gd in plants. Eu and Sm are not essential elements and in our study, both these elements are not detected, so Eu and Sm will be considered safe limits because we don't have any references for their permissible limits.

#### 4.1 Calculation of daily intake of metals

Daily intake of metals depends on the concentration of the metal in the vegetables, its daily consumption and body weight and DMI is calculated by using the following equation

Daily Metal Intake from vegetables (DMI) = (C metal x D food intake) /PBW

where C= metal concentration in vegetables in mg/kg, D= daily intake of vegetables in kg/person, and PBW= average person's body

weight in kg (65 kg adults, 22 kg children).The amount of vegetables required in our daily diet is at least 400 grams, which is suggested by the WHO per person in adults[24].

**Table 3: Average Daily Intake of Metals**

Elements	Avg. Conc. Of 6 vegetables (mg/Kg)	Intake by human being (mg/g)	RfD *
Cr	82.16	11.68	105
Ce	45.34	8.63	
1`2q	53.66	38.64	
Gd	207.16	59.06	
Fe	5	3.60	10.0-60.0
Co	91.5	10.80	3.010
Mn	263	67.67	0.5-5.0
Zn	9.16	0.66	15.00
Ni	27.66	3.561	1.40
Pb	24.83	13.28	0.245
Cd	77.16	3.16	0.070
Mg	868.5	1157.33	
Ca	9.16	4.40	
Na	48	11.62	

**Bio-Concentration Transfer Ratio**

BCTR is defined as the uptake of contaminants from the dissolved phase; it can be calculated by the following equation:

**BCTR=Metal(veg.conc.)/Metal(Soil conc.)**

**Bio-Concentration Transfer Ratio from soil to vegetables**

Soil to plant bio-concentration ratio of metals mainly depends on temperature, pH and electrolyte concentration of the soil. It observed that Na and Mn have higher BCTR for all types of vegetables and range from 0.45(Luffa Acutangula L) to 5.81 (Lagenaria Siceraria L) and 0.156 (Raphanus sati us L) to 2.4(SpinaciaOleracea L) respectively. The transfer ratio for Fe, Zn, and Ni is comparatively low in all varieties of vegetables. Gd showsa high value of transfer

ratio in non-leafy vegetables whereas it is absent for SpinaciaOleracea L. Cr shows a high BCTR value but is found in only three varieties of vegetables. The transfer ratio for Cr is found in three non-leafy vegetables and ranges from 2.54 (Luffa Acutangula L) to 6.09 (Solanum Lycopersicum L). For other elements/ metals like Ce, Dy, Eu, Sm,K, Co, Pb, and Cd; there is no soil to plant transfer factor observed. Soil to plant BCTR is mainly observed in edible parts of studied vegetables in the order Raphanussativus (L) > Luffa Acutangula> Lagenaria Siceraria> Solanum Lycopersicon L> Spinacia Oleracea> Raphanus sativus L (leaf).

**Table 4: The BCTR value of Cr,Gd,Ca,Na,Fe,Mn, and Ni for various vegetables show great variations**

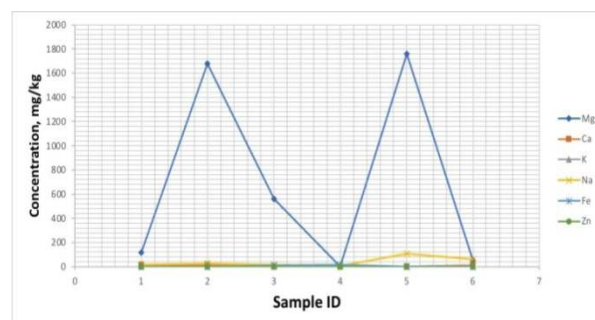
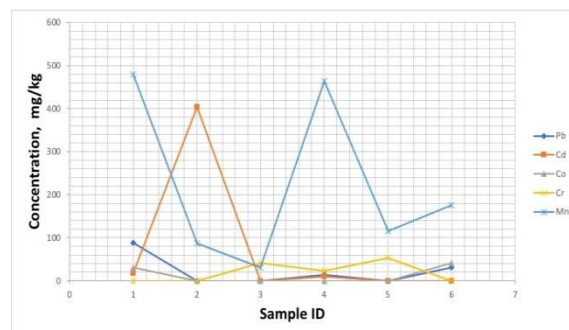
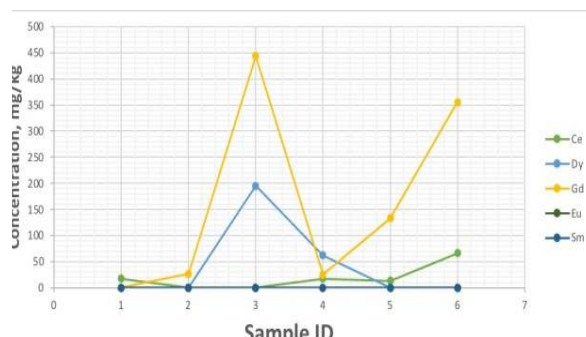
Vegetables/metals	Cr	Gd	Ca	Na	Fe	Mn	Zn	Ni
Spinach	—	0.11	2	1.5	—	—	—	1.07
Radish leaves	—	1.85	—	0.77	1.18	0.156	0.5	0.08
Radish	4.63	—	2	1	—	2.4	—	0.17
Ridge gaurd	2.54	0.14	—	0.45	1.54	2.32	0.33	0.13
Gaurd	—	0.55	1	3.54	—	0.57	—	0.088
Tomato seeds	6.09	1.48	—	5.81	—	0.88	—	0.266

### 5.Conclusion

Among the 17 elements, the concentration of Fe, Cr, Ni, Mn, Cd, Pb, Gd has crossed the permissible limits. The concentration of all these elements in water is higher than permissible limits whereas in the soil only Cr, Ni and Mn have increased, in which Cr, Cd, Pb and Gd are very toxic metals and the presence of these elements in the water is very hazardous, as water used in irrigation in that case elements are transmitted into soil and vegetables. Water that has increased the concentration of metals should not be used in irrigation, as it will reach the biological system through the food chain. The transfer ratio of Na, Mn, Ni, Cr, and Gd from soil to vegetables was found to increase, in which Gd and Cr are toxic and are mainly observed in edible parts.

Throughout the study, it was observed that the edible parts had a higher concentration of these elements in comparison to leafy vegetables. As these plants are consumed by humans, toxic

elements can be transferred to the human body disrupting various biological systems. Therefore workers and residents of these areas might be a health risk from toxic metals exposure.





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