

Heavy Metal Concentrations in Pharmaceutical Effluents of Industrial Area of Dehradun (Uttarakhand), India

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Abstract

"Heavy metals" which have specific gravity about 5 times that of water were determined in the different effluent samples taken from Selaqui industrial area. When water is contaminated with heavy metals then water becomes toxic and dangerous for our biological system. Quality of water affects our biological system and our surrounding is also affected. In the present study concentrations of some heavy metals in the effluents of pharmaceutical industries operating in the industrial area (Selaqui region) of Dehradun were determined using atomic absorption spectrophotometer. The heavy metals analyzed in this study included Cadmium, Chromium, Lead, Nickel, Zinc and Copper. Most of the samples were found to contain the metals in varying concentrations. The highest concentration of heavy metal detected was Iron with concentration of 10.80 mg/L. The highest concentration for Pb was found to be 0.26 mg/L while 0.55 mg/L for Cd. Zinc was obtained in the range of 1 to 1.3 mg/L, Copper in the range of 0.08 to 0.38 mg/L and Nickel 0.03 to 0.12 mg/L. Chromium, lead, cadmium and nickel were found to be above the permissible limit recommended by WHO standards. Different metals were found within the permissible limit in ground water sample but if these effluents containing above mentioned heavy metals are drained regularly without proper treatment, then after some years the ground water will not be suitable for drinking purpose and it may cause diseases in the human being and animals and will also affect the flora of the region. This study reveals the need for enforcing adequate effluent treatment methods before their discharge to surface water to reduce their potential environmental hazards.

Keywords: Heavy metals; Pharmaceutical effluents; Surface water; Hazard

Introduction

"Heavy metals" are chemical elements with a specific gravity at least 5 times that of water. The specific gravity of water is 1 at 4°C (39°F). Specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metals with a specific gravity 5 or more times those of water are arsenic (5.7), cadmium (8.65), iron (7.9), lead (11.34), and mercury (13.546). When water is contaminated with these heavy metals then that water becomes toxic and dangerous for our biological system.

There are 35 metals that concern us because of occupational or residential exposure; 23 of these are the heavy elements or "heavy metals": antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc [1]. Small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon, and repeated long-term contact with some metals (or their compounds) may cause cancer [2].

Pharmaceutical effluents are wastes generated by pharmaceutical industries during the process of drug manufacturing. Their risk to human health and environment are immense. The increase in demand for pharmaceuticals has resulted in a consequent increase in pharmaceutical manufacturing companies in the country and hence increased discharges from these industries constitute hazard to man

and other living organisms in the environment because they contain toxic substances detrimental to health [3].

Water the most indispensable natural resource is being deteriorated in quantity and quality by us. This important resource needs to be taken care of and therefore monitored carefully. Dehradun the capital of Uttarakhand has seen rapid industrial development since it became the capital of the state. The Selaqui region of Dehradun especially has seen mushrooming of pharmaceutical industries in the past few years since many effluents are not treated properly, these products are discharged on the ground or in the water bodies and most of these discharges to water bodies accumulate in the system through food chain [2]. These effluents are usually discharged into the surrounding environment and ground water affected. A similar case study was done by another study was done by Anawara et al. [4], in Bangladesh and they highlighted the impact on water quality. When effluent is improperly handled and disposed, they affect both human health and the environment. The uncontrollable growing use of pharmaceutical products now constitutes a new challenge. Most pharmaceutical effluents are known to contain varying concentrations of organic compounds and total solids including heavy metals. Heavy metals such as Lead, Mercury, Cadmium, Nickel, Chromium and other toxic organic chemicals or phenolic compounds discharged from pharmaceutical industries are known to affect the surface and ground waters. Due to mutagenic

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and carcinogenic properties of heavy metals, much attention has been paid to them since they have direct exposures to humans and other organisms [5]. Heavy metals are natural components of the earth crust. These metals enter into living organism through food or proximity to emission sources. They tend to bioaccumulate and are stored faster than excreted [6].

This study was aimed to determine the presence of heavy metals, namely Iron, Lead, Chromium, Cadmium, Zinc, Copper and Nickel in the effluents of the selected pharmaceutical Industries in the Selaqui region of Dehradun. Similar case study was done by Oyeku and Eludoyin [7], in Africa. Another study was done by Momodu and Anyakora [5], on heavy metal contamination in Ground water of Nigeria.

The results obtained may form the basis for intervention by encouraging the pharmaceutical companies to effectively treat their effluent before being discharged into the environment. Each industry should treat their effluents, in accordance with the legal requirements, before discharging these into the streams otherwise 'Polluter pays' principle should be implemented (Sate Report).

Materials and Method

Chemicals

All chemicals and reagents of analytical grade (AR grade of Rankem) were used for analysis. Concentrated HNO_3 was used for the digestion of the samples while corresponding metal salts [$\text{CdCl}_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{SO}_4)_2$, $\text{Zn}(\text{SO}_4)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3$] were used as standards [8].

Instrumentation

AAS instrument (PERKIN ELMER A. Analyst 200; Germany consisting of a hollow cathode lamp, slit width of 0.7 nm and an air acetylene flame was used for this work. The samples were analyzed for six heavy metals namely Cr, Ni, Cd, Zn, Pb & Cu. Chromium which was analyzed at wavelength of 357.87 nm, Nickel at 232.00 nm, Cadmium at 228.80 nm, Zinc at 213.86 nm, Lead at 283.31 nm and Copper at 324.75 nm.

Sampling

Sampling was done as per standard way to ensure representation of industrial effluent. Samples were collected from various industrial units (A, B, C, D & E) situated in the industrial area i.e. Selaqui region. These industrial units synthesize cough syrups, medicinal tablets and cosmetics. Effluent samples were mostly collected from drains coming out of the industrial site. Plastic cans of 2 litre capacity were used for sampling of effluent. The samples were taken in the 3 batches i.e. during different seasons of the year. The first set of samples was collected during summer time, second sample during the rainy (monsoon)

season and third during winter season. Samples were collected from the effluent release point or a little away from it (this was generally the drains coming out from the industrial unit). Samples were collected and preserved after nitric acid treatment. Analysis of samples was done by flame atomic absorption spectroscope at ICAFI University, Dehradun.

Sample preparation

Samples were prepared by using standard APHA methods. To ensure removal of organic impurities and prevent interference during analysis, each of 50 ml volume sample was digested using 10 ml conc. HNO_3 in a 250-ml conical flask placed on a fume cupboard. The samples were covered properly with aluminum foil to avoid spillage and heated on a hot plate until the solution reduced to 10 ml. This was allowed to cool and made up to mark with distilled water before filtering into a 50-ml standard flask, labeled and ready for analysis. The blank constituted 5% HNO_3 .

Standard preparation

Standard solutions were taken for different metals. Solution of 1000 ppm strength served as the stock solution, subsequently lower concentrations of 2 ppm, 4 ppm and 6 ppm were prepared from the stock by serial dilution. The same method was adopted for Cr, Ni, Pb, Cu and Zn standards.

Results and Discussion

Metal concentrations in different effluent samples (A to F) are shown in 3 Tables and all values are expressed in ppm (mg/l). Tables 1-3 data are corresponding to 3 batches of sampling taken in different seasons. Metals were determined at selective wavelengths, which are given below as

Cr (λ) = 357.87 nm, Cu (λ) = 324.75 nm, Co (λ) = 240.73 nm, Fe (λ) = 248.33 nm

Cd (λ) = 228.8 nm, Zn (λ) = 213.86 nm and Pb (λ) = 283.31 nm

Cr, Cu, Co, Fe, Ni & Zn-Analyzed using Hollow Cathode Lamp (HCL), in a Flame atomizer AAS. Cd and Pb-Analyzed using Electrode Less Discharge Lamp (EDL), in the Flame atomizer AAS.

Data given in Tables 1-3 indicates that most of the metals were found in varying concentrations. Comparative concentration of heavy metals is shown in Figure 5 while Figures 1-4 show maximum concentrations of heavy metals Cr, Pb, Cd and Ni respectively. The highest concentration was detected for Iron i.e. 10.80 mg/l or ppm, it varied from 8.5 to 10.8 ppm while in ground water it was found to be about 8 ppm.

Chromium varied from 0.12 to 0.31 ppm in all effluent samples except one pharma company sample(C company sample). The EPA standard for total Cr is 0.1ppm while 0.05 ppm as per WHO standards,

Metals	Effluent sample-A	Effluent sample-B	Effluent sample-C	Effluent sample-D	Effluent sample-E	Water sample-F
Cr	0.28	0.18	0.001	0.12	0.28	ND
Pb	0.186	0.216	0.179	0.179	0.206	0.139
Cd	0.62	0.18	ND	0.08	0.29	ND
Cu	0.35	0.16	0.12	0.16	0.08	0.07
Zn	1.16	0.98	1.34	1.28	1.12	0.39
Co	0.263	0.154	0.197	0.117	0.119	ND
Ni	0.05	0.07	ND	0.07	0.09	ND
Fe	8.5	8.7	8.9	8.6	9.1	8.1

Table 1: Metal concentration in 1st batch effluent samples, all values in mg/l.

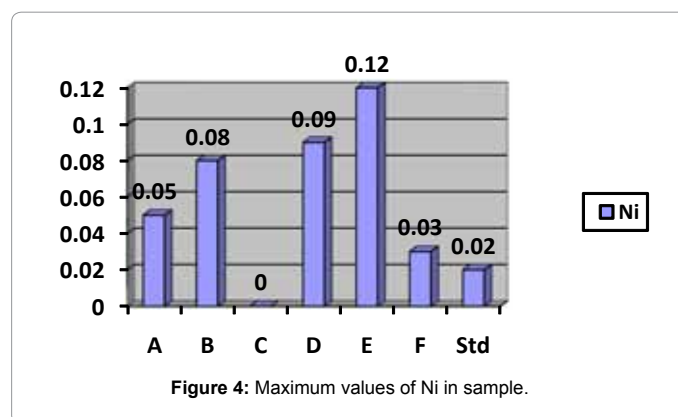
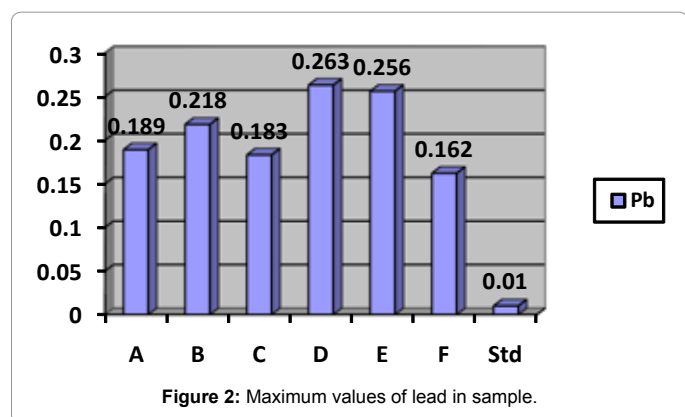
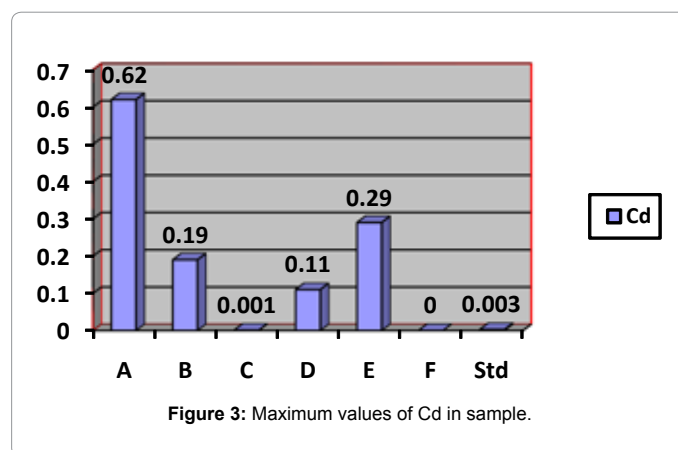
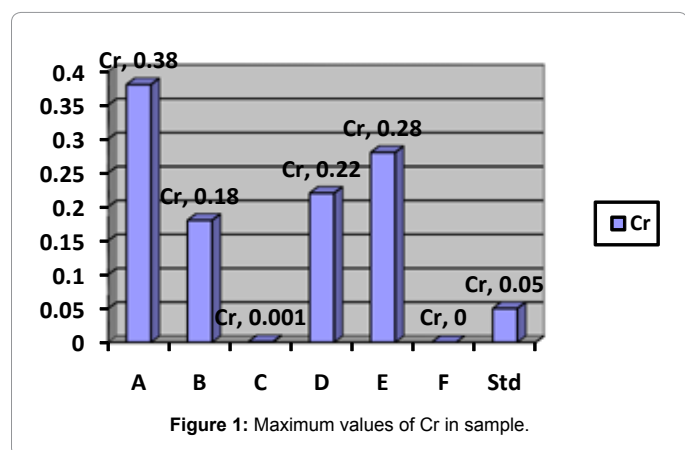
Metals	Effluent sample-A	Effluent sample-B	Effluent sample-C	Effluent sample-D	Effluent sample-E	Water sample-F
Cr	0.29	0.15	ND	0.21	0.26	ND
Pb	0.183	0.213	0.172	0.262	0.188	0.152
Cd	0.55	0.16	0.001	0.09	0.24	ND
Cu	0.32	0.18	0.09	0.11	0.07	0.05
Zn	1.13	0.96	1.27	1.05	1.06	0.34
Co	0.266	0.156	0.195	0.116	0.110	ND
Ni	0.03	0.06	ND	0.09	0.09	0.03
Fe	8.6	10.8	10.2	10.5	8.9	8.3

Table 2: Metal concentration in 2nd batch effluent samples.

Metals	Effluent sample-A	Effluent sample-B	Effluent sample-C	Effluent sample-D	Effluent sample-E	Water sample-F
Cr	0.31	0.18	ND	0.22	0.25	ND
Pb	0.189	0.218	0.183	0.263	0.256	0.162
Cd	0.58	0.19	ND	0.11	0.25	ND
Cu	0.38	0.14	0.23	0.20	0.09	0.07
Zn	1.13	0.98	1.31	1.08	1.05	0.35
Co	0.272	0.164	0.193	0.115	0.112	ND
Ni	0.05	0.08	ND	0.09	0.12	0.01
Fe	8.8	9.3	10.8	10.7	8.9	7.8

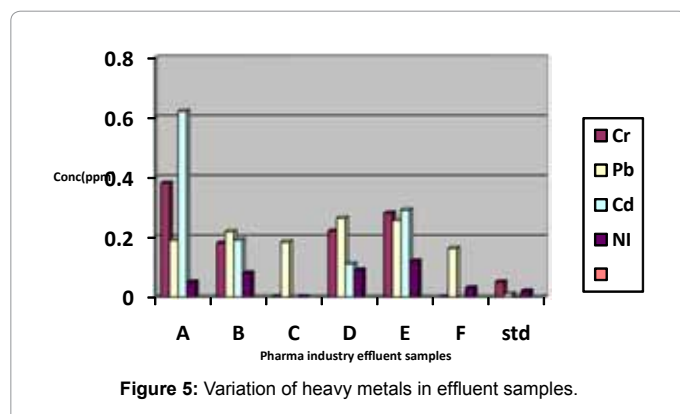
A, B, C, D & E are different industries generating effluents. F is water sample taken from hand pump situated in the industrial area. F sample is ground water sample taken from hand pump, ND = Not detected or below detection limit

Table 3: Metal concentration in 3rd batch effluent samples.



in this way we observe that Cr is above the standard value in most of the effluent samples, if Cr is discharged continuously then it will increase in ground water sample, although it is not detectable in the present hand pump sample (F). Chromium in drinking water may lead to allergic dermatitis [9]. It can cause bladder, lung and skin cancer.

Lead was found to be in the range of 0.158 to 0.262 ppm which is above limit of Pb (0.01 ppm as per WHO standards) [10]. It was also observed in the higher range in hand pump water sample taken from the pharma industrial area (selaqui) of Dehradun valley. Pb is very toxic metal and it interferes with a variety of body processes and is



toxic to many organs and tissues including the heart, bones, intestine, kidneys, reproductive and nervous systems [11].

Nickel was observed in the range from 0.05 to 0.12 ppm, which appears to be higher than the WHO prescribed limit of 0.02 ppm. Ni was not detected in 2 effluent samples including ground water sample.

Cadmium content is in the range of 0.16 to 0.56 ppm while not detected in ground water sample. Its permissible limit as per WHO is less than 0.003 ppm, in this way we conclude that cadmium is higher in all effluent samples except one pharma company effluent (C). Acute exposure to Cd fumes may cause flu like symptoms including chills, fever and muscle ache. More severe exposure can cause trachea-bronchitis, pneumonitis and pulmonary edema. Cd dust inhalation causes respiratory tract and kidney problems which can be fatal. Ingestion of Cd causes immediate poisoning and damage to the liver and kidney. In humans, the liver is the primary organ of copper-induced toxicity. Other target organs include bone and the central nervous and immune system [12,13]. Excess copper intake also induces toxicity indirectly by interacting with other nutrients [14]. Excess copper intake produces anemia by interfering with iron transport and/or metabolism [15].

Zinc was observed in the range of 1 to 1.3 ppm which is in the permissible range. Although Zinc is essential for human health but too much Zn can cause health problems, like stomach cramps, skin irritation, vomiting, nausea and anemia.

Copper was found in the range of 0.08 to 0.38 ppm in the effluent samples while it could not be detected in hand pump water. Cu was found lower than the prescribed limit (2 ppm). Excess copper intake causes stomach upset, nausea, and diarrhea and can lead to tissue injury and disease [16].

The permissible range of Iron in drinking water is 10 ppm. The analysis of pharma effluents shows maximum level of 10.8 ppm for Iron. This is almost crossing the permissible limit. Though Iron is not considered to be hazardous to health, we experience red, brown or yellow staining of laundry, glassware and dishes. This water has metallic taste and an offensive odor. Water system piping and fixtures can also become restricted or clogged, if water has more than 10 ppm of iron content.

From the Figures 1-5, it is clear that four heavy metals i.e Cr, Pb, Cd and Ni were observed to be in the higher range in most of the pharma industrial effluent samples.

Conclusion

By this study it can be concluded that heavy metals like Chromium,

lead, cadmium and Nickel were found to be above the permissible limit recommended by WHO standards while Copper, Zinc and Iron were found almost within the permissible limit. Almost all ground water samples taken from hand pump situated in the industrial area were found to contain most of the heavy metals within the permissible range but if the effluents containing above mentioned heavy metals are drained regularly in huge quantity without proper treatment, then after some years the ground water will be polluted with such toxic heavy metals and will not be suitable for drinking purpose. Such type of polluted water may cause diseases in the human being and animals and will also affect the flora of the region. This study reveals the need for enforcing adequate effluent treatment methods before their discharge to surface water to reduce their potential environmental hazards.

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