Presence Of Heavy Metal In Soil On Three Different Sites Of Prayagraj For Forensic Considerations

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ABSTRACT

Atomic absorption spectrometry (AAS) is a unique tool for the study of heavy and traces metal components of soil samples. This technique is often utilized for the quantitative determination of elements in environmental materials at trace levels. Heavy metal analysis of soil in forensic science can provide a clue in investigation. Atomic absorption spectrometry (AAS) is a technique through which can measure the amount of trace metals present in soil samples. Variety types of atomizers are in used in AAS most often the flame and the graphite furnace types being utilized in analysis. In field of forensic science heavy metal analysis play a key role as it provide a unique fingerprint of different soil. The present study is conducted to study the correlation between the three different types of land use and the presence of heavy metals in soil. It also highlights the various components of atomic absorption spectrophotometer, different types of AAS in soil examination and applications of atomic absorption spectroscopy in the fields of forensic science.

KEYWORDS: AAS, Heavy Metal, Soil, Flame, Graphite Furnace, Forensic Science.

INTRODUCTION

Atomic absorption spectroscopy has been at the leading edge of inorganic examinations in criminological sciences since the late 1960s. With the advancement of non flame atomizers (carbon furnace) and high intensity lamps (electrode less discharge, hollow cathode), different elements of attentiveness, due to their high toxic nature, are frequently regularly examined (As, Th, Sb, Cd, etc.) It has discovered applications in soil, hair, fingernail, paint, powers, greases, fibers, polymers, papers, pharmaceutical, gunfire buildup, and falsified coins examinations. **[1]** Atomic absorption spectroscopy has gotten one of the most every now and again utilized apparatuses in investigative science. It is commonly recognized that if adequate amount of analytic is existing in the specimen, at that point it ought to be resolved utilizing a flame technique since this has included favorable circumstances of being quick (expecting just a couple of components need be resolved) and, in examination with elective procedures, extremely easy to utilize.**[2]** Atomic Absorption Spectrometry (AAS) is an instrument for evaluating the ingestion of follow segments present in soil tests by assessing the radiation devoured by the compound part of interest. This is done by examination of the spectra made when the specimen is empowered by radiation. It relies upon the Beer-Lambert law standard in which atomic absorption method measures the essentialness as photons of light that are devoured by the specimen. An identifier quantifies the wavelength of light transmitted by the specimen and then correlates with the wavelength which initially went through the specimen. A signal processor then points out the changes that occurred in wavelength ingested, which show up in the readout as pinnacles of vitality retention at discrete wavelength. **[3]** AAS is an optical atomic spectrometric procedure dependent on the estimation of the particular assimilation beginning from free non ionized atom in the gas stage. **[14]** Heavy metals in soil tests can be examined by exceptionally sensitive spectroscopic methods, such as atomic absorption spectroscopy [e.g. Flame Atomic Absorption Spectroscopy (FAAS) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS)].**[5]** Flame and furnace spectroscopy has been utilized for quite a long time for the investigation of metals. Today these methods are utilized like never before in materials and natural applications. This is because of the requirement for lower identification limits and for metal trace examination in a wide scale of sample tests. This method, of examination has greater specificity than ICP method. **[6]** In follow component examination of soil for trace element by flame atomic absorption spectroscopy (FAAS), sample dissolution is frequently the most tedious step.**[7]** The benefit of GF-AAS over F-AAS is that F-AAS can only examine solution just while GF-AAS can examine solution, slurries, and solid sample. **[8]** A portion of the weaknesses incorporate constrained application as just around 70 components barring earth metals have been distinguished by this strategy. Another burden in that AAS can't yet recognize non-metals. **[13]**

Soil Heavy Metal Analysis

Soils may get tainted by the accretions of substantial metals and metalloids through discharge from the quickly extending mechanical regions, mine tailings, removal of high metal squanders, leaded fuel and paints, land use of composts, creature excrements, sewage slop, pesticides, wastewater water system, coal burning buildups, spillage of petrochemicals, and air statement. Heavy metals comprise a characterized gathering of inorganic compound which are extremely dangerous, and some of those are normally found at polluted areas and are such as lead (Pb), chromium (Cr), zinc (Zn), cadmium (Cd), copper (Cu), iron (Fe) and nickel (Ni). Albeit heavy metals are normally found in the dirt, land, soil, geological and anthropogenic exercises increment the convergence of follow components in amounts risky for plants and creatures. Some substantial metals, for example, Cu, Fe, Ni and Zn are required in little amounts by creatures. Be that as it may, extraordinary measures of these components can get hurtful to living beings**. [3]** The soil stem can move segments onto an article or people. Because of its unpredictable material through assessment of its segments it can give data about its geographical source, prevailing vegetation, the board, and condition. Soil comprises of high volume of data that greatly affects Forensic investigation. Individual systematic procedures have various sizes of goals and pertinence relying upon the idea of the criminal case and setting, every technique has its qualities and shortcomings. The soil that moves from the stem onto an item or individual can be recuperated and utilized as proof in a criminological examination. Soil recognizable proof of source, connecting to a wrongdoing is needy of the attributes of the natural and inorganic sample which can be contrasted and different sample. **[4]** Atomic absorption spectroscopy (AAS) gauges the measure of light of a particular frequency consumed by atom of a specific substance. This method is particularly valuable in identification of heavy metal contaminants in soil samples. It is likewise valuable in examination of paint chips. This method can enable criminological researchers to decide if soil or paint at the scene of crime can be connected to another area. **[9].** The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg.**[10]** Various extraction methods are utilized for the determination of concentration of heavy metal in soil. The method which is mostly preferred for the extraction is usually utilizing mixture of conc. acid reflect the whole amount of concentration of Inorganic elements. Different extraction methods like diluted acid, EDTA, and NH_4ACcan only partially extract heavy metals from soil**. [11]** Both AA and ICP spectrometers require the sample to be in a fluid structure before introducing into the instrument. This is practiced by digestion in concentrated acids, with aqua regia (HCL/HNO3) being the most widely recognized, albeit different acids can be utilized. Note that this technique for processing may not bring about a proportion of all out metals, as not all segments might be solvent in the corrosive of decision, especially those bound as silicates. On the off chance that this is viewed as fundamental (once in a while suggested for residue), at that point it is important to utilize hydrofluoric acid, which will process the silicates. Be that as it may, aqua regia is perceived as an industry standard and most regularly utilized, with the outcomes once in a while alluded to as 'aqua regia solvent'. **[12]**

Forensic Application of Soil Analysis through AAS

Soil is significant physical evidence utilized in criminal examination. It is contact evidence found in shoes, shirts, and head hairs, vehicle tires, moved from the scene of crime. Soil is a blend of multi-minerals, plant materials, creature matters and little man-made materials like paint chips, glass pieces, solid materials, oil stains and some more. Soil is made out of little particles and these particles differ in size, shape, and substance piece. Three sorts of soil particles are known viz. sand, sediment, and earth. Through Atomic Absorption Spectroscopy (AAS) we can determine the trace metal concentration of potassium, sodium, calcium, iron, lead, copper, chromium and cadmium from soil samples collected from different points and depths**.[17]**Atomic absorption spectroscopy has served the criminological network for more than 40 years and keeps on working viably for such various applications as gunfire powder residue investigation and toxicological assessments in presumed substantial metal toxicological cases. These and other established criminological applications have additionally used different types of spectrochemical examination, for example, neutron activation. From settled AA method to the expanding number of forensic applications being created for laser ablation/inductively coupled plasma mass spectrometry; present day atomic absorption spectroscopy has demonstrated itself to be a convincing and advancing instrument in the examination of legal proof. **[15]** The forensic science is considered as the enthusiastic and mysterious by the common people, to the forensic scientist who perform it is often consider it with meticulous and annoying examinations. This is mostly is in the established area of forensic science, basically that of contact evidence where the examination of minuscule samples can lead the criminal case by providing the clue and assist in the conviction of an accused person. Physical evidence such as hairs and other fibres, paint samples, glass fragments, stains, soils, and other deposits**.** New era of instrumentation such as infra-red spectrophotometry, gas chromatography, and atomic absorption spectroscopy and energy dispersive X-ray analysis now allows a relatively simple identification of the composition of these materials. **[16]**

Material And Methods

A. Sample location- Prayagraj

The soils employed in this study were collected from Prayagraj district (23 blocks, 3 sample from each block) in total 115 samples were collected. The specified areas which were included for the sampling were block area, agriculture land, and playground. These areas were selected for the sampling because there were great chance of characterization of soil as it undergoes through different environment and also for forensic consideration.

B. Digestion of Soil Samples

1 g of soil sample (oven dried) was weighed and placed in a 250 mL Beaker with 15 mL aquaregia (35 percent HCL and 70 percent high quality HNO3, in a 3:1 ratio). After that, the solution was digested at 70°C till it became transparent. The resultant solution was filtered using Whatman filter paper no. 42 before being transferred to a 50ml dilute to 50 ml volumetric flask and diluted with deionized water to the necessary level. An atomic absorption spectrophotometer (Perkin–Elmer A Analyst 400) was used to determine the amounts of Cu, Zn, Fe and Mn in the sample solution.

C. Analysis of soil samples

AAS The analyzer 400 model was used to detect the quantity of heavy metals in previously digested soil samples. The compressor was switched on when the nitrous oxide, acetylene gas, and nitrous oxide were all fixed, and the liquid trap was blasted to eliminate any trapped liquid. The Extractor and the AAS control were both turned on. The slender tube and nebulizer component were cleaned with purifying wire, and the burner aperture was cleaned with an arrangement card. The attached PC's AAS programming worksheet was opened, and an empty cathode light was put into the light holder. The light was turned on, the cathode beam was adjusted to hit the layout card's target zone for maximum light output, and then the machine was turned off. The rate of craving was measured by placing the fine in a 10 mL graduated container filled with deionized water. A set of calibration solutions (standards) containing known amounts of analyte element were generated, as well as the analytical blank. The responses of the blank and standards were measured one by one after they were atomized. After creating a calibration graph for each solution, the sample solutions were atomized and examined. The varied metal concentrations in the sample solution were derived from the calibration based on the absorbance recorded for the unknown sample.

RESULT AND DISCUSSION

The results of concentration of heavy metals in soil sample collected at Prayagraj district are presented in table 1.1.

Table 1: Concentration of heavy metals in the soil sample

		Concentration of heavy metal in the soil samples (ppm)			
S.NO	**Sample**	**Zn**	**Cu**	**Fe**	**Mn**
1	Chaka B1	0.21	0.02	28.52	3.32
2	Chaka P1	0.28	0.03	43.01	23.41
3	Chaka A1	0.66	0.09	71.09	41.44
4	Jasra B1	0.25	0.02	12.05	66.67
5	Jasra P1	0.35	0.06	4.72	28.43
6	Jasra A1	0.66	0.05	50.37	53.19
7	Shankargarh B1	0.58	0.04	11.78	43.75
8	Shankargarh P1	0.47	0.08	50.82	33.71
9	Shankargarh A1	0.04	0.02	31.93	74.17
10	Kaundhiyara B1	0.24	0.06	8.91	75.46
11	Kaundhiyara P1	0.30	0.04	30.28	54.95
12	Kaundhiyara A1	0.28	0.03	62.47	5.00
13	Karchana B1	0.20	0.02	35.68	32.99
14	Karchana P1	0.29	0.04	51.36	65.92
15	Karchana A1	0.34	0.04	2.59	68.38
16	Meja B1	0.21	0.02	15.37	83.96
17	Meja P1	0.33	0.05	14.92	32.25
18	Meja A1	0.27	0.03	30.21	38.52
19	Uruva B1	0.52	0.02	40.59	31.27
20	Uruva P1	0.31	0.04	93.74	74.12
21	Uruva A1	0.34	0.05	14.72	41.31
22	Koraon B1	0.01	0.02	65.26	89.97
23	Koraon P1	0.34	0.06	6.77	26.21
24	Koraon A1	0.31	0.05	35.97	51.21
25	Manda B1	0.20	0.04	18.02	37.88
26	Manda P1	0.36	0.03	3.65	12.53
27	Manda A1	0.19	0.02	4.33	3.85
28	Saidabad B1	0.41	0.06	4.36	13.46

29	Saidabad P1	0.38	0.03	54.07	30.24
30	Saidabad A1	0.33	0.04	94.21	45.47
31	Handia B1	0.21	0.02	58.34	44.31
32	Handia P1	0.43	0.06	16.76	29.42
33	Handia A1	0.32	0.06	16.94	85.14
34	Dhanupur B1	0.30	0.02	7.91	23.51
35	Dhanupur P1	0.61	0.06	27.53	9.07
36	Dhanupur A1	0.36	0.04	129.60	69.31
37	Pratappur B1	0.31	0.04	BDL	3.03
38	Pratappur P1	0.49	0.04	6.19	28.23
39	Pratappur A1	0.42	0.03	3.85	32.78
40	Shasho B1	0.28	0.03	42.54	67.89
41	Shasho P1	0.25	0.02	39.53	41.69
42	Shasho A1	0.46	0.04	9.88	43.65
43	Phulpur B1	0.29	0.03	3.76	27.55
44	Phulpur P1	0.35	0.05	100.51	2.90
45	Phulpur A1	0.33	0.05	7.76	60.98
46	Bahariya B1	0.27	0.04	BDL	45.36
47	Bahariya P1	0.26	0.02	1.40	24.80
48	Bahariya A1	0.23	0.04	9.09	32.12
49	Bahadurpur B1	1.7	0.05	22.16	34.75
50	Bahadurpur P1	0.32	0.03	70.06	27.27
51	Bahadurpur A1	0.27	0.04	4.67	2.45
52	SVD B1	0.30	0.04	BDL	37.09
53	SVD P1	0.35	0.02	32.29	93.97
54	SVD A1	0.27	0.04	30.21	38.52
55	Soraon B1	0.30	0.04	41.08	2.86
56	Soraon P1	0.27	0.05	2.86	7.79
57	Soraon A1	0.24	0.04	7.62	73.03
58	Kaurihara B1	0.45	0.03	BDL	8.08
59	Kaurihara P1	0.38	0.03	7.73	38.93
60	Kaurihara A1	0.20	0.05	72.54	5.55
61	Maumima b1	0.58	0.08	29.93	78.75
62	Maumima p1	0.37	0.02	3.00	29.03
63	Maumima a1	0.23	0.03	41.39	10.56
64	Holagarh b1	0.60	0.03	38.9	77.62
65	Holagarh p1	0.33	0.04	BDL	8.96
66	Holagarh a1	0.30	0.05	34.34	39.98
67	Bhagwatpur b1	0.40	0.03	9.62	71.04
68	Bhagwatpur p1	0.33	0.03	94.24	7.38
69	Bhagwatpur a1	0.27	0.02	43.76	5.66
	Min.	0.01	0.02	1.40	2.45
	Max.	1.7	0.09	129.60	93.97
	Mean	0.35	0.03	32.18	38.46
	SD	0.20	0.015	28.86	25.46
	*BDL -Below Detectable Limit *A1- Agriculture land, B1- Block land and P1-Playground				

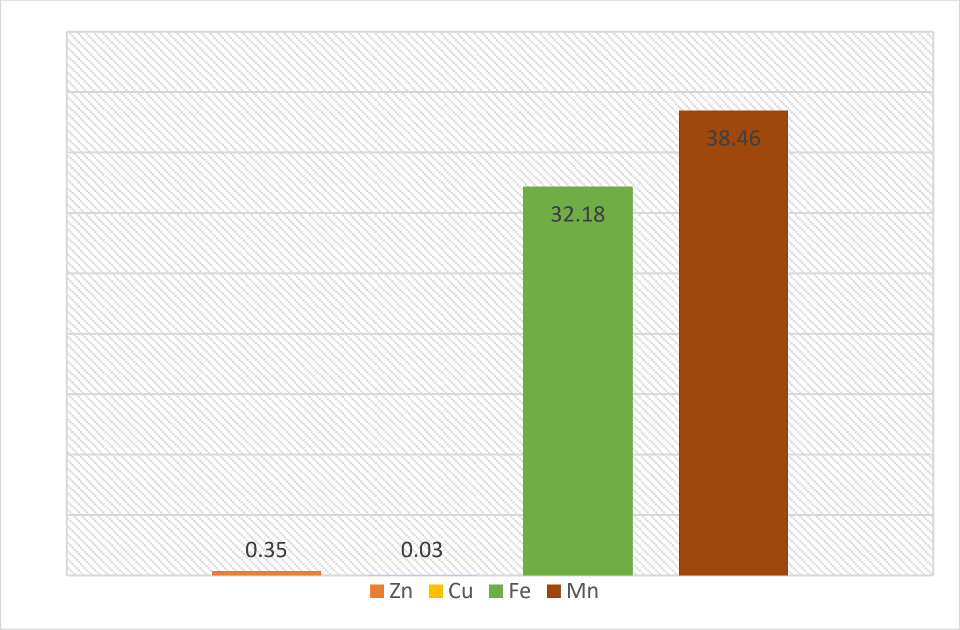

Fig. 1.1: Concentration of Heavy Metals in Soil (mg/Kg)

From the above figure, important remarks are noted. The mean value of Mn is higher among all heavy metals and was found to be (38.46 ± 25.46) mg/Kg. The mean value of Cu was the minimum among all heavy metals and was found to be (0.03± 0.015) mg/Kg. The mean concentration of heavy metals in soil were in the following order of Mn>Fe>Zn>Cu.

Manganese: An important plant mineral nutrient, manganese (Mn) is vital to several physiological functions, most notably photosynthesis. A common issue, manganese insufficiency is mostly found in sandy soil, organic soil that has a pH higher than 6, and extensively weathered tropical soil**.** The concentration of manganese is found in the range of 2.45 – 93.97 mg/kg. Min. concentration (2.45 mg/Kg) of manganese is found at Bahadurpur A1and Max. Concentration (93.97 mg/Kg) of manganese is found at SVD P1. The mean concentration of manganese is found as (38.46 ± 25.46) mg/Kg. According to ICAR, IARI manual the requirement of manganese in the Soil is 20-3000 mg/Kg. The mean concentration of manganese at all location is found to be smaller than the limit prescribed by ICAR, IARI manual. The lower Mn concentrations showed that there is no heavy metals pollution at the sampling site.

Iron: Although it is mostly present in forms that are indigestible by plants, iron is the fourth most common metal in soil. Most of the iron in soil is present in forms that are not easily utilized by plants, such as silicate minerals, iron oxides, and iron hydroxides. synthesis of chlorophyll. Compaction or floods can result in poor soil aeration, or a lower oxygen content in the soil**.** The concentration of iron is found in the range of 1.40 – 129.60 mg/kg. Min. concentration (1.40 mg/Kg) of iron is found at Bahariya P1 and Max. Concentration (129.60 mg/Kg) of iron is found at Dhanupur A1. The mean concentration of iron is found as (32.18±28.86) mg/Kg. According to ICAR, IARI manual the limit of iron in the soil is 50 mg/Kg. The concentration of iron some location is found to be higher than the limit prescribed by ICAR, IARI manual. The higher Fe concentrations showed that there is a heavy metals pollution at all sampling site.

Copper: Nearly all copper found in soil is found in its divalent form. The primary and secondary mineral crystal lattices typically have the highest percentage of Cu. Furthermore, a significant amount of Cu is bound by the organic matter in the soil. The concentration of copper is found in the range of 0.02 – 0.09 mg/kg. Min. concentration (0.02 mg/Kg) of copper is found at 15 different location and Max. Concentration (0.09 mg/Kg) of copper is found at Chaka A1. The mean concentration of copper is found as (0.03±0.015) mg/Kg. According to ICAR, IARI manual the limit of copper in the soil is 3 mg/Kg. The mean concentration of copper at all location is found to be smaller than the limit prescribed by ICAR, IARI manual. The lower Cu concentrations showed that there is no heavy metals pollution at the sampling site.

Zinc: Zinc was used in various industrial processes, including the mining, burning, and steel-making processes. Many foods contain varying quantities of zinc. There are additional zinc concentrations in drinking water that may increase if stored in metal containers. Drinking water containing higher than allowed levels of zinc can have negative health effects on crops or hazardous waste sites. Zinc is an essential trace element that is necessary for human health. Zinc shortages may result in congenital abnormalities. Global zinc development is likewise increasing, ensuring that zinc ends up high in the water more and more. Because power plants have enormous volumes of wastewater, water. The concentration of zinc is found in the range of 0.01- 1.7 mg/kg. Min. concentration (0.01 mg/Kg) of zinc is found at Koraon B1and Max. Concentration (1.7 mg/Kg) of zinc is found at Bahadurpur B1. The mean concentration of zinc is found as (0.35±0.20) mg/Kg. According to ICAR, IARI manual the limit of zinc in the soil is 1000 mg/Kg. The mean concentration of zinc at all location is found to be smaller than the limit prescribed by ICAR, IARI manual. The lower Zn concentrations showed that there is no heavy metals pollution at the sampling site.

New Approach

Forensic science does not investigate potential value of soil research, even though soil may be a crucial piece of physical evidence in instances involving animal crimes, hit-and-run incidents (soil on the car), both indoor and outdoor murder, assault cases, etc. Soil analysis can be used to establish a connection between the suspect and the crime. As a result, figuring out the soil's origin is crucial. There are many different types of particles and materials in the environment that may be important as trace evidence, and sophisticated methods are now present for their testing and comparison. Currently, the main issue bonding the use of soil as evidence in a forensic context are the lack of awareness among the legal and investigative communities, the insufficient of resources to develop relevant databases, and there are relatively least number of professionally experienced and trained scientist able to undertake the work. From this research we can not only characterize the soil sample but also develop one of its kind databases. A similar method can be applied in the real cases of forensic laboratories to check whether two soil samples are from same location or not. Currently, no such research has been conducted on soil sample in forensic aspect of Prayagraj district.

CONCLUSION

On the basis of this result, it is concluded that heavy metal concentration and their distribution in the soil samples of Prayagraj (block sites, agriculture land and playground) differ from one another due to anthropogenic activity and climatic conditions. The experiment of heavy metal analysis of soil samples is valuable evidence for forensic purposes Significantly high levels of hazardous metals can affect soil quality as well as human health through the tropic food chain. Heavy metals give each soil its own distinct imprint. It provides a distinctive soil profile from one place to another, which aids forensic investigations. When it comes to many different types of crime, such as murder, cases of poisoning, hit and run, burglary, cases of poisoning, etc.

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