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## RESEARCH ARTICLE

### HEAVY METAL ANALYSIS OF GANGA AND YAMUNA RIVER WATER

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#### ABSTRACT

Analysis was conducted for the concentration of Chromium (Cr) and Nickel (Ni) in the river Ganga on four sampling sites at Prayagraj Uttar Pradesh and the bioaccumulation of these heavy metals in the crops grown in the area. The main aim of this analysis was to analyze the concentration of these heavy metals and study their bioaccumulation and biodistribution in the crops and assess their effects on human and aquatic life. The concentrations of these heavy metals were compared with WHO 1993. The concentrations were found to be above the maximum permissible limits, showing detrimental effect of their presence on crops grown near the sampling sites.

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#### INTRODUCTION

Water is the most important resource to maintain life on this planet. The river Ganga is the most important river system in India. Due to the abundant availability of water throughout the year, it has played a major role in the development of Indian civilization and economy (Paul, Sinha, 2013). In India, water of many rivers has a special place in all religious activities. A large number of rivers and ponds have religious significance. Religious feelings of many pilgrims are so strong that they still consider these waters pure and sacred and consume it particularly during all religious ceremonies. Ganga river is one of those rivers which is most sacred river of India. Due to increase in population, urbanization and industrialization, water quality of Ganga river has been damaged and compromised by domestic sewage and industrial effluents, which contain a large number of chemicals and heavy metals (Pandey *et al*, 2011). After entering the water stream, metals are taken by many organisms and flora and eventually, they are stored in marine organisms and plant systems which are readily consumed by humans (Asaolu, *et al*, 1997). Due to the increased use of metal-based fertilizers in the agricultural revolution of government, due to water-scarcity, the

concentration of metal population in the fresh water has increased substantially. In river waters, metals are in the form of a mixtures, soluble and insoluble form such as ionic species, inorganic and organic compounds that are connected to the colloids and suspended particulate matter (Mitra, 2000), (Avantika, 2013). Metals are probably the most harmful pollutants because of their ability to create adverse effects on account of their non-biodegradability and its implications on nature and human beings, if their concentration exceeds the permissible limit (Lokhande, 2000), (Avantika, 2013). Metals enter the water system by natural or man-made sources, various industries and domestic sewages are included in the anthropogenic sources. Industries that emit metals in electrical industry, paints and pigment industries, ceramic pulp and paper industry, cotton textiles, steel plants, galvanization of iron products, iron and mining industries (Tyagi *et al*, 2000), (Avantika, 2013). These metals even in low levels, have cumulative effect on drinking water and groundwater (Prabha, 1997), (Avantika, 2013). Various environmental factors like temperature, pH, water hardness, dissolved oxygen, salinity, and organic matter can affect toxicity in metals (Bryan, 1976), (Dojlildo, 1993), (DWAf, 1996), (Avantika, 2013). In addition, the reduction of natural eradication procedures for metals increases the situation. As a result, the metal often comes in second place through harmful bioaccumulation in the second compartment, from one compartment to another within the aqueous environment.

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Food chain transfers increase toxic exposure in humans (Rainbow, 1985), (Sanders, 1997), (Avantika, 2013). As a result of adsorption and accumulation, the concentration of metals in the sediment below is expected to be higher than the above water and it can sometimes cause secondary pollution, therefore, the sediments below are the reserves of heavy metals in high concentration. Metals in natural water can actually exist in dissolved colloidal and suspended forms (Avantika, 2013). This invaluable resource was reduced to a convenient means of disposal of waste. Waste water, such as municipal sewage, is a major culprit followed by industrial waste and agricultural run-off. Permanent restructuring of the river and its environment was the result of the diversity of various construction activities, and the replacement of the natural environment by a newly built environment with long-term and long-lasting results in the current biological species and physical conditions of the region (Bhadula *et al*, 2014), (Matta *et al*, 2011).

**Study Area:** Allahabad is situated at a height of 98 meters (322 feet) in the southern part of Uttar Pradesh at 25.45 ° N 81.84 ° E and the two rivers Ganges and Yamuna are located here and the confluence of these two visible and the invisible river Saraswati is referred as *Sangam*. This region was known in ancient times as the Vats country. It has Bundelkhand region in its south and south-east, east of it is the middle Ganges valley of North India or Purvanchal, it has Bundelkhand region in its south-west, it is the northwest and north-east region of Awadh and is located in the direction west with Awadh region, and Kaushambi makes it a lower Doab area. The two rivers Ganga and Yamuna serve as the primary source of drinking water and its water is also used for irrigation in the areas adjacent to the river bed. Water samples were collected from Baluaghat, Shastri Pool, Sangam and Tiveni Ghat regions surrounding the river beds of Ganga and Yamuna.

## MATERIALS AND METHODS

**Sample Collection:** Water samples were collected from Ganga and Yamuna rivers and their confluence site, *Sangam*. Samples were collected from about 20 – 30 cm below the water surface in triplicates by keeping the mouth of the sample bottles against the water flow direction. All containers were washed and de-contaminated with distilled water and acid (APHA, 2012). The samples from four different sites of the River Ganga and Yamuna were taken on different dates and at regular time intervals. The sites were:

- Baluaghat - 25°25'23.99' N, 81°50'27.26' E
- Shashtri Bridge - 25°26'8.31' N, 81°53'25.25' E
- Sangam - 25°25'13.00' N, 81°53'22.83' E
- Triveni - 25°24'31.84' N, 81°53'34.73' E

The sampling dates were 04 February 2019, 25 February 2019, 18 March 2019 and 15 April 2019.

**Determination of Heavy Metals:** For sampling, the containers were washed thoroughly and again filled with 8N HNO<sub>3</sub>. Then to reduce the adsorption of metals in container, 5 ml HNO<sub>3</sub> per liter was added at the time of collection. For analysis of heavy metals, HNO<sub>3</sub> at the rate of 4 ml per liter sample was evaporated to about 50 ml in the beaker on the water bath and then cooled. In a 100 ml measuring cylinder, 2 ml HCl was added, the solution was added to 100 ml distilled water.

The analysis of acidic samples was done for heavy metals with the help of Atomic Absorption Spectrophotometer (AAS) Perkin Elmer AA 400. The samples were directly aspirated into the air–C<sub>2</sub>H<sub>2</sub> flame of AAS and absorbance was measured at different wavelength. The metals determined were Nickel (Ni) and Chromium (Cr) (Avantika, 2013).

## RESULT AND DISCUSSION

**Chromium (Cr):** In this study the chromium values ranges between 0.04 mg/l - 0.08mg/l of water which is more than the permissible limit (WHO, 1993) (Table 2). In water, lower concentrations of Cr do not affect the human health while higher concentration of Cr in water causes disorder of skin and respiratory tract. The high concentration of Chromium is found in ground water, which may be possible due to the presence of dairies, small tanneries, sugar manufacturing and refractory industries in the region which discharge their effluents in the open drainage and on the land surface and in the rivers. The maximum values of Chromium may be attributed to huge amount of domestic sewage with organic pollutant containing heavy metals and particularly which is disposed off into the river (Avantika, 2013), (Odeyemi *et al*, 2011).

**Table 1. Permissible limits of Heavy Metals in Drinking Water (WHO, 1993)**

Heavy metal	WHO
Chromium	0.05(mg/l)
Nickel	0.02(mg/l)

**Nickel (Ni):** In this study the nickel values ranges between 0.03 mg/l - 0.08 mg/l of water which is more than the permissible limit (WHO, 1993) (Table 2). Free Nickel mostly occurs in Ni<sup>2+</sup> cationic form. Ni interacts with organic matter (which ranges from 3-5% to 5.3%) in the aqueous phase and settles down, resulting in its higher concentration in sediments (Avantika, 2013), (Israilli and Khursheed, 1991). High concentration of both Chromium and Nickel is detrimental to human health and can cause severe effects on human physiology and also on physiology of plants grown in such areas. The bioaccumulation and biodistribution of heavy metals in vegetable plants is also of great concern and its analysis will be done at a later stage.

**Effects of Chromium on Human:** Major factors governing the toxicity of chromium compounds are oxidation state and solubility. Cr(VI) compounds, which are powerful oxidizing agents, tend to be irritating and corrosive, appear to be much more toxic systemically than Cr(III) compounds, given similar amounts and solubilities. Although mechanisms of biological interaction are uncertain, this variation in toxicity may be related to the ease with which Cr(VI) can pass through cell membranes and its subsequent intracellular reduction to reactive intermediates. Since Cr(III) is poorly absorbed by any route, the toxicity of chromium is mainly attributable to the Cr(VI) form. It can be absorbed by the lung and gastrointestinal tract, and even to a certain extent by intact skin. The reduction of Cr(VI) is considered to serve as a detoxification process when it occurs at a distance from the target site for toxic or genotoxic effects while reduction of Cr(VI) may serve to activate chromium toxicity if it takes place in or near the cell nucleus of target organs. If Cr(VI) is reduced to Cr(III) extracellularly, this form of the metal is not readily transported into cells and so toxicity is not observed.

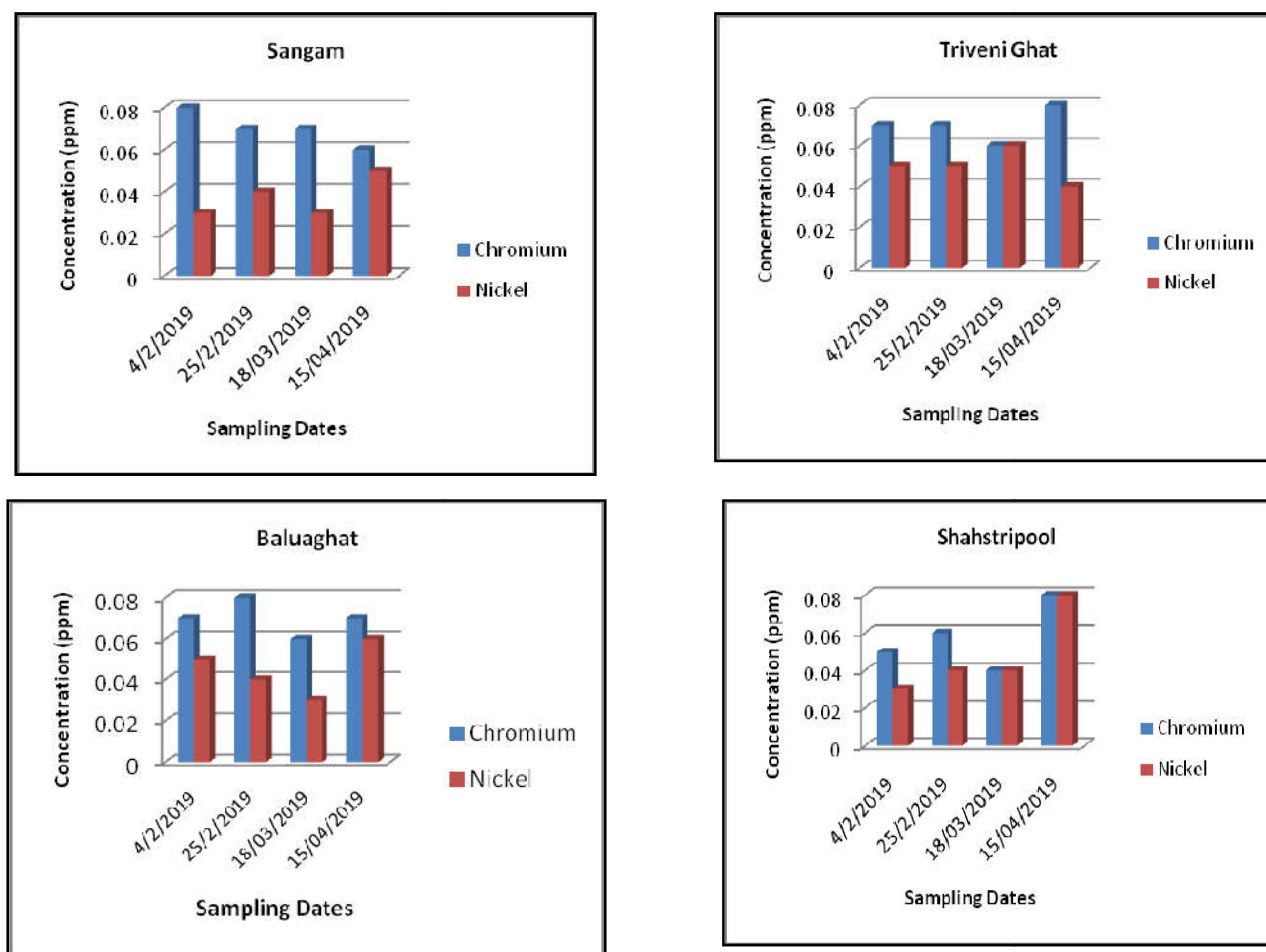


Figure 3. Graphical representation of variation of heavy metals at certain sites

The balance that exists between extracellular Cr(VI) and intracellular Cr(III) is what ultimately dictates the amounts and rates at which Cr(VI) can enter cells and impart its toxic effects. Cr(VI) enters many types of cells and under physiological conditions can be reduced by hydrogen peroxide ( $H_2O_2$ ), glutathione (GSH) reductase, ascorbic acid, and GSH to produce reactive intermediates, including Cr(V), Cr(IV), thiyl radicals, hydroxyl radicals, and ultimately, Cr(III). Any of these species could attack DNA, proteins, and membrane lipids, thereby disrupting cellular integrity and functions.

**Skin Effects of Chromium Toxicity:** Dermal exposure to chromium has been demonstrated to produce irritant and allergic contact dermatitis. Primary irritant dermatitis is related to the direct cytotoxic properties of chromium, while allergic contact dermatitis is an inflammatory response mediated by the immune system (Israilli and Khursheed, 1991). Allergic contact dermatitis is a cell-mediated immune response that occurs in a two-step process. In the first step (induction), chromium is absorbed into the skin and triggers the next step - an immune response (sensitization). Sensitized individuals will exhibit an allergic dermatitis response when exposed to chromium above a threshold level. Localized erythematous or vesicular lesions at points of contact or generalized eczematous dermatitis should suggest sensitization (Avantika, 2013). Chromium allergic dermatitis is characterized by symptoms of dryness, erythema, fissuring, papules, scaling, small vesicles, and swelling (Israilli and Khursheed, 1991). Solubility and pH appear to be the primary determinants of the capacity of individual chromium compounds to elicit an allergic response (Odeyemi *et al*, 2011).

The low solubility Cr(III) compounds are much less efficient contact allergens than Cr(VI) (Peralta *et al*, 2001).

**Effects of Chromium on Plant:** Chromium is known as a poisonous metal that can damage plants and animals. In chromium-induced oxidative stress, plants contain lipid peroxidation which causes severe damage to the cell membrane. Chromium-induced oxidative stress initiates the erosion of photosynthetic pigments that lead to development. High chromium concentrations may disturb the chloroplast ultra structure to the photosynthetic process. Since germination of seed is the first physical process affected by Cr, the ability of seed to germinate in a medium through Cr will indicate the level of tolerance to this metal (Peralta *et al*, 2001). Germination of *Echinocola Colona* seed with weeds was reduced to 25% with 200  $\mu$ M Cr (Rout *et al*, 2000). The high level of hexavalent Cr (500 ppm) in the soil reduces germination by 48% in the bushing of *Phaseolus vulgaris*. Peralta (Peralta *et al*, 2001) found that 40ppm Cr had reduced the capacity of 23% of the seeds of *Lucerne (Medicago sativa)* to germinate and grow in the contaminated medium (Wang, 1996). The decrease of 32-57% in germination of sugarcane was seen with 20 and 80 ppm Cr respectively (Srivastava *et al*, 2000). The reduced germination of seeds under Cr stress could be a depressive effect of Cr on the activity of amylases and on the subsequent transport of sugars to the embryo axes. On the other hand, protease activity increases with the Cr treatment, which can contribute to decrease in germination of treated seeds (Zaid, 2001). Due to heavy metals in trees and crops, due to lack of root development, there is a well documented effect (Tang *et al*, 2001), (Thomas *et al*, 1998).

Prasad (Prasad *et al*, 2001) pointed out that the new Root primordia in *Salix Viminalis* has a sequence of metal toxicity  $Cd > Cr > Pb$ , while the length of the root was affected more than the Cr compared to other heavy metals studied. Chromium stress is one of the key factors affecting photosynthesis in terms of  $CO_2$  fixation, Electron transport, Photophosphorylation and Enzyme activities (Clijsters and Assche, 1985). In higher plants and trees, chromium's effect on photosynthesis is well documented. However, it has not been well understood that the extent of Cr-induced barrier of photosynthesis is due to the disorganization of the chloroplast's ultra structure, the barrier of electron transport or the effect of Cr on the enzymes of the Calvin cycle.

The Chromate is used as a Hill reagent by isolated chloroplast. Chromium stress can induce three possible types of metabolic modification in plants (i) alteration in the production of pigments, which are involved in the life sustenance of plants (e.g., chlorophyll, anthocyanin) (Boonyapookana *et al*, 2002) (ii) increased production of metabolites (e.g., glutathione, ascorbic acid) as a direct response to Cr stress, which may cause damage to the plants and (iii) alterations in the metabolic pool to channelize the production of new biochemically related metabolites, which may confer resistance or tolerance to Cr stress (e.g., phytochelatins, histidine) (Schmfger, 2001).

**Effect of Nickel on Human:** An allergic reaction (contact dermatitis) usually begins within hours to days after exposure to nickel. The reaction may last as long as two to four weeks. The reaction tends to occur only where your skin came into contact with nickel, but sometimes may appear in other places on your body. Nickel allergy signs and symptoms include: (a) Rash or bumps on the skin Itching, (b) Dry patches of skin that may resemble a burn, (c) Blisters and draining fluid in severe cases which may be severe, (d) Itching, which may be severe, (e) Redness or changes in skin color (Schmfger, 2001).

**Effect of Nickel on Plant:** Nickel is an essential nutrient for plants. However, the low volume required for normal development of plants is very low. Therefore, it is necessary to understand the functional roles and toxic effects of Ni in plants, with the level of Ni pollution in the environment. The concentration of  $Ni^{+2}$  in the polluted soil can be up to 20 to 30 times (200-26,000 mg / kg) from the overall range (10-1,000 mg / kg) found in natural soil (Izosimova, 2005).

However, the concentration of  $Ni^{+2}$  is increasing in some areas such as mining works, emissions of smelters, burning of coal and oil, sewage, phosphate fertilizers and pesticides. Excess of  $Ni^{+2}$  in the soil causes various physical changes and symptoms of various toxicity such as chlorosis and necrosis in different plant species, including rice (Zornoza *et al*, 1999), (Rahman *et al*, 2005), (Das *et al*, 1997). Plants grown in high  $Ni^{+2}$  containing soil showed impairment of nutrient balance and resulted in disorder of cell membrane functions. Thus,  $Ni^{+2}$  influenced the lipid composition of the plasma membrane and the H-ATPase activity (Ros *et al*, 1992), as stated in the *Oryza sativa* shoot (Das *et al*, 1997). Other symptoms seen in  $Ni^{+2}$  treated plants were related to changes in water balance. High uptake of  $Ni^{+2}$  has led to the decline in the water content of species of dicot and monocot plants. The reduction in water indigestion is used as an indicator of the progress of  $Ni^{+2}$  toxicity in plants (Pandey and Sharma, 2002), (Gajewska *et al*, 2006). In Pigeon pea (*Cajanus cajan*) plant, Ni decreases chlorophyll content and stomatal conductance; decrease

enzyme activity which affected Calvin cycle and  $CO_2$  fixation (Sheoran *et al*, 1990). Due to nickel concentration, Rye grass (*Lolium perenne*) also showed reduction in plant nutrient acquisition along with decrease in shoot yield and chlorosis (Khalid and Tinsley, 1980).

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