

Analysis of Some Selected Heavy Metals in Effluent of Badarpur Thermal Plant

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ABSTRACT

The most prominent issue being studied today is water pollution as water is the basic need of life. The presence of metal in the atmosphere, soil and water poses a serious problem to the human health. Some metals are biologically important in trace amount but in excessive amount they are poisonous and can even cause death to most of the living organisms. Heavy metals such as cadmium, copper, lead chromium and mercury are important environmental pollutants which poses a threat to the environment. Essential sources of heavy metals in waste water are present in urban areas and industrial effluents, deterioration of sewerage pipe and treatment works, and the wear of household plumbing fixtures. The free metal ions and their labile complexes are more in the receiving water than the stable complexes which impart toxicity to the water body. Depending on the relative concentration of the different forms of these metals in water, have deleterious effect. The metal effluent treatment before dumping is likely to be most effective tool at the sources of the pollution where concentration is highest. This paper observes the analysis of certain heavy metals (Fe, Cu, Zn, Cr, Cd, Hg, As, Pb) in effluent of ash pond overflow and discharge channel of Badarpur Thermal Power station, weather the concentration of these metals lies between the standard ranges or not .This comprehensive literature will help in analyzing the concentration of heavy metals from different sampling sites.

Keywords: Badarpur Thermal Power Station (BTPS), Heavy Metals.

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Introduction

The word "Pollution" is derived from the Latin word "Pollutio" meaning defilement. Pollution of water bodies is steadily due to rapid population growth, industrial proliferations, urbanizations, increasing living standards and wide spheres of human activities. According to President's Science Advisory Committee, Washington (1965), water pollution may be defined as "Alteration in physical, chemical and biological characteristics of water, which may cause harmful effects on human and aquatic biota" (Mishra, 2008).

Metals present in the atmosphere, soil and water can cause serious problems to all the organisms. The mobilization of heavy metals into the biosphere by human activities has become an important process in the geochemical cycling of these metals. This actually evident in urban areas where various stationary and mobile sources release large quantities of heavy metals into the atmosphere, soil and water, exceeding the natural emission rates. Heavy metal intake by human population through the food chain has been reported in many countries. This problem is receiving increasing attention from the public as well as Government agencies, particularly in developing countries. Heavy metals possibly the most persistent in the environment pose a threat to the aquatic species and have detrimental effects on aquatic organisms. They have reached higher trophic levels through food chain (Harvey, 1974). Attention has been focused on heavy metals

as environmental pollutants since the occurrence of Minamata disease caused by

methyl mercury poisoning (Takeuchi *et al.* 1962). There are 106 elements in the periodic table; of this 38 are heavy metals. Only 18 of these elements are toxic. Many authors employ the less evocative term "trace metals". These heavy metals have a specific gravity of 4-5 times greater than that of water and usually belong to atomic numbers 22-34 and 40-52 and are members of lanthanides and actinides of the periodic table (Murphy, 1981).

Elevated level of heavy metals in the water can be attributed to both natural and anthropogenic sources. The most significant source of metals is weathering of rocks and volcanic activities from which they are released and find their way into the water bodies (Viner, 1975 a). A large quantity of metals also suspend into the atmosphere from where they can reach the water through dry deposition and precipitation. The natural sources of atmospheric contamination are mainly the dried water droplets from oceans, dust particles from volcanic eruptions, erosion of soil, weathering of rocks and forest fires. The important toxic metals are Be, Pt, Hg, Ti, V, Te, U, Co, Fe, Se, Cd, Sb, Pd, As, Cr, Ni, Zn and Mn. Many of these metals are essential for the growth of the organisms at lower concentrations but they become poisons when their concentration exceeds beyond certain levels. Their toxicity varies with threshold limiting value (TLV) =2 µg/m³ to 5000 µg. This is the maximum

tolerable limit for a human being. The different metals have different degree of toxicity.

India is one of the tenth industrialized countries of the world. Due to rapid progress made in industrialization without adequate environmental safety measures, pollution of water bodies in India have become a common feature. Metallic cations and anions (example chromate) appear in the effluent of a variety of processes. As the effluents are discharged into rivers, aquatic organisms readily absorb heavy metals from a biotic environment by a number of mechanisms. The increasing use of coal for power generation results in an increasing potential for adverse environmental impacts. One of these emanates from the disposal of ash from thermal power plants through settling ash ponds. Overflow and leachate from these ash ponds are discharged to adjacent receiving water bodies. And environmentally important by component of these discharges is toxic metals. Although they are generally present at relatively low concentration in coal, significant mobilization still occurs because of the very large quantities of coal consumed. Therefore, it is imperative to excess their impact, particularly on the receiving water.

Dennis *et al.* (2000) studied a new Biotechnology for recovering heavy metal ions from waste water. By this technology they recover all heavy metals from waste water. The concentration of metals was found high.

Fernandez-Turiel *et al.* ((2001) found elevated levels of heavy metals in urban soils located within the vicinity of a Pb smelter in Lastenia, Argentina. The heavy metals were found at elevated, concentration that i.e Pb (31-8714mg/Kg), Cd (0.27-30.68mg/Kg), Cu (21-242mg/Kg) and Zn (44-4637mg/Kg).

Yadav *et al.* ((2003) carried out a study on potentials and hazards associated with sewage irrigation in Haryana and found higher levels of heavy metals in sewage water, soil and crops.

Aslam *et al.* (2004) have studied the removal of Cu from industrial effluent by adsorption with economical viable material. The removal of heavy metals from electroplating waste water with economically feasible material was investigated. Leachate samples were analyzed for concentration of these elements by A.A.S. The results revealed that the removal efficiency of Cu was high from 97-70%.

Sial *et al.* ((2006) have studied the quality of effluents from Hattar industrial state. The major industries including textile, food industries, ceramics, steel, leather, tanning developed with proper planning discharging their effluents in nearby natural drains and ultimately to collected in a big drain near Wah. These effluents were analyzed for heavy metals and the result revealed that toxic metal load in all the effluents is above the limit ie 2.0 mg/L. Copper and Iron were higher than NEQS.

Oliveri *et al.* (2007) have determined that the presence of heavy metals in waste water which is one of the main cause of water pollution. They aimed removal of Cu, Cd, Pb, Zn, Hg, Mn, Cr in urban effluent by biological waste water treatment as well as to quantified levels of As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Sn, Zn and Pb in dewatering in sludge from biological waste water treatment plant. The percentage of removal efficiency was following- Hg-61.5%, Cd-60.0%, Zn-44.9%, Pb-39.7%, Cr-16.5% and Mn-104%. In turn the mean concentration (mg/Kg) of metals in dewatering sludge followed this increasing order. Hg-0.31%, As-1.14%, Cd-1.34%, Pb-132.1%, Cr-0195.0%, Cu-391.7%, Zn-864.4%, and V-59.2%.

Islam *et al.* (2007) studied on assessing potential dietary toxicity of heavy metals in selected food crops in China. These metals enter the human body mainly through two routes namely inhalation and ingestion, and

Material and Methods

The materials and method include the following aspects:

- 1) Location of sites
- 2) Collection of samples
- 3) Metals analyzed
- 4) Instrument used

1. **Location of sites:** Site selected for the present study is Badarpur Thermal Power Station (BTPS) of NTPC. BTPS is a 720-mw power station is situated at the southern most fringe of metropolitan

with ingestion being the main route of exposure to these elements in human population.

Thus keeping the above in the view the aim of the present study is to analyze some heavy metals in effluent of Badarpur thermal power plant, Delhi. The speciation of eight environmentally important heavy metals, viz, Fe, Cu, Zn, Cr, Cd, Hg, As, Pb has been investigated in the discharge channel and ash pond overflow. They find their way through a canal to the receiving water of the river Yamuna. Depending on the relative concentration of the different forms of these metals in water and various sizes of suspended particulates, these have a deleterious effect on water quality. In this paper we have attempted to summarize the analysis of concentration of different heavy metals from different places.

city. It is located near Tuglakabad railway station. The ash disposal area is located between Agra canal and Yamuna River at a distance of about 2.5 km from the BTPS. The site is accessible from Delhi-Mathura highway.

2. **Collection of samples:** The samples were collected from the Ash pond overflow and from Discharge channel of BTPS. The sampling point was chosen carefully so that a representative sample of the effluent to be tested is obtained. During taking the sample every possible precaution was taken so as to reduce the possibility of any error during

analysis and to prevent the result from being biased. The clean and dried glass bottles were used for the collection of effluents which were thoroughly rinsed with concentrated HNO_3 and then rinsed well with (DDW) Double Deionized Water. For the sample preservation the effluent was treated with conc. HNO_3 i.e. 5ml HNO_3 in 100 ml of sample to reduce the pH. 10 ml of sample is required for each metal detection hence approximately 100ml of each sample was collected for various metal detection.

3. **Metals analysed:** Following metals were analysed by AAS-Fe, Cu, Zn, Cr, Hg, As and Pb.

Iron:

Principle: All the Fe is converted into ferrous state by boiling with hydrochloric acid and hydroxyl amine. The reduced ion chelates with 1, 10-phenanthroline and pH 3.2 to 3.3 to form a complex of orange-red colour. The intensity of this colour is proportional to the concentration of iron and follows Beer's law, and therefore, can be determined colorimetrically.

Strong oxidizing agents like cyanide, nitrite and phosphates, chromium, zinc, cobalt, copper and nickel interfere with the determination of iron. The boiling of the sample with an acid initially removes interference of cyanide, nitrite and polyphosphates. Hydroxylamine eliminates the interference caused by strong oxidizing agents. Bismuth, cadmium mercury and silver precipitate the phenanthroline and error caused by them and other metals can be overcome by using excess of phenanthroline.

Procedure-Fe was analyzed by AAS.

Zinc:

Principle: A blue colored complex is formed by zinc with 2-carboxy 2'-hydroxy-5-sulphoformazyl benzene (zincon), in a solution buffered at pH 9. The intensity of this color can be measured by a spectrophotometer.

Many other heavy metals are also complexed to give colors with zincon. All the metals are first complexed with cyanide and then chloral hydrate or cyclohexanone is added to free the Zn from cyanide complex.

Procedure-Zn was analyzed by AAS.

Chromium:

Principle: A compound of red violet color is formed by the reaction of dissolved hexavalent chromium with diphenylcarbazide in acid solution. Total (dissolved + particulate) chromium can be obtained after digestion of sample with $\text{H}_2\text{SO}_4\text{-HNO}_3$. For determination of total dissolved chromium, the trivalent chromium can be oxidized to hexavalent by potassium permanganate. The excess KMnO_4 is then destroyed by sodium azide (NaN_3).

The reaction is highly specific for Cr, however Mo can be tolerated up to 200mg/l. The vanadium should not be more than 10 times to that of the concentration. Iron in excess of 1mg/l produce yellow color, but the color is not strong enough to interfere at specific wavelength for chromium determination.

Procedure-Cr was analyzed by AAS.

Cadmium:

Principle: Cadmium ions react with dithizone to form a pink-red color. The color so determined is extracted with chloroform and can be determined by colorimetrically.

Mercury:

Principle: The colorometric methods suggested for Hg, for example, dithiozone extraction method, are not reported to give accurate results due to large number of interferences. The best method for detection of Hg is to employ flameless atomic absorption spectrophotometry where no flame is required for atomization. The Hg is reduced to elemental state and then volatilized by simple aeration with air. These volatile Hg vapours pass through a cell in the light path radiation at 253.7 nm by Hg cathode lamp of a spectrophotometer. Absorbance of the light is measured as a function of mercury concentration.

A large No. of designs of the flameless atomic absorption spectrophotometers are available. Some are made exclusively for the measurement of Hg and are called as mercury analysers.

Procedure: Hg was analysed by AAS.

Arsenic:

Principle: Arsenic in presence of Zn in acid medium gets reduced to arsine, AsH_3 . Arsine is then passed through a scrubber containing glass wool soaked with lead acetate, and later is absorbed in silver diethyl-dithiocarbamate dissolved in pyridine. Arsenic reacts with the silver salt to form a red complex which can be determined by colorimetrically.

Many other metals such as Cr, Co, Cu, Hg, Mo, Ni, Pt, Sb and Ag interfere in the detection of As, but the concentrations of these metals normally encountered in the waters are often less to produce any significant interference.

Procedure-As was analyzed by AAS.

4. Instrument used: Atomic Absorption Spectrophotometry (AAS)

Model: Perkin Elmer 1331

Metal concentration in water samples were determined by AAS. The analytical processes used included absorption or emission technique, the flameless or carbon furnace technique and special procedures such as cold vapour (Mercury determination) and hydride generation (Arsenic and Selenium)

Atomic Absorption Spectroscopy (AAS): It was introduced by Dr. Alan Walsh of Australia in 1955. This powerful instrument technique is used for the quantitative determination of trace metals in liquids. Direct application of this technique is limited to metals, with the exceptions of Bi, Si, Te, As and Se.

Principle: The absorption of energy by ground state atoms in the gaseous state forms the basis of atomic absorption spectroscopy. When a solution containing metallic species is introduced into a flame, the vapor of metallic species will be obtained, to some of the metal atoms may be raised to an energy level sufficiently high to

emit the characteristic radiation of the metal but a large sufficiently high to emit the characteristic radiation of the metal but a large percentage of the metal atoms will remain in the non-emitting ground state. These ground state atoms of a particular element are receptive of light radiation of their own specific resonance wavelength. Thus, when a light of this wavelength is allowed to pass through a flame having atoms of the metallic species, part of that light will be absorbed and the absorption will be proportional to the density of the atoms in the flame. Thus, in AAS the amount of light absorbed is determined.

Instrument and Working: Major components of AAS are radiation source, the flame, a monochromator and a detector circuited with a recorder. The source of radiation is always a hollow cathode lamp. The radiation from this lamp enters the flame through a copper which sends the radiation intermittently. Various kind of flames such as acetylene-air, acetylene-oxygen, acetylene-nitrous oxide, hydrogen-air, hydrogen-oxygen and propane-air are employed depending on the temperature

required for atomization of a particular element. The sample is aspirated into the flame through the burner for atomization. The atomic vapors of the element absorb a portion of the radiation and the remaining is transmitted to monochromator which selects only the required wavelength. The monochromator is set on the wavelength emitted by hollow cathode lamp which is specific. The element being estimated. The radiation after passing through the monochromator reaches to a detector which produces an electrical signal. This signal is then amplified and displayed by the recorder. The radiation produced by the flame itself is also reaching the detector, but the amplifier is turned to the frequency of the chopper so that only A.C. radiation will be monitored. The D.C. radiation from the flame is automatically excluded. The chopper may be a mirror which alternately sends the radiation through the flame and directly to the detector circuit. These type of instruments are called double beam AAS which measure I_0/I . In the signal beam instruments, the radiation simply reaches intermittently through the flame, and in this case only transmitted radiation is measured.

Results

In the present study the samples were taken from two different sampling sites and were analyzed for heavy metals.

Table-1

The mean value of eight observations (Concentration±Standard Deviation) of some selected heavy metals of Ash pond overflow (Site- First) and Discharge Channel (Site-Second)

Heavy Metals	Ash Pond Overflow Mean Value±S.D	Discharge Channel Mean Value±S.D
Fe	1.768±1.682	1.765±1.682
Cu	0.026±0.016	0.023±0.016
Zn	0.243±0.178	0.145±0.111
Cr	0.005±0.004	0.004±0.003
Cd	0.003±0.015	0.001±0.002
Hg	0.01±0.277	0.01±0.275
As	0.003±0.001	0.002±0.004
Pb	0.032±0.018	0.027±0.016

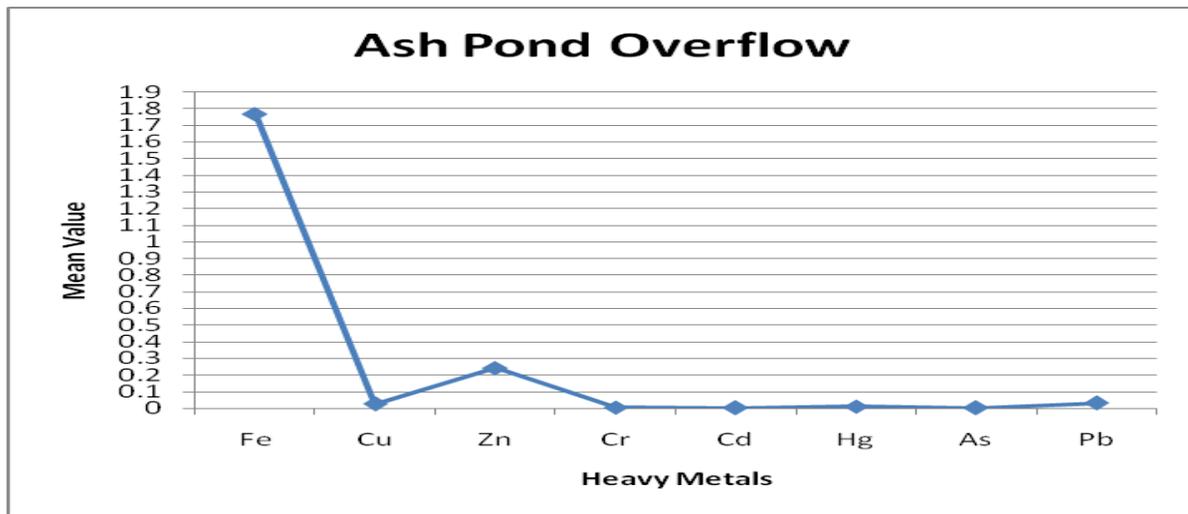


Fig.1- Variation of heavy metals (Fe, Cu, Zn, Cr, Cd, Hg, As, Pb) mg/l in ash pond overflow of BTPS.

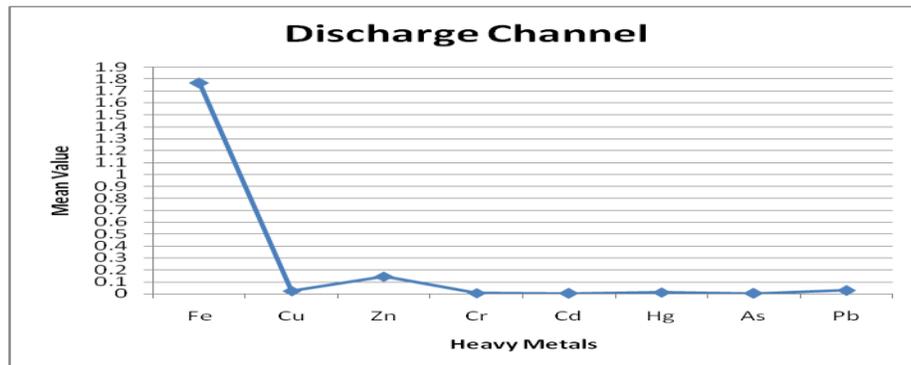


Fig.2- Variation of heavy metals (Fe, Cu, Zn, Cr, Cd, Hg, As, Pb) mg/l in Discharge channel of BTPS.

Discussion

The present study was conducted to evaluate the concentration of heavy metals in industrial effluent of BTPS. The result indicated that industrial effluent may be regarded as the major source of water pollution. The main concentrations of heavy metals viz. Pb, Cu, Zn, Fe, Hg, Cr, As and Cd in discharge channel and ash pond overflow are given in table 1. This industrial effluent discharged into the aquatic systems; change the physico-chemical properties of water such as pH value, turbidity, DO and BOD etc., thereby affecting the flora and fauna.

From table 1 it is evident that Fe at site first (Ash pond overflow) was 1.78mg/l and site second was (Discharge channel) 1.765mg/l. The observed values were found under the permissible limits as prescribed by CPCB (1998) which is 3mg/l. Heavy metal such as Cd, Cu, Pb, Cr, Hg are important environmental pollutants, particularly in areas with anthropogenic pressure (Islam et al, 2007). Fe is used in industries for coating.

From table 1 Cu at site first was 0.026mg/l and site second was 0.023mg/l. The observed values were found under the permissible limits as prescribed by CPCB (1998) which is 3mg/l. The high causes the precipitation of Cu thereby increasing its concentration in the soil. Cu is mainly associated with the organic matter probably due to its high complexing tendency for organic matter (Gadh *et al.* 1993) Aleem

(1990) reported Cu level ranging between 0.032 to 0.74mg/l in ponds of Bhopal.

From table 1 Zn at site first was 0.243mg/l and site second was 0.145mg/l. The observed values were found under the permissible limits as prescribed by CPCB (1998) which is 5.0mg/l. Zn is used as protective coating on less reactive metals through the process galvanized coating. Khopker (1995) reported that industrial effluent contains 200-250ppm of Zn.

From table 1 Cr at site first 0.005mg/l and site second was 0.004mg/l. The observed values were found under the permissible limits as prescribed by CPCB (1998) which is 60.1mg/l.

From table 1 Cd at site first was 0.003 mg/l and site second was 0.001mg/l. The observed values were found under the permissible as prescribed by CPCB (1998) which is 2.0 mg/l. Cd is present in the waste, water from electroplating, steel manufacturing plants. It is used in industries as protective coating of iron, copper and steel. The higher pH results in precipitation of Cd thus increasing the concentration in sediments (Dean *et al.* 1972). According to Gadh *et al.* (1993) Cd is mostly bound with carbonates. Klein (1974) carried out a study on average quantities of some heavy metals in industrial effluents and he also found a very low amount of Cd in most of the effluent. The tolerance limit of Cd for industrial effluent discharged into sewers is 1 mg/l.

From table 1 Hg at site first was 0.01 mg/l and site second was 0.001mg/l. The observed values were found under the permissible limits as prescribed by CPCB (1998) which is 0.01mg/l. Hg, a liquid volatile metal found in rocks and soils. It also present in air due to the result of human activities such as in the production of fungicides, paints, cosmetics, paper, pulp etc.

From table 1 As at site first was 0.003 mg/l and site second was 0.002 mg/l. The observed values were found under the permissible limits as prescribed by CPCB (1998) which is 0.2mg/l.

From table 1 Pb at site first was 0.032 mg/l and site second was 0.027 mg/l. The observed values were found under the permissible limits as prescribed by CPCB (1998) which is 0.1 mg/l. Khopkar also observed 19.0 ppm of Pb. ISI proposed value for effluent discharge into sewer is 1ppm. The TLV for Pb dust and fumes is 0.15 mg/m³ in US and 0.2 mg/m³ in Sweden. The concentration of Pb at site was 0.005 and 0.006 respectively, below the limits.

Conclusion

It has been now established beyond doubt that the water resources in the developing countries are mismanaged because of human interference and his quest for development, excellence and luxuries. Although chemical, biological and ecological methods for proper

Ash in slurry form was discharged into the lagoons where ash particles get settled from the slurry. Heavy metals accumulated in it in the form of oxides and clear effluent water was discharged from the ash pond. So heavy metals were found greater in ash pond overflow than discharge channel. From the above discussion it can be said that the water used for industrial purpose cannot be reused without treatment. From the forgoing discussion it is evident that water is highly susceptible to environment. Industrial effluent contains objectionable and hazardous constituents, which exert direct toxicity or being about physical, chemical and biological changes in the aquatic environment. Heavy metals salt such as Cd, Pb, Hg, Ni, Zn V, and As etc. are highly toxic to fish and aquatic organisms. If precautionary measures are not taken then the chances of chronic toxicity might be developed as a major public health problem. Treatment of metal effluents is likely to be most effective at the sources of the population where concentration is highest.

management of water bodies have been tried.

The present study was to analyze some heavy metals in ash pond overflow and

discharge channel of BTPS. The speciation of eight environmentally heavy metals viz,

Fe, Cu, Zn, Cd, Cr, Hg, As and Pb. The heavy metals of ash pond overflow and discharge channel have variation in their quantities but their concentration lies

between the standard ranges, so it is clear that BTPS play a significant role in minimizing the water pollution.

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