Concentrations of some heavy elements in fly ash samples from thermal electric power stations in the middle and south of Iraq

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Abstract. The objective of this present work is determining some heavy elements concentrations like (Cd, Co, Mg, Mn, Fe, Cu, Ni, Pb & Zn) in thermal electric power stations in the middle and south of Iraq. 18 Fly Ash samples were collected from thermal electric power stations in the middle and south of Iraq, the concentration values of (Cd, Zn, and Fe, Mg, Cu) in some samples were over the international limits in the Fly Ash samples. In general the increasing of the heavy metals in some fly ash samples due to the releasing of these metals is the combustion of the fuel and fuel type which provides thermal electric power station different from units to other, and geology of the region collected samples from it and the geochemical characteristics of the crude oil.

1. Introduction

A heavy element is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts. The term has particular application to cadmium, mercury, lead, zinc and arsenic, all of which appear in the organization's list of 10 chemicals of major public concern [1].

Toxic heavy elements are found naturally in the earth. They become concentrated as a result of human caused activities and can enter plant, animal, and human tissues via inhalation, and manual handling. Then, lead-acid batteries; they can bind to and interfere with the functioning of vital cellular components. The toxic effects of arsenic, mercury, and lead were known to the ancients, but methodical studies of the toxicity of some heavy metals appear to date from only 1868. In humans, heavy element poisoning is generally treated by the administration of chelating agents. Some elements regarded as heavy metals are essential, in small quantities, for human health [1].

Toxic heavy elements are found naturally in the earth, and become concentrated as a result of human caused activities. Common sources are from mining and industrial wastes; vehicle emissions; fertilizers; paints; treated woods; and aging water supply infrastructure. Arsenic, cadmium and lead may be present in children's toys at levels that exceed regulatory standards. Lead can be used in toys as a stabilizer, color enhancer, or anti-corrosive agent. Cadmium is sometimes employed as a stabilizer, or to increase the mass and luster of toy jewelry. Arsenic is thought to be used in connection with coloring dyes [2].

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Lead is the most prevalent toxic heavy element contaminant. As a component of tetraethyl lead, \((\text{CH}_3\text{CH}_2)_4\text{Pb}\), it was used extensively in gasoline during the 1930s–1970s. Lead levels in the aquatic environments of industrialized societies have been estimated to be two to three times those of pre-industrial levels. Although the use of leaded gasoline was largely phased out in North America by 1996, soils next to roads built before this time retain high lead concentrations [3]. Heavy elements enter plant, animal and human tissues via air inhalation and manual handling. Motor vehicle emissions are a major source of airborne contaminants including arsenic, cadmium, cobalt, nickel, lead, antimony, vanadium, zinc, platinum, palladium and rhodium. Stations are exposed to heavy elements through the uptake of water; animals eat these plants; ingestion of plant- and animal-based foods are the largest sources of heavy elements in humans. Absorption through skin contact, for example from contact with fly ash from electrics power station is another potential source of heavy element contamination. Toxic heavy metals can bio accumulate in organisms as they are hard to metabolize [3].

Although there is no clear definition of what a heavy element is, density is in most cases taken to be the defining factor. Heavy elements are thus commonly defined as those having a specific density of more than 5 g/cm³. The main threats to human health from heavy elements are associated with exposure to lead, cadmium, mercury and arsenic (arsenic is a metalloid, but is usually classified as a heavy metal).

Inhalation of heavy elements fumes or particles can be life threatening, and although acute pulmonary effects and deaths are uncommon, sporadic cases still occur. Exposure may cause kidney damage. Several reports have since shown that kidney damage and/or bone effects are likely to occur at lower kidney levels. Long-term high heavy elements exposure may cause skeletal damage. The exposure was caused by heavy elements -contaminated water used for irrigation of local rice fields experiments have suggested that may be a risk factor for cardiovascular disease, heavy elements exposure may give rise to lung damage or may cause contact eczema. These intriguing contradictory findings need to be followed up by more studies of other similarly exposed populations [4].

The symptoms of lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system. Lead encephalopathy is characterized by sleeplessness and restlessness. Children may be affected by behavioral disturbances, learning and concentration difficulties. In severe cases of lead encephalopathy, the affected person may suffer from acute psychosis, confusion and reduced consciousness. People who have been exposed to lead for a long time may suffer from memory deterioration, prolonged reaction time and reduced ability to understand [5]. Atomic absorption spectrometry (AAS) is an analytical technique made in Australia that measures the concentrations of heavy elements us we show in fig (2). Atomic absorption is so sensitive that it can measure down to parts per billion of a gram (ppb or µg/ L) in a sample [6]. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level. Atomic absorption spectrometry has many uses in different areas of chemistry [7].

Atoms of different elements absorb characteristic wavelengths of light. Analyzing a sample to see if it contains a particular element means using light from that element. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample. In AAS, the sample is atomized – i.e. converted into ground state free atoms in the vapor state – and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporized sample. Some of the radiation is absorbed by the lead atoms in the sample [7, 8].

The greater the number of atoms there is in the vapor, the more radiation is absorbed. The amount of light absorbed is proportional to the number of lead atoms. A calibration curve is constructed by running several samples of known lead concentration under the same conditions as the unknown. The amount the standard absorbs is compared with the calibration curve and this enables the calculation of the lead concentration in the unknown sample. Consequently an atomic absorption spectrometer needs
the following three components: a light source; a sample cell to produce gaseous atoms; and a means of measuring the specific light absorbed [9].

2. Material and Methods
Fly ash samples from thermal electric power station after block out the chimney of it to measure the concentrations of studied heavy elements using (ICP-MS) equipment, after collecting samples stage, all the samples were taken to the laboratories of Baghdad university / chemistry lab by The chemical process of digestion to prepare the fly ash samples for measuring the studied Heavy elements, preparing as follow:

fly ash sample are taken from different thermal electric power station in the middle and south of Iraq, Crumbled and put it in the oven till the dryness and then Crush them to small volumes by mill and after harmonizing these samples, ( 10) gm from each sample was taken for analysis, A (7) ml of concentrated Hydrochloric acid (HCl) and a (8) ml of concentrated Nitric acid (HNO₃) were added to the sample after putting it in a Beaker (100) ml, then the mixture was heated to the end drought and avoid boiling, Returned to the previous steps. Then the acid was added for the second times and the samples were placed on Hot Plate and bring it up to the boiling point only and Put this mixture on the magnetic stirrer for (24) hours then Filtered the mixture by Filtering paper (No. 42) and put it in volumetric flask (100) ml and Finally were wished by Filtered water and adding the washing water to the filter and complete the Volume to (100) ml us we show in figure (1) then sending the prepared samples were sent to the analysis by (Optical Emission Spectrometer, PerkinElmer, Optima 2100DV) equipment's (AAS) us we show in figure (2) [9,10].

![Figure 1](image_url) prepared the fly ash samples for AAS
3. Results and Discussion

After collecting fly ash samples from thermal power stations in the middle and south of Iraq all samples were taken to the laboratory to preparing these samples for analyzing by (AAS) equipment’s (Buck Scientific Model 210 VGP, Atomic Absorption Spectrophotometer).

| S No | (Ni) µg/ml | (Zn) µg/ml | (Pb) µg/ml | (Mg) µg/ml | (Cu) µg/ml | (Fe) µg/ml | (Cd) µg/ml | (Mn) µg/ml | (Co) µg/ml |
|------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| S1   | 3.27       | 12.9       | 1.893      | High       | 1.211      | 487.6      | 0.927      | 0.095      | 0.804      |
| S2   | 3.929      | 0.303      | 0.422      | 0.031      | 0.418      | 6.56       | 0.432      | 3.829      | 0.07       |
| S3   | 4.675      | 2.39       | 0.232      | 0.27       | 0.246      | 1.201      | 0.242      | 0.9        | 0.074      |
| S4   | 6.499      | 0.531      | 0.639      | High       | 0.975      | 964.5      | 0.937      | 0.135      | 0.224      |
| S5   | 2.227      | 31.925     | 6.197      | 0.058      | 2.092      | 3.242      | 2.043      | 3.339      | 0.155      |
| S6   | 0.473      | 0.037      | 0.112      | High       | 0.039      | 0.105      | 0.025      | 0.031      | -0.013     |
| S7   | 3.562      | 0.932      | 0.577      | 0.02       | 0.316      | 1.114      | 0.052      | 2.455      | 0.194      |
| S8   | 2.539      | 0.58       | 0.458      | 0.423      | 1.339      | 7.416      | 0.052      | 0.104      | 0.128      |
| S9   | 4.902      | 0.132      | 0.363      | 0.049      | 3.849      | 6.575      | 0.106      | 0.222      | 0.15       |
| S10  | 5.579      | 0.005      | 0.814      | 0.256      | 1.489      | 4.352      | 0.073      | 0.09       | 0.255      |
| S11  | 4.818      | 0.118      | 0.512      | 0.054      | 3.956      | 9.407      | 0.051      | 0.12       | 0.146      |
| S12  | 3.644      | 0.134      | 0.842      | 0.273      | 1.698      | 1.283      | 0.066      | 1.455      | 0.193      |
| S13  | 0.911      | 1.195      | 0.432      | 0.035      | 4.8        | 1100.5     | 0.051      | 0.099      | 0.102      |
| S14  | 3.163      | 1.515      | 1.085      | 0.305      | 1.764      | 344.7      | 0.047      | 3.053      | 0.076      |
| S15  | 3.97       | 0.104      | 1.017      | 0.15       | 0.597      | 0.745      | 0.042      | 1.137      | 0.143      |
The concentration of Cadmium in the samples is ranging $(2.043 \pm 0.025\mu g/ml)$ with a mean $(0.293 \mu g/ml)$, the greatest value in S5 which is in fact represents S3 in Al-Dura thermal power station. It is within the range $(0.5 \mu g/ml)$ [11, 12] in fly ash and the smaller concentration represented S5 in Al-Rasheed thermal power station. Table 1 shows us the concentration of Cadmium and fig. 3 shows us the greatest and smaller concentration.

|   | 3.045 | 2.00 | 0.253 | 0.088 | 0.105 | 0.647 | 0.026 | 0.772 | 0.101 |
|---|-------|------|-------|-------|-------|-------|-------|-------|-------|
| S16 | 1.087 | 0.099 | 0.363 | 0.029 | 2.375 | 4.475 | 0.033 | 2.845 | 0.095 |
| S17 | 2.524 | 0.06  | 2.241 | High  | 104.7 | 6.052 | 0.069 | 26.8  | 0.146 |
| ave | 3.378 | 4.04 | 1.025 | 0.143 | 7.33  | 163.9 | 0.293 | 2.637 | 0.169 |

Table 1. Heavy elements concentration

The concentration of Cobalt in the samples is ranging $(0.804 \pm 0.013\mu g/ml)$ with a mean $(0.169 \mu g/ml)$, the greatest value in S1 which is in fact represents S2 in Al-Dura thermal power station. It is less than the range $(8 \mu g/ml)$ [11, 12] in fly ash and the smaller concentration in S6 represented S5 in Al-Rasheed thermal power station. Table 1 shows us the concentration of Cobalt and fig 3 shows us the greatest and smaller concentration.

![Figure 3. Cd concentration](image.png)
The concentration of Manganese in the samples is ranging (28.6 \pm 0.031 \mu g/ml) with a mean (2.637 \mu g/ml), the greatest value is S18 which is in fact representing S10 in Musaeb thermal power station. It is less than the limit (3.85 \mu g/ml)[11,12] in fly ash and the smaller concentration is S6 represented S5 in Al-Rasheed thermal power station Table 1 show us the concentration of Manganese and fig 5 show us the greatest and smaller concentration.

The concentration of Nickel in the samples is ranging (5.579 \pm 0.473 \mu g/ml) with a mean (3.378 \mu g/ml), the greatest value is S10 which is in fact representing S6 in Naseraya thermal power station. It is less than the limit (7.15 \mu g/ml)[11,12] in fly ash and the smaller concentration is S6 represented S5 in Al-Rasheed thermal power station Table 1 show us the concentration of Manganese and fig 6 show us the greatest and smaller concentration.
The concentration of Zinc in the samples is ranging (31.92±0.005 µg/ml) with a mean (4.04 µg/ml) the greatest value is S5 which is in fact representing S3 in Al-Dura thermal power station. It is more than the limit (1.65 µg/ml) [11,12] in fly ash and the smaller concentration is S10 represented S6 in Naseraya thermal power station Table 1 show us the concentration of Manganese and fig 7 show us the greatest and smaller concentration.

The concentration of Lead in the samples is ranging (2.241±0.112 µg/ml) with a mean (1.025 µg/ml), the greatest value is S5 which is in fact represents S3 in Al-Dura thermal power station. It is less than the limit (9.35 µg/ml) [11,12] in fly ash and the smaller concentration is S6 represented S5 in Al-Rasheed thermal power station Table 1 show us the concentration of Manganese and fig 8 show us the greatest and smaller concentration.
The concentration of Magnesium in the samples is ranging \((\text{High}_{0.029\,\mu g/ml})\) with a mean \((0.143\,\mu g/ml)\), the greatest value is S1, in fact represents S2 in Al-Dura thermal power station, S6 in fact represents S5 in Al-Rasheed thermal power station, S18 which is in fact represents S10 in Musaeb thermal power station. It is more than the limit \((0.440\,\mu g/ml)[1,12]\) in fly ash and the smaller concentration is S17 represented S3 in Hartha thermal power station. Table 1 show us the concentration of Manganese and fig 9 show us the greatest and smaller concentration.

**Figure 8. Pb concentration**

**Figure 9. Mg concentration**
The concentration of Copper in the samples is ranging (104.7 ± 0.039 µg/ml) with a mean (7.33 µg/ml), the greatest value is S18 which is in fact representing S10 in Musaeb thermal power station. It is more than the limit (1.98 µg/ml) [11,12] in fly ash and the smaller concentration is S6 represented S5 in Al-Rasheed thermal power station. Table 1 show us the concentration of Manganese and fig 10 show us the greatest and smaller concentration.

![Figure 10. Cu concentration](image)

The concentration of Iron in the samples is ranging (1100.5 ± 0.105 µg/ml) with a mean (163.9 µg/ml), the greatest value is S13 which is in fact represents S2 in Hartha thermal power station. It is more than the limit (9.90 µg/ml) [11,12] in fly ash and the smaller concentration is S6 represented S5 in Al-Rasheed thermal power station, Table 1 show us the concentration of Manganese and fig 11 show us the greatest and smaller concentration.

![Figure 11. Fe concentration](image)
4. Conclusion
The results which obtained from the present work show that fly ash samples from thermal electric power stations in the middle and south of Iraq were found to be significantly contaminated with metals like Cd, Zn, and Fe, Mg, Cu at levels above the background concentration in the international limits, which may give rise to various health hazards, while the concentrations other heavy elements were under the background concentration in the international limits. The high concentration of some heavy elements can be due to the type of fuel used in the thermal power station. The increase in the concentration of some heavy metals can be due to the type of fuel used in the thermal power plant. The increase of some heavy elements can lead to serious diseases, especially lung cancer, so it is necessary to get rid of fly ash in other ways or replace the fuel with another.

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