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## Analysis of Heavy Metals in Sludge and Bottom Ash from a Pharmaceutical Industry

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### ABSTRACT

The present study was conducted to estimate the quantity of ETP sludge generated by the pharmaceutical industry per week and per year and to analyze the ETP sludge of pharmaceutical industry and bottom ash that comes after the incineration of that sludge. Secondary sludge samples were collected from effluent treatment plant of the industry and bottom ash samples were collected from industrial incinerator using composite sampling technique. The pH, electrical conductivity, Cr, Cu, Ni, Zn, Fe, Mn of ETP sludge and incinerator's bottom ash were determined. Results were analyzed statistically for mean, standard deviation, correlation and t-test. Results of incinerator's bottom ash were compared with USEPA standards (1996) to evaluate its toxicity. In bottom ash Cd, Cr, Cu, Ni, and Mn concentrations were above and Pb, Fe and Zn were found under the permissible limits set by USEPA. Positive correlation existed between the pH, electrical conductivity and heavy metals concentration in ETP sludge and incinerator's bottom ash. Pharmaceutical industry is producing hazardous sludge, due to the presence of heavy metals. Controlled burning of ETP sludge under high pressure and temperature (incineration) reduced the metal content of the sludge along with reduced cost of sludge handling and disposal.

**Keywords:** Bottom Ash, Effluent Treatment Plant, Heavy Metals, Incinerator, Pharmaceutical Industry, Sludge Disposal.

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### INTRODUCTION

Pharmaceutical companies are major contributors of hazardous and toxic effluents into the environment [1]. Wastewater from pharmaceutical industry contained antibiotics, analgesics, antidepressants hypertension drugs, heavy metals, high BOD<sub>5</sub> and COD. ETP sludge samples had high pH values almost double than pH values of bottom ash produced as a result of burning of ETP sludge. Wastewaters released from pharmaceutical industries are more hazardous than the domestic wastewater in term of BOD<sub>5</sub>, COD, TDS and phenol contents present in it. If it dispose off with insufficient treatment may lead to great damage to the environment and ground water resources. General treatment cannot be used for every pharmaceutical wastewater water treatment due to its

variable composition. Specific treatment required for specific type of wastewater. Treatment of Pharmaceutical wastewater requires the information about the characteristics and composition of the effluent [2].

All over the world wastewater ends with two products: treated water and slurry (sludge), sludge often considered a byproduct of the treatment. It contains all of the compounds removed from wastewater as well as those added during treatment [3]. Sludge is a semi-solid material left from industrial water treatment, or wastewater treatment processes. The primary aim of wastewater treatment is to remove the solids from the wastewater. [4].

There are principally three final disposal strategies for wastewater sludge. Sludge may be deposited on land (in landfills), in the sea (ocean disposal), or incinerated. Sludge and sludge components may also be used in different ways. The most obvious one is the direct use of treated sludge on land as a fertilizer and soil conditioner. Sludge may also be used indirectly on land in the build-up of top soil of agricultural value. Finally may be recycled in the form of products made from sludge such as; bio-soils (mixture of sludge with other materials), nutrients (phosphate, nitrogen), metals (coagulants) etc. [5].

For incineration of sludge, incineration is a high temperature burning process whereby combustible wastes reduced to inert residues (ashes). The material that cannot be combusted is known as bottom ash, its volume is usually 10% of the original material. Although incineration provides an economic, nuisance-free, clean method of disposing waste, however gases and bottom ashes remain as potential sources of pollution [6].

Pharmaceutical factories wastewater poses pollution problem mainly due to the presence of solvents (used in manufacturing), oil and its high COD and BOD<sub>5</sub>. Because of these problems the conventional treatment of wastewater which employs activated sludge process and trickling filter for the pharmaceutical factory's effluent treatment usually malfunctions. Physico-chemical treatment using different coagulants is more suitable for the treatment of pharmaceutical wastewater. Commonly used coagulants are; lime, alum, ferric chloride and ferrous sulphate [7].

Sludge utilization for agricultural use contains the beneficial use of the product and ultimate disposal, and is generally considered the least expensive sludge management option. However the accumulation of metals and industrial organic contaminants may render sludge suitable for agricultural use [8].

## MATERIAL AND METHOD

For the collection of sludge and bottom ash samples, sampling plans were made. Samples were collected by using grab sampling method to form composite samples. The equipment used for the sampling should be cleaned before use and should be large enough to collect an adequate sample amount. The pH, electrical conductivity, Cr, Cu, Ni, Zn, Fe, Mn of ETP sludge and incinerator's bottom ash were determined. HACH pH meter and conductivity meter were used to determine the pH level and electrical conductivity of pre-treated samples. Hot plate used for the digestion of samples. Spectroquant (NOVA 60), spectrophotometer (DR 2800) and test kits were used for the determination of heavy metals in sludge and bottom ash.

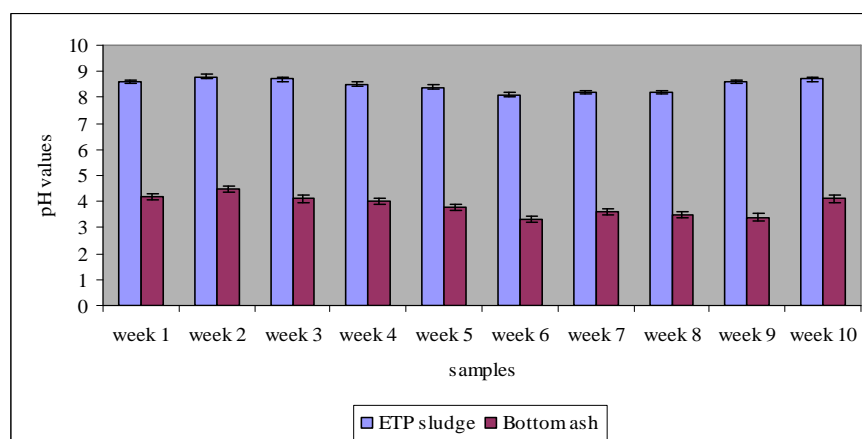
### Methodology

Daily effluent discharge from the industry was 90m<sup>3</sup>, and generation of sludge was 0.9kg. 630m<sup>3</sup> wastewater released from the manufacturing units and generation of sludge per week was 6.3kg. Annual production of sludge from the industry was 328.5kg. Secondary sludge samples were taken for analytical work. Analysis of ETP sludge and bottom ash for the determination of pH, electrical conductivity and heavy metal's concentration in the ETP sludge and bottom ash carried out.

Composite sampling technique was used for the collection of sludge and bottom ash samples. Each sample was divided into six sub-samples. Sludge samples from wastewater treatment plant of pharmaceutical industry and bottom ash samples from incinerator plant were collected at six different spots within the discharge pit and collection bin respectively and mixed together to form composite samples. Ten composite samples of ETP sludge and ten composite samples for incinerator bottom ash were collected in ten weeks.

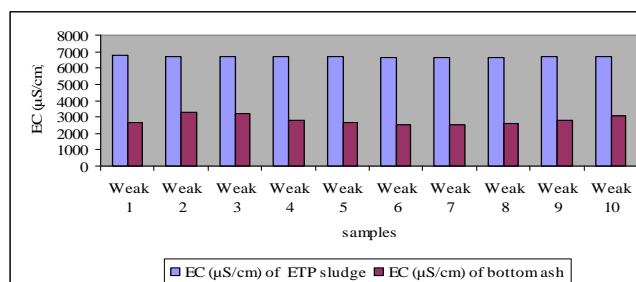
## RESULTS AND DISCUSSIONS

In ETP sludge minimum value of pH was 8.1 and maximum value was 8.4 (Annexure I), and mean value obtained 8.48 (Annexure II). The minimum value of pH in bottom ash was 3.3 and maximum value was 4.5 (Annexure I). The value mean obtained 3.85 (Annexure II). Standards limits by USEPA for pH of industrial sludge and incinerator bottom ash are not available. pH values of ETP sludge and bottom ash are non-significance. A strong correlation ( $r = 0.801$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).



**Fig 1: Showing correlation between pH of ETP sludge and bottom ash samples**

In ETP sludge minimum value of electrical conductivity was  $6620\mu\text{S/cm}$  and maximum value was  $6710\mu\text{S/cm}$  (Annexure I). The mean value obtained  $6669\mu\text{S/cm}$  (Annexure II). The minimum value of electrical conductivity of bottom ash was  $2500\mu\text{S/cm}$  and maximum value was  $3300\mu\text{S/cm}$  (Annexure I). The mean obtained  $2600\mu\text{S/cm}$  (Annexure IV). Standard limits by USEPA of electrical conductivity of industrial sludge and bottom ash of industrial incinerator are not available. A modest correlation ( $r = 0.695$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).



**Fig 2: Showing correlation between EC ( $\mu\text{S/cm}$ ) of ETP sludge and bottom ash samples**

In ETP sludge minimum value of cadmium was 0.31ppm and maximum value was 0.48ppm (Annexure I). The mean obtained 0.3880ppm (Annexure II). The minimum value of cadmium of bottom ash was 0.05ppm and maximum value is 0.12ppm (Annexure I).The mean obtained 0.03900ppm (Annexure II). Cadmium concentration in all samples is above the USEPA permissible limits for cadmium in incinerator’s bottom ash. A modest correlation ( $r = 0.503$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).

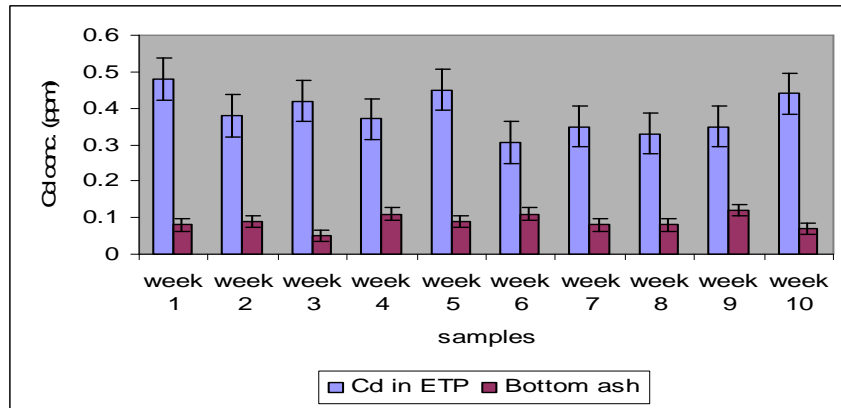


Fig 3: Showing correlation between Cd conc. (ppm) of ETP sludge and bottom ash samples

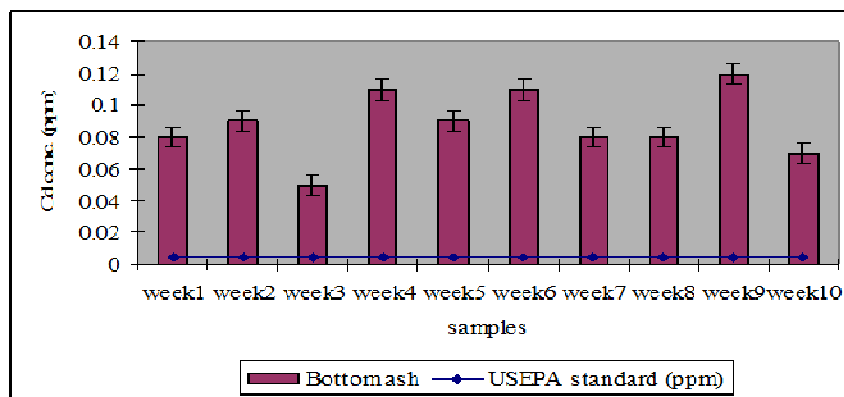


Fig 4: Showing comparison of Cd conc. (ppm) of bottom ash samples with USEPA standard

In ETP sludge minimum value of chromium was 0.07ppm and maximum value was 0.14ppm (Annexure I). The mean obtained 0.10900ppm (Annexure II). The minimum value of chromium in bottom ash was 0.03ppm and maximum value was 0.07ppm (Annexure I).The mean obtained 0.052ppm (Annexure II). Chromium concentration in all bottom ash samples is below the USEPA permissible limits for chromium in incinerator’s bottom ash. A strong correlation ( $r = 0.943$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).

The sludge minimum value of copper was 16.99ppm and maximum value was 17.21ppm (Annexure I). The mean obtained 17.1010ppm. The minimum value of copper of bottom ash was 0.29ppm and maximum value was 6.31ppm (Annexure I).The mean obtained 5.43600ppm (Annexure II). Copper concentration in all bottom ash samples is above the USEPA permissible limits for copper in incinerator’s bottom ash. A very weak correlation ( $r = 0.095$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).

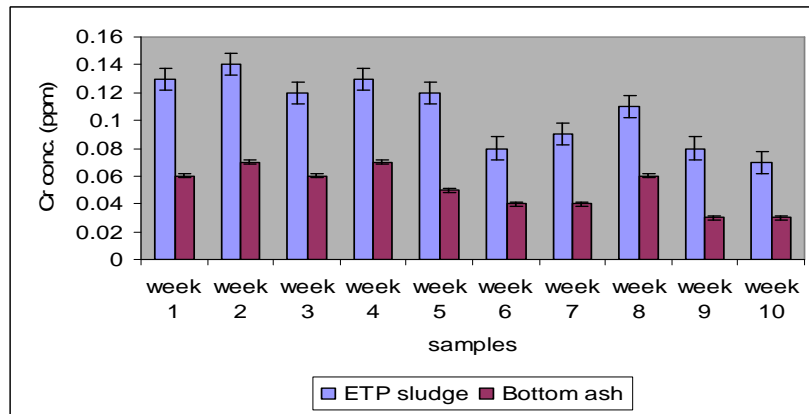


Fig 5: Showing correlation between Cr conc. (ppm) of ETP sludge and bottom ash samples

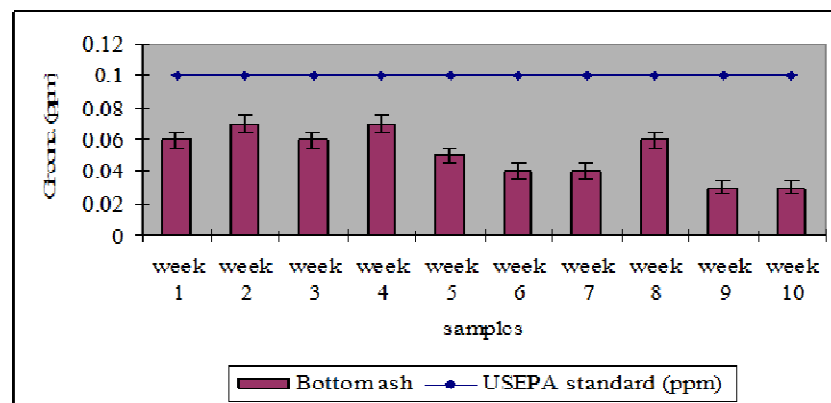


Fig 6: Showing comparison of Cr conc. (ppm) of bottom ash samples with USEPA standard

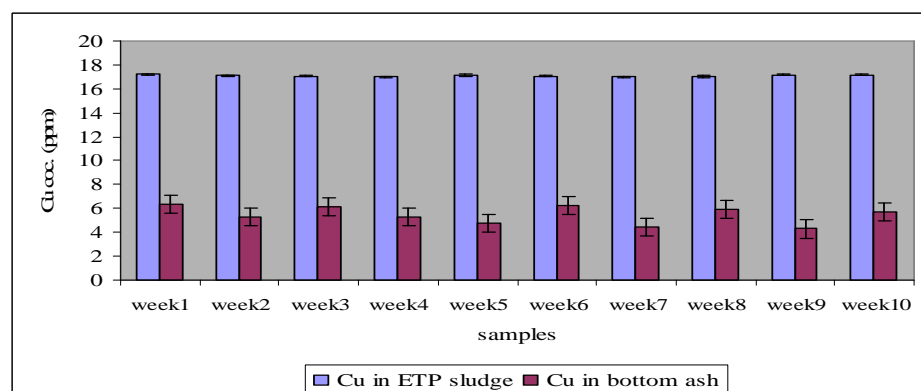
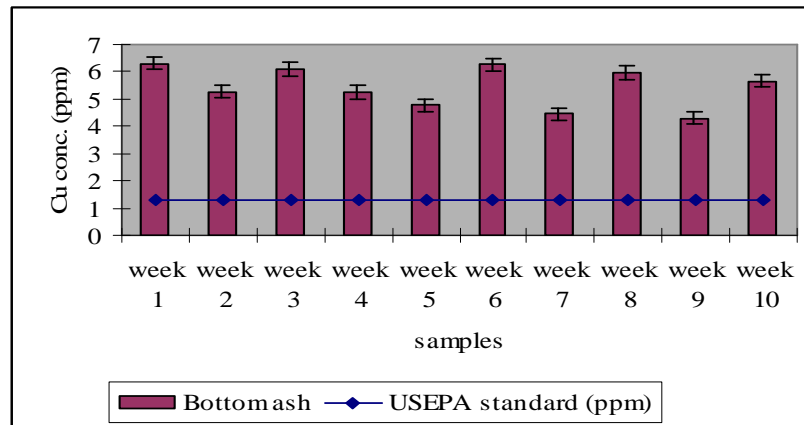
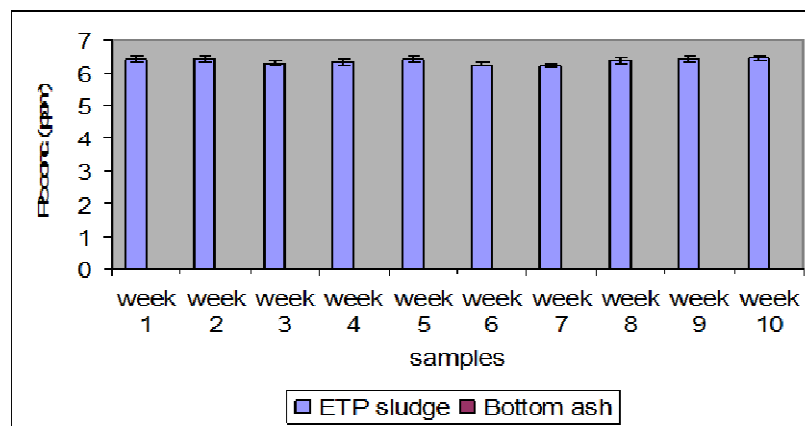


Fig 7: Showing correlation between Cu conc. (ppm) of ETP sludge and bottom ash samples

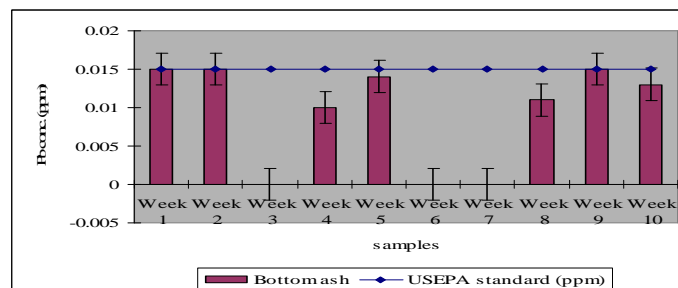


**Fig 8: Showing comparison of Cu conc. (ppm) of bottom ash samples wit USEPA standard**

In ETP sludge minimum value of lead was 6.4ppm and maximum value was 6.44ppm (Annexure I). The mean obtained was 6.343ppm (Annexure II). The minimum value of lead of bottom ash was BDL and maximum value was 0.02ppm (Annexure I). The mean value obtained is 0.0140ppm (Annexure II). Lead concentration in 40% bottom ash samples is below and in 60% samples was equal to concentration fixed by USEPA permissible limits for lead in incinerator’s bottom ash. Mixing bars of sample number 3, 6 and 7 of bottom ash represent the zero concentration of lead (Annexure II). A strong correlation ( $r = 0.942$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).



**Fig 9: Showing correlation between Pb conc. (ppm) of ETP sludge and bottom ash samples.**



**Fig 10: Showing comparison of Pb conc. (ppm) of bottom ash samples withUSEPA standard**

In ETP sludge minimum value of nickel was 6.04ppm and maximum value was 6.72ppm (Annexure I). The mean obtain is 6.140ppm (Annexure I). The minimum value of nickel of bottom ash was 4.31ppm and maximum value was 5.21ppm (Annexure I). The mean obtain is 5.067ppm (Annexure II). Nickel concentration in all samples is above the USEPA permissible limits for nickel in incinerator’s bottom ash. A modest correlation ( $r = 0.673$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).

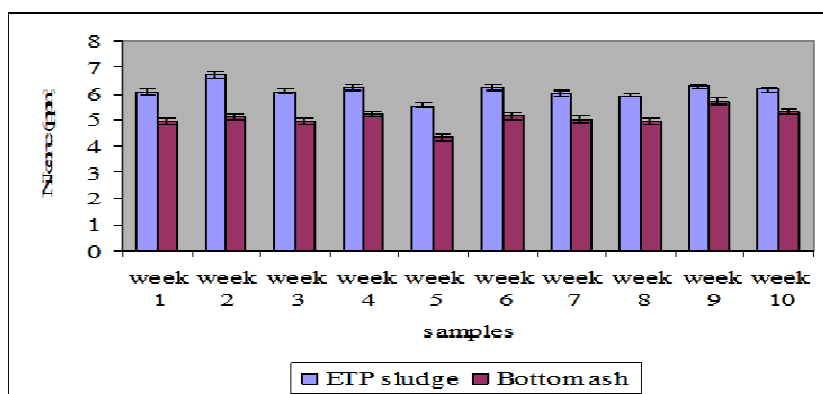


Fig 11: Showing correlation between Ni conc. (ppm) of ETP sludge and bottom ash samples

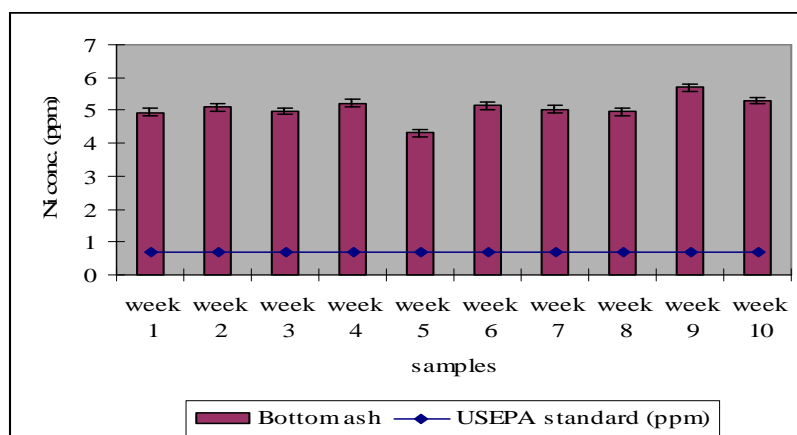


Fig 12: Showing comparison of Ni conc. (ppm) of bottom ash samples with USEPA standard

In ETP sludge minimum value of Zn was 7.33ppm and maximum value was 7.72ppm (Annexure I). The mean obtained is 7.52ppm (Annexure II). The minimum value of zinc of bottom ash was 2.75ppm and maximum value was 3.86ppm (Annexure I).The mean obtained is 3.46ppm (Annexure II). Zinc concentration in all bottom ash samples was above the USEPA permissible limits for zinc in incinerator’s bottom ash. A weak correlation ( $r = 0.494$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).

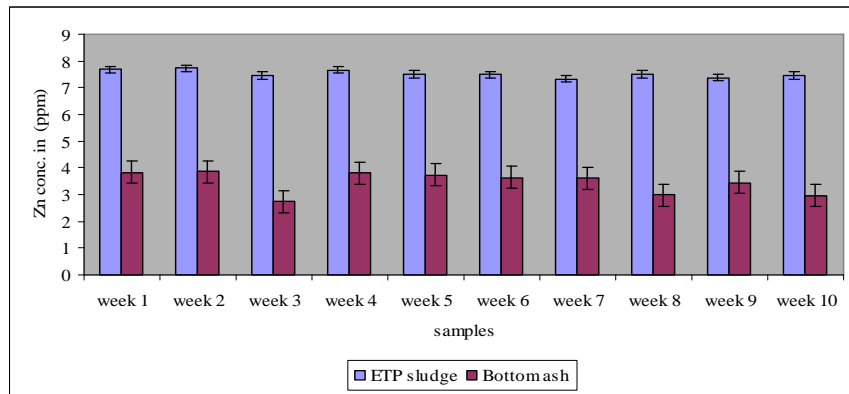


Fig 13: Showing correlation between Zn conc. (ppm) of ETP sludge and bottom ash samples

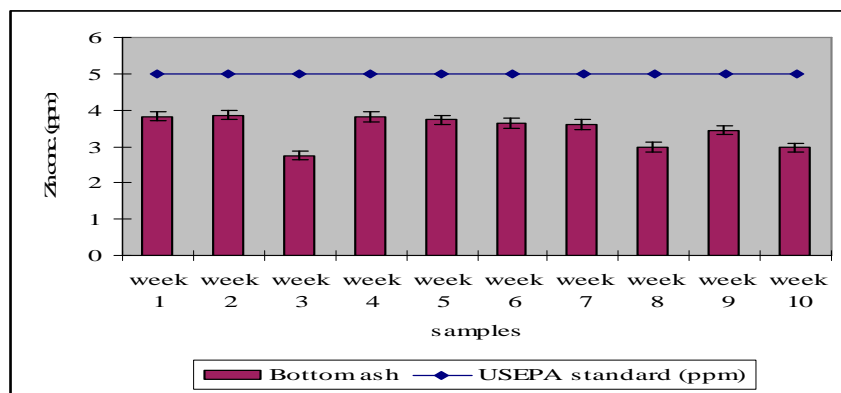


Fig 14: Showing comparison of Zn conc. (ppm) of bottom ash Samples with USEPA standard

In sludge minimum value of iron was 4.15ppm and maximum value was 4.52ppm (Annexure I). The mean obtained is 4.29ppm (Annexure II). The minimum value of iron of bottom ash was 0.21 and maximum value was 0.54ppm (Annexure I).The mean obtained is 0.38ppm (Annexure II). Iron concentration in all bottom ash samples was below the USEPA permissible limits for cadmium in incinerator’s bottom ash. A modest correlation ( $r = 0.794$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).

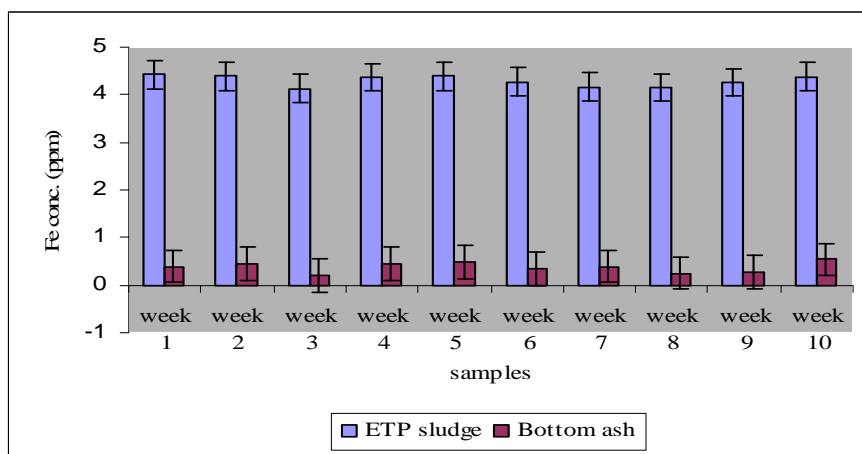
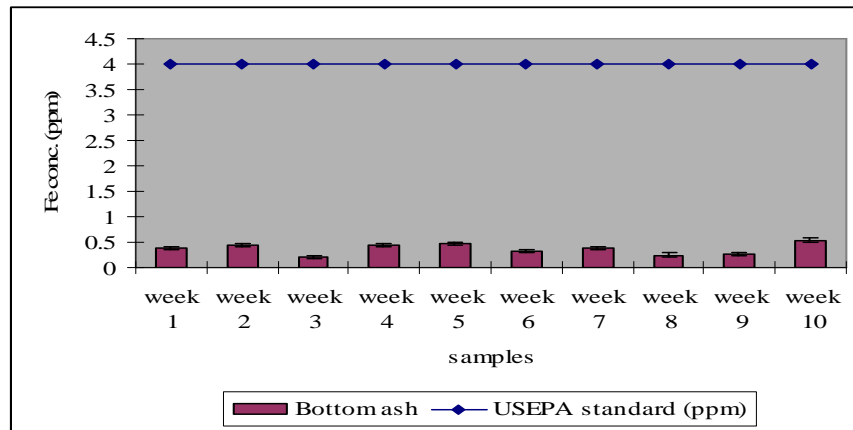


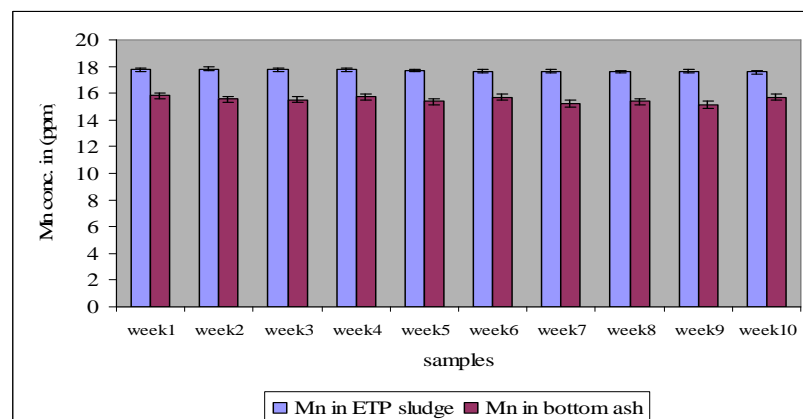
Fig 15: Showing correlation between Fe conc. (ppm) of ETP sludge and bottom ash samples



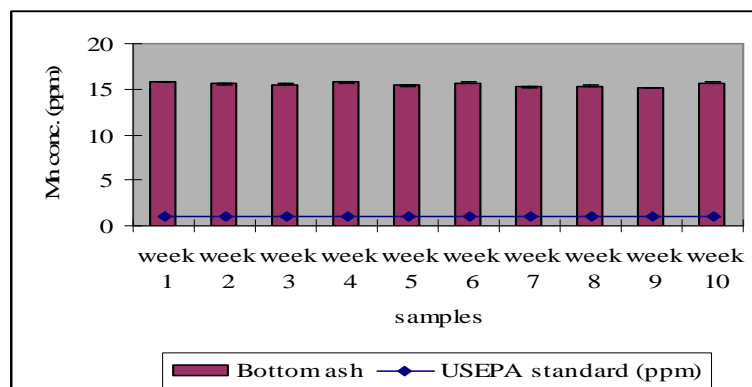


**Fig 16: Showing comparison of Fe conc. (ppm) of bottom ash Samples with USEPA standard**

In ETP sludge minimum value of manganese was 17.61ppm and maximum value was 17.81ppm (Annexure I). The mean obtained is 17.71ppm (Annexure II). The minimum value of manganese of bottom ash was 15.1ppm and maximum value was 15.81ppm (Annexure I).The mean obtained is 15.51ppm (Annexure II). Manganese concentration in all bottom ash samples is above the USEPA permissible limits for manganese in incinerator’s bottom ash. A week correlation ( $r = 0.404$ ) existed between the pH of ETP sludge and bottom ash of all samples (Annexure III).

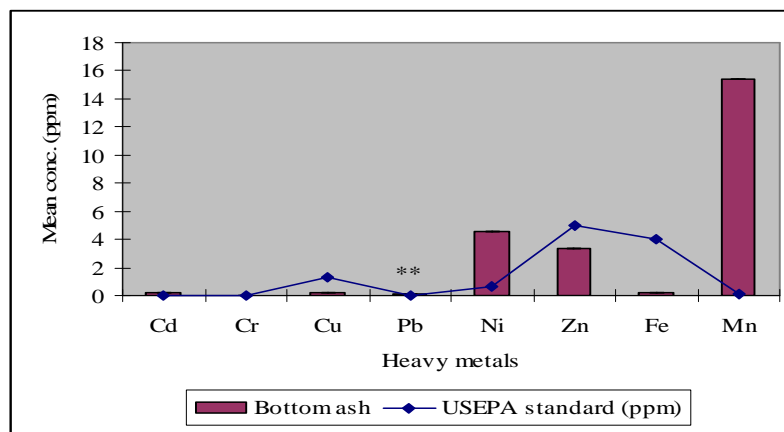


**Fig 17: Showing correlation between Mn conc. (ppm) of ETP sludge and bottom ash samples**



**Fig 18: Showing comparison of Mn conc. (ppm) of bottom ash samples with USEPA standard**

Concentrations of heavy metals; cadmium ( $P=1.283$ ), Copper ( $P=3.452$ ), nickel ( $P=2.823$ ), iron ( $P=5.633$ ), and manganese ( $P=2.436$ ) in the bottom ash samples are non-significant (Annexure III) and these are above the USEPA permissible limit (Cd=0.005ppm, Cr=0.10ppm, Cu=1.3ppm, Ni=0.70ppm, and Mn=1.0ppm). Bottom ash samples contained chromium concentration above the USEPA permissible limit except (5, 6, 7, 9). Mean concentration value of chromium is non-significant ( $P=5.043$ ) (Annexure III) and above the USEPA standard (Annexure 9).



**Fig 19: Showing comparison of mean concentrations (ppm) of heavy metals in bottom ash samples with USEPA standard**

Lead concentration ( $P=0.003$ ) (Annexure III) in bottom ash samples is below the USEPA permissible limit 0.015ppm. All samples contained zinc concentration non-significantly ( $P=3.217$ ) below the USEPA standard 5.0ppm (Annexure 9). All samples contained iron concentration non-significantly ( $P=3.217$ ) below the USEPA standard 4.0ppm.

## Discussion

Analysis performed on sludge and bottom ash of incinerator, which shows that selected pharmaceutical industry is producing toxic sludge due to the presence of heavy metals; Cd, Cr, Cu, Pb, Ni, Zn, Fe, and Mn. Bottom ash generate from incineration of that sludge was also toxic but its toxicity become reduced up to 50% after incineration, and it was only 10% of the waste burned.

pH of ETP sludge ranged from 8.1ppm to 8.4 (Annexure I), and standard deviation in the pH values of samples collected  $\pm 0.092$  (Annexure II). This shows that pH of ETP sludge falls in alkaline range and there is little variation in the pH of sludge of effluent treatment plant. Variation in pH values was due to the change in manufacturing patterns of the industry. High pH values of the samples were due to the increased production of antibiotic and low pH values depicts that industry was producing antibiotics in small amounts in those days. pH of the substances decrease with the passage of time due to the decaying of organic contents. pH of incinerator's bottom ash was ranged from 3.3 to 4.5 (Annexure I), and standard deviation in the values of pH values of samples collected  $\pm 0.393$  (Annexure II). This was also due to the change in composition of sludge of the industry. Graph does not show any trend in the pH values of ETP sludge and bottom ash samples (Fig 1). Heavy metals uptake increases by the sludge particulates with the increase of pH. However Cu and Ni uptake decreases with the increase of pH, primarily due to high dissolved organic matter concentration in high pH condition. Under neutral and low pH conditions ( $\text{pH} < 8$ ) the dissolved organic matter effect on metal uptake for all heavy metals is insignificant. Hydrogen ion

concentration or pH is the single most important factor influencing metal absorption [9]. It is an important factor to decide whether sludge or bottom ash should be applied on land, land filled and composted.

Electrical conductivity of sludge was ranged from 6620 $\mu$ S/cm to 6710 $\mu$ S/cm (Annexure I), standard deviation in the values of sludge samples  $\pm 30.71$  (Annexure II). Variations in electrical conductivity values were due to the change in the amount and electrical conductivity potential of suspended particles in the sludge. High electrical conductivity values shows increased production of the industry and more use of those metals in the manufacturing which have high conductivity strength. Electrical conductivity values of bottom ash ranged from 2500 to 3300 $\mu$ S/cm (Annexure I), standard deviation in values of bottom ash samples  $\pm 294.39$  (Annexure II). Graph of EC values of ETP sludge and bottom ash samples does not follow any trend in the values (Fig. 2). Electrical conductivity of bottom ash varied due to the non-homogenous nature of sludge.

Cadmium concentration of sludge ranged from 0.31ppm to 0.48ppm (Annexure I), and standard deviation in the values of samples collected  $\pm 0.057$  (Annexure IV). In pharmaceutical industry cadmium used as a stabilizer, pigment, and coating agent. During processing of zinc and copper compounds for use in ointments and iron tablets respectively, cadmium also released in the wastewater as an inevitable by-product. High value bars of cadmium concentration in ETP sludge graph show increased production of ointments in which zinc compounds being used. Cadmium concentration of bottom ash range from 0.05ppm to 0.12ppm (Annexure I), and standard deviation in the values of bottom ash samples  $\pm 0.016$  (Annexure II). Cadmium concentration in bottom ash also varied due to the non-homogenous nature of sludge. Cadmium concentration values of bottom ash depict more than 75% reduction in the Cd content in ETP sludge during incineration, but still cadmium level in bottom ash is above the USEPA permissible limit (Annexure IV). Graph of cadmium concentration in ETP sludge and bottom ash samples does not show any trend in the values (Fig. 3). Cadmium naturally found in all soils and rocks, typically as cadmium oxide. When cadmium contaminated sludge applied on cultivated land it becomes concentrate in edible portions of the plants grown there, and it can pollute surface waters as well as soils, and it can be transported over great distance when it is absorbed by sludge. Cadmium has the tendency of bioaccumulation, and enters into the body through inhalation and ingestion from soils. Side effects of Cd are very serious it destroys red blood cells [10]. Target organs of cadmium are kidney, placenta, bones, lung and brain; it also becomes a reason for abdominal pain and high blood pressure [11].

Chromium concentration in ETP sludge ranged from 0.07ppm to 0.14ppm (Annexure I), and the standard deviation in values of sludge samples  $\pm 0.233$  (Annexure II). Chromium concentration varied because of the variation in production pattern of the industry. Chromium used as catalyst and oxidizing agent in the manufacturing of medicines that is why it is detected in ETP sludge. It is also found in iron, zinc and lead ores as chromate ion, which is another reason for its presence in the sludge of pharmaceutical industry. Chromium concentration in bottom ash samples ranged from 0.03ppm to 0.07ppm (Annexure I), and standard deviation in the bottom ash samples  $\pm 0.0143$  (Annexure II). Chromium concentration in bottom ash samples varied due to the non-homogenous nature of ETP sludge. Chromium level reduced up to 75% during burning of sludge and bottom ash received Cr content below USEPA permissible limit (Annexure IV). Graph of chromium concentration in ETP sludge and bottom ash samples does not show any trend in the values (Fig 5). Cr is a micronutrient for humans and animals, its trivalent form are essential for normal metabolism of carbohydrate and lipid. Its fewer amounts can cause disturbance of metabolism and diabetes, but excess exposure results in skin rashes, upset stomach kidney damage, liver damage, lung cancer and weaken immune systems. When sludge applied on cultivated land, it becomes concentrate in edible portions of the plants grown there [12].

Copper concentration in ETP sludge ranged from 16.99ppm to 17.21ppm (Annexure I), and standard deviation value  $\pm 0.081$  (Annexure II). Copper used in the manufacturing of iron tablets and suspensions that is why it is detected in the sludge generated. Copper concentration in bottom ash ranged from 4.29ppm to 6.31ppm (Annexure I), and standard deviation in the bottom ash samples  $\pm 0.747$  (Annexure II). Copper concentration in bottom ash samples varied due to the non-homogenous nature of ETP sludge samples. Copper level reduced up to 65% during burning of sludge and bottom ash received Cu content above the USEPA permissible limit (Annexure IV). Graph of copper concentration in ETP sludge and bottom ash samples does not show any trend in the values (Fig. 9). Copper is a trace element and it is essential for human health. Although humans can handle proportionally large amount of it but too much copper can cause vomiting, diarrhea, liver damage and kidney damage. Its presence in water may be due to the corrosion of pipelines. When it ends up in soil it strongly attaches with organic matter and minerals, as a result it does not travel far after release into soil and hardly even enter groundwater [13].

Lead concentration in ETP sludge ranged from 5.97ppm to 6.51ppm (Annexure I), and standard deviation value  $\pm 0.079$  (Annexure II). Lead concentration varied because of the variation in production pattern of the industry. Lead concentration in bottom ash ranged from BDL to 0.02ppm (Annexure I), and standard deviation in bottom ash samples  $\pm 0.0082$  (Annexure II). Lead concentration in bottom ash varied due to the non-homogenous nature of sludge. Graph of Pb concentration in ETP sludge samples and bottom ash does not show any trend in the values (Fig. 9). Incineration of sludge was very much encouraging with respect to the lead concentration in bottom ash where it became reduced to below detectable limit in three samples out of ten and in remaining samples reduction was more than 75%, and bottom ash received Pb content below the USEPA permissible limit (Annexure IV). Lead is very toxic to our health, it has not essential trace element having function in neither human body nor in plants. It induces various toxic effects in humans at low doses. Lead absorption in the body increases by the iron deficiency situation. Target organs of lead are bones, kidneys, blood, and thyroid gland, its results in high blood pressure, disturbance of nervous systems and brain damage [10].

Nickel concentration of ETP sludge ranged from 6.04ppm to 6.72ppm (Annexure I), and standard deviation in concentration values of ETP sludge  $\pm 0.295$  (Annexure II). Variation in nickel concentration was because of change in production pattern of the industry. Nickel used as catalyst in the production processes of certain antibiotics medicines and released in the wastewater. Nickel concentration in bottom ash ranged from 4.31ppm to 5.21ppm (Annexure I), and standard deviation in bottom ash samples is  $\pm 0.348$  (Annexure II). Nickel concentration in bottom ash varied because of the non-homogenous nature of sludge. Graph of nickel concentration in ETP sludge and bottom ash samples does not show any trend in the values (Fig. 16). Values of bottom ash depict that only 15% Ni reduced during incineration of sludge, and bottom ash received Ni content above USEPA permissible limit (Annexure IV). Nickel is required in minute quantity for body as it mostly present in pancreas and hence plays an important role in production of insulin. But uptake of large amount of it results in lung cancer, birth defects, and heat disorder, most common ailment arising from Ni is allergic dermatitis. Nickel is not known to accumulate in plants or animals so it will not biomagnify up the food chain [14].

Zinc concentration of sludge ranged from 7.33ppm to 7.72ppm (Annexure I), and standard deviation  $\pm 0.131$  (Annexure II). Variation in zinc concentration was because of the changing production pattern of the industry, therefore graph of zinc concentration in sludge samples also show variation in the values (Fig. 13). Zinc used in the making of ointments and food supplements by the industry. Zinc concentration in bottom ash ranged from 2.75ppm to 3.86ppm (Annexure I), and standard deviation  $\pm 0.411$  (Annexure II). Zinc concentration in bottom ash samples varied because of the non-homogenous nature of sludge produced as a result of change in wastewater

composition. Values of bottom ash depict that 50% Zn content in sludge reduced during incineration, and bottom ash received Zn content above the USEPA permissible limit (Annexure IV). Graph of zinc concentration in ETP sludge and bottom ash samples also does not show any trend (Fig. 13). Zinc is a mineral that is a component of more than 300 enzymes needed to repair wounds maintains fertility in adults and growth in children, synthesize protein, and helps cell reproduce, preserve vision and boost immunity. [15]

Iron concentration of ETP sludge ranged from 4.13ppm to 4.52ppm (Annexure I), and standard deviation in concentration values of ETP sludge samples  $\pm 0.111$  (Annexure II). Variation in the Iron concentration was because of the changing production pattern of the industry. Iron is being used in the production of iron tablets and suspensions. Iron concentration in bottom ash ranged from BDL to 0.5ppm (Annexure I), and standard deviation in the values of bottom ash samples  $\pm 0.197$  (Annexure II). Iron concentration in bottom ash varied because of non-homogenous nature of sludge coming from effluent treatment plant. Graph of iron concentration in ETP sludge and bottom ash samples does not show any trend in the values. Burning of sludge reduced iron concentration below one, due to its oxidizing nature, that is below the USEPA permissible limit (Annexure IV).

Manganese concentration of sludge ranged from 4.13ppm to 4.52ppm (annexure I), standard deviation value obtained  $\pm 0.122$  (Annexure II). Fluctuation in manganese concentration in ETP sludge samples was because of variation in production pattern of the industry. Manganese concentration in bottom ash samples ranged from 15.1 to 15.81ppm (Annexure I), standard deviation value obtained  $\pm 0.225$  (Annexure II). Manganese is resistant to heat that is why only 20% manganese content of sludge reduced during burning process and its concentration remained above USEPA standard (Annexure IV). Manganese concentration in bottom ash varied because of non-homogenous nature of ETP sludge. Graph of manganese concentration in ETP sludge and bottom ash samples does not show any trend in the values.

#### ANNEXURE I

**Table: Parameters Ranges in ETP sludge and bottom ash samples of Pharmaceutical Industry**

Sr.No.	Parameter	ETP sludge	Bottom ash
		Ranges	Ranges
1	pH	8.1 - 8.4	3.3 - 4.5
2	EC ( $\mu\text{S}/\text{cm}$ )	6620 – 6710	2500 - 3300
3	Cd	0.31 – 0.48	0.07 - 0.12
4	Cr	0.07 – 0.14	0.03 - 0.07
5	Cu	16.99 – 17.21	4.29 - 6.31
6	Pb	6.4 – 6.44	BDL - 0.02
7	Ni	6.04 – 6.72	4.31 - 5.21
8	Zn	7.33 – 7.72	2.75 - 3.86
9	Fe	4.15 – 4.42	0.21 - 0.54
10	Mn	17.61 – 17.81	15.22-15.81

#### ANNEXURE II

**Table: Average values of physical parameters and heavy metals in sludge and Bottom ash generated after incineration of sludge of Pharmaceutical industry**

Sr. No.	Parameters (ppm)	ETP Sludge		Bottom Ash	
		Average value		Average value	
		Mean	SD	Mean	SD
1	pH	8.2800	±0.092	3.850	±0.392
2	EC (µS/cm)	6669.0	±30.71	2800.0	±294.39
3	Cd	0.388	±0.057	0.093	±0.016
4	Cr	0.109	±0.233	0.055	±0.014
5	Cu	17.101	±0.081	5.436	±0.747
6	Pb	6.343	±0.079	0.010	±0.009
7	Ni	6.140	±0.295	5.067	±0.348
8	Zn	7.560	±0.1313	3.463	±0.411
9	Fe	4.292	±0.111	0.375	±0.107
10	Mn	17.71	±0.122	15.508	±0.225

**ANNEXURE III****Table: Probability values of heavy metals in bottom ash.**

Sr. No.	Parameters (ppm)	Probability	Statistical significance
1	Cd	1.283	Non significance
2	Cr	3.452	Non significance
3	Cu	4.691	Non significance
4	Pb	0.003	Highly significance
5	Ni	2.823	Non significance
6	Zn	3.217	Non significance
7	Fe	5.633	Non significance
8	Mn	2.436	Non significance

**ANNEXURE IV****USEPA maximum detection limit for heavy metals in bottom ash, 1996.**

Sr. No.	Contaminants	USEPA standard (ppm)
1	pH	Not available
2	EC	Not available
3	Cd	0.005
4	Cr	0.1
5	Cu	1.3
6	Pb	0.015
7	Ni	0.70
8	Zn	5.0
9	Fe	4.0
10	Mn	1.0

## CONCLUSION

Study revealed that pharmaceutical industry producing hazardous sludge, due to the presence of heavy metals (Cd, Cr, Cu, Pb, Ni, Zn, Fe and Mn). Concentration of (Cd, Cr, Pb, Ni, Zn and Fe) was not so much high but as we know that small amount of heavy metals can be hazardous due to its accumulative property and poisonous nature. Proper treatment of pharmaceutical industry sludge is important from public health and environmental protection point view.

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