

ASSESSMENT OF AGRICULTURAL SOIL QUALITY BASED ON HEAVY METALS CONCENTRATION IN AND AROUND YERRAGUNTLA CEMENT INDUSTRIAL ZONE, YSR KADAPA, ANDHRA PRADESH, INDIA

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ABSTRACT

Heavy metals (HMs) are the important polluting substances which are commonly emitted to the environment from industrial zones, particularly cement manufacturing units. They not only enter into the soils but also reached to the food chain via biomagnifications. Here in the present study we made a thorough investigation of soil and plant samples in and around the agricultural lands nearby the cement factories located in Yerraguntla for heavy metals concentration. This industrial town is notable for cement manufacturing units located in the Rayalaseema region, YSR Kadapa District, Andhra Pradesh, India. The selected soil sampling locations for the study are Nallingayapalle, Jamba puram, Thurakapalle and Appayapalli labeled as S1, S2, S3 and S4 respectively. In addition, the famous crops cultivated in the agricultural lands closer to this industrial zone also selected for the study. They are *Oryza sativa*, *Gossypium hirsutum*, *Arachis hypogaea*, *Helianthus annuus*, *Allium cepa* and *Solanum lycopersicum* with the common names of rice, cotton, ground nuts, sunflower, onions and tomatos respectively. The soil samples were collected from the surface in 5-10cm depth and the plant sampling was done with the selected healthy plants during December 2019. The samples analyzed to determine their HMs (Lead, Nickel, Chromium, Cobalt, Boron, Copper, Iron, Manganese and Zinc etc) by Inductively Coupled Plasma Optical Emission Spectrometer (ICP - OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The results showed that the level of heavy metals concentration

does not exceed the United States Environmental Protection Agency (USEPA) standards and it was ascribed that the source for the pollutants is not only cement industry but also motor vehicle emissions.

Keywords: Heavy metal pollutants, Soil and plant samples, Yerraguntla industrial zone, ICP-OES and ICP-MS.

INTRODUCTION: Agriculture, aquaculture and livestock activities are the main economic source in India. Andhra Pradesh is one of the top states in India which is known for its largest producers in agriculture and aqua culture [1]. One of the popular districts is YSR Kadapa provided with red ferruginous and black soils ranging from poor to good fertile nature. 53% percent of the cultivated land is occupied with red soils which are low nutrient and the remaining 24% of black corson soil, 19% of black soil and 4% of sandy soil lands with low fertile nature. The overall cropping area is nearly 4.08 lakh hectares and the major rain based crop is Groundnut with the annual cropped area of 52%. Commercial crops are grown in 5% of the annual cropped area; Pulse account for 3 percent and the area under food crops is 0.99 lakh hectares, accounting for 25 percent of the cropped area. The remaining area is accounted under non-food crops is 2.97 lakhs hectares [2]. The soil is most important and valuable resource in nature which play key role in agriculture and aquaculture activities. Soil is mainly composed of mineral constituents (sodium, potassium etc), organic matter (humus), living fauna, air, water, and it regulates the natural cycles of these components [3, 4]. Nearly 20

crops varieties are cultivating at YSR Kadapa district due to the different varieties of soils and the different varieties of soils are given in figure.1.

Now-a-days cement emissions have drawn great interests over the years due to their involvement in the environmental pollution/contamination. Nevertheless, cement manufacturing industries has supported the economic growth of the country as well as aimed to reach the demands of worldwide growing population. Despite all the advantages, cement manufacturing industries also generates adverse environmental pollution and contributes to the deterioration of the air quality by producing hazardous air pollutants [5-7]. Cement manufacturing industries are also extensive energy consumption as well as green house gas emitter in the atmosphere.

Among released contaminants in atmospheric air by cement manufacturing, various heavy metals (HMs) are also widely spread in the atmosphere covering upto thousands of kilometers around the emission source and gradually deposited. HMs are originated from raw materials, fuel and waste combustion, during the clinkering process [8-10]. The behavior of these metals in the burning process depends largely on their volatility and temperature. Non-volatile metals remain mainly within the clinker. Moreover, the typical raw cement is composed of 25 mg/kg Cr, 21 mg/kg Cu, 20 mg/kg Pb, and 53 mg/kg Zn [11]. Further to this elemental composition, it was also reported that about 0.07 kg of dust is generated into the atmosphere when 1 kg of cement is manufactured [12].

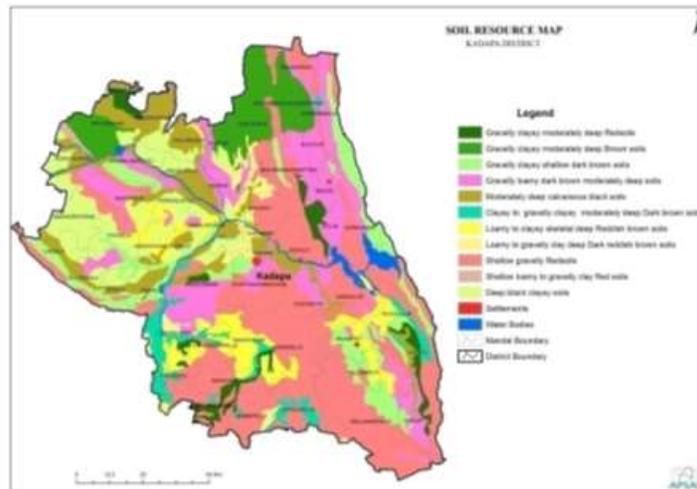


Fig. 1 Soil resource map of YSR Kadapa district

Soil contamination by heavy metals can cause long term problems on the biogeochemical cycle, which may affect soil functioning systems, leading to changes in soil fauna [13]. The effects and concentrations of the dust containing trace metals as pollutants vary and depend largely on technology employed from the cement industries to ameliorate environmental degradation. In humans, trace metals such as Pb may affect the brain and cause retarded growth, especially in children [14]. In plants, excessive [Pb] alters normal metabolic pathways by disrupting specific cellular enzymes and may also inhibit the photosynthetic ability of plants [15]. In general, excessive levels of heavy metals may result

in the induction of oxidation stress, damage to DNA, and disturbances in the biosynthetic pathways [16]. Migration of heavy metals in the soil takes place due to mass transfer, which involves water carrier, diffusion and this migration of metals in soils depends on various properties of soil. Soil pollution by heavy metals has serious health implication especially with regards to crops/vegetables grown on such soils [17, 18]. Heavy metals occupy a special position in soil chemistry because they play very important physiological roles in nature [18].

In addition, study of heavy metals in soil is very important because soil is interlinked with

ground water, surface water, crop and Aquaculture. If the soils are contaminated with heavy metals or higher concentrations of heavy metals there may be a chance to bioaccumulation of these heavy metals into crop that might be effect on the human health otherwise there may be a chance to leaching of heavy metals into water bodies. Heavy metals can be found generally at trace levels in soil and vegetation, and living organisms feel the need for micro-portions of these metals. However, these heavy metals have a toxic effect on organisms at high content levels. Heavy metal toxicity has an inhibitory effect on plant growth, enzymatic activity, stoma function, photosynthesis activity and accumulation of other nutrient elements, and also damages the root system [19]. Hence, in order to investigate the heavy metals concentration present in the collected soil and plant samples in and around Yerraguntla industrial zone of YSR Kadapa district, Andhra Pradesh, Inductively coupled plasma optical emission Spectrometer (ICP - OES) and Inductively coupled plasma mass spectrometry (ICP-MS) were used for sample analysis. The results showed that the level of heavy metals concentration does not exceed the United States Environmental Protection Agency (USEPA) standards and it was ascribed that the source for the pollutants is not only cement industry but also motor vehicle emissions.

METHODOLOGY: Soils may be defined as a thin layer of earth's crust that serves as a natural medium for the growth of plants. It is the unconsolidated mineral matter that has been subjected to and influenced by genetic and environmental factors. Soils serve as a reservoir of nutrients for plants and crops and also provide mechanical anchorage and favorable tilth. Reconnaissance survey was done (during December, 2019) for collection of soil samples and the composite soils were collected from the study area of the villages in the vicinity of Yerraguntla cement manufacturing units. The sampling locations are situated in around 10 km radius of the located cement industries. The soil samples were collected from the surface in 5-10cm depth and the plant sampling was done with the selected healthy plants. The selected soil sampling locations for the study are Nallingayapalle, Jamba puram, Thurakapalle and Appayapalli labeled as S1, S2, S3 and S4 respectively. In addition, the famous

crops cultivated in the agricultural lands closer to this industrial zone also selected for the study. They are *Oryza sativa*, *Gossypium hirsutum*, *Arachis hypogaea*, *Helianthus annuus*, *Allium cepa* and *Solanum lycopersicum* with the common names of rice, cotton, ground nuts, sunflower, onions and tomatos respectively.

SAMPLE PREPARATION/SAMPLE

DIGESTION: The homogeneous samples are used for metal digestion. In a typical procedure, 1.0 g finely grinded and dried soil samples were taken in cleaned microwave digestion vessel and added 7 mL of concentrated HNO₃, 1 mL of HCl and 2 mL of Hydrogen Peroxide solutions. Closed the lid of vessel and digested by using microwave digestion system. After completion of digestion, the system was cooled and removed the vessels from Microwave digestion. Then the samples were filtered by using watman no. 42 filter paper and collected the filtrate in 50 mL Volumetric flash and made the final volume upto 50 mL by using diluents as 2% Nitric acid solution.

The plant samples were partitioned as root and leaves. From these parts, 0.2 g of each of the part was acid-digested using 2 ml HCl, 1 ml HClO₄, 2 ml of HF, and 5 ml of HNO₃, and the resulting solutions were then analyzed for trace metal contents using ICP-MS. Quality assurance was done using Certified Reference Materials for both soil and plant samples and the analysis was also carried out in triplicate.

PRINCIPLE AND SAMPLE ANALYSIS BY ICP-

OES AND ICP-MS: Radio frequency induction of Argon takes place and generates a high temperature nearly 6000°K. Sample is introduced into mixing chamber and the sample is mixed with argon gas, sample is converted into aerosol form. Only fine droplets or aerosol can enter into the plasma temperature. At that temperature interferences of other element can eliminate.

Each element has its characteristic wavelength. At that characteristic wavelength the intensity of each element can be measured. Before doing the analysis external calibration can be made by using five linear multi element standards were used which is traceable to National Institute of Standards and Technology (NIST). We observed good linear correlation coefficient for all metals (>0.995). Quality control check results were observed within the satisfactory levels.

OPERATING CONDITIONS OF ICP-OES

Power: 1200 watts
Nebulizer Flow: 0.8 L / min
Auxiliary Flow: 1.2 L / min
Viewing Height: 10 (mm)

The instrument used was a Perkin-Elmer Sciex Elan 5000 ICP-mass spectrometer (Perkin-Elmer, Uberlingen, Germany) equipped with quartz torch, nickel sampler and skimmer cones, a peristaltic pump (maintaining a 1 ml min⁻¹ sample uptake rate), a cross-flow type pneumatic nebulizer and a double pass Scott-type spray chamber.

RESULTS AND DISCUSSION: Four soil samples were collected from four villages nearby Yerraguntla cement industrial zone, YSR Kadapa district and analyzed for Pb, Cd, As, Co, Fe, Cr, Cu and Hg by ICP-OES. Sampling location details and the heavy metals concentration levels are summarized in Table -1 and results were discussed below. In the same way the detection limits for plant samples were summarized in Table-2.

PHYSICAL PARAMETERS FOR SOIL SAMPLES

PARTICLE SIZE: A Particle size of the different constituents (clay, silt, sand and gravel) controls the porosity and water holding characteristic of the soil. Clay (size < 0.003 mm) amount in the soil samples ranges from 25% to 40%; Silt (size 0.003 to 0.06 mm) in the soil samples is 14% to 24% and Sand (size 0.06 to 0.5 mm) in the soil samples is 5% to 10%, while Gravel (size > 3.55 mm) in the soil samples is 30% to 35%. Analysis shows that the soil has moderate water holding capacity.

POROSITY: Porosity is a measure of space in between soil particles caused by structural conditions

and determined under identical conditions. Porosity of soil samples of the study area ranges from 35.4% to 40.2%.

WATER HOLDING CAPACITY (WHC): Water Holding Capacity (WHC) of soil samples of the study area ranges from 35% to 44%.

BULK DENSITY: Bulk Density of soils in the study area is found to be in the range from 1.65 to 1.97 g/cm³.

CHEMICAL PARAMETERS FOR SOIL SAMPLES

pH: pH of soils in the study area is found to be in the range of 7.02 to 7.26.

CHLORIDE: Chloride content in soils of the study area is found to be in the range of 36 to 491 mg/kg.

SOLUBLE CALCIUM: The soluble calcium as CaCO₃ in soil samples is found to be in the range of 172 to 245 mg/kg.

MAGNESIUM: Magnesium content in soil samples of the study area ranges from 123 to 149 mg/kg.

TOTAL PHOSPHORUS: Available Phosphorus content in soil samples of the study area ranges from 12 to 16 mg/kg.

TOTAL NITROGEN: Available nitrogen content in soil samples of the study area is found to be in the range from 124 to 146 mg/kg.

POTASSIUM: Potassium content in soil samples of the study area is found to be in the range from 125 to 239 mg/kg.

SODIUM: Sodium content in soil samples of the study area is found to be in the range from 233 to 524 mg/kg.

TOTAL ORGANIC MATTER (TOM): Total organic matter content in soil samples of the study area is found to be in the range of 1.22 to 1.54 mg/kg.

Table-1: Results of Heavy Metals Concentration in Cultivated Agricultural Soils

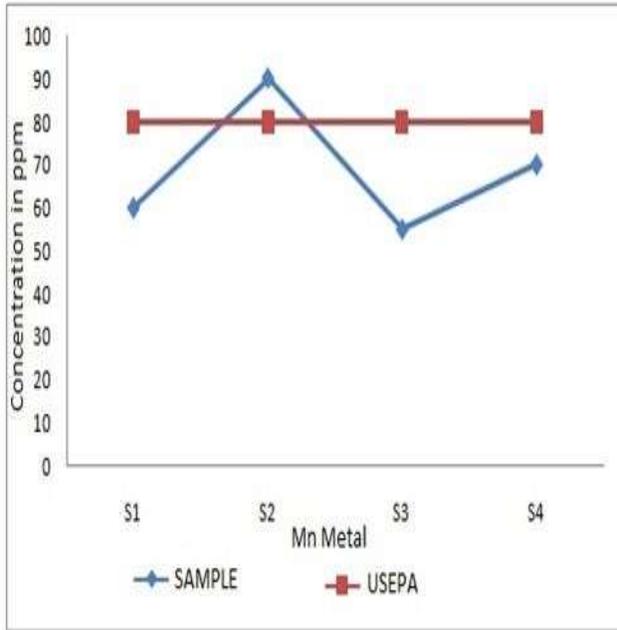
Elements	S1 (in ppm)	S2 (in ppm)	S3 (in ppm)	S4 (in ppm)	USEPA (in ppm)
Mn	60	90	55	70	80
Ni	52	40	49	45	50
Cu	60	52	43	45	50
Zn	223	190	185	206	200
As	10	10	12	10	Not available
Se	10	Not detected	10	10	Not available
Pb	321	250	310	190	300
Cr	Not detected	Not detected	Not detected	Not detected	400
Co	Not detected	Not detected	Not detected	Not detected	Not available

Table-2: Results of Heavy metals concentration in plants (in µg/g)

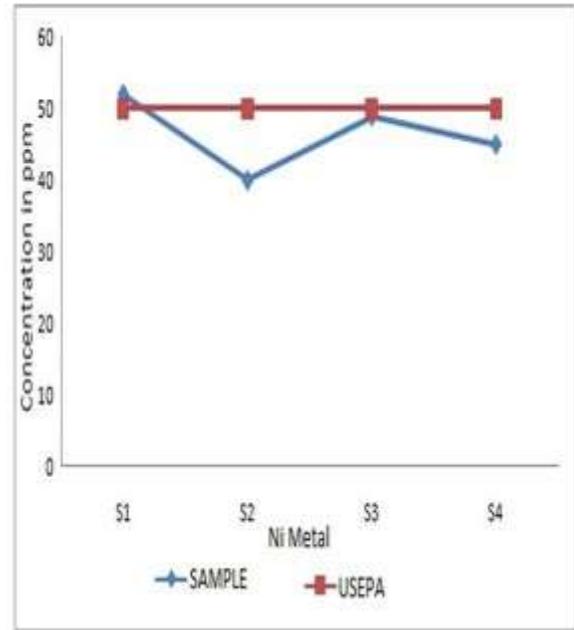
Elements	Oryza sativa (Rice)	Gossypium hirsutum (Cotton)	Arachis hypogaea (Ground nuts)	Helianthus annuus (Sun flower)	Allium cepa (Onions)	Solanum lycopersicum (Tomatos)
Mn	5.77	7.35	10.8	12.8	15.5	6.89
Ni	2.86	4.36	4.12	3.66	7.44	2.37
Cu	7.67	12.67	7.43	5.45	8.97	7.74
Zn	6.48	10.23	6.45	3.32	7.46	4.95
As	0.03	0.0	0.0	0.0	0.0	0.01
Se	0.0	0.0	0.0	0.0	0.0	0.0
Pb	0.32	0.11	0.01	0.01	0.02	0.0
Cr	0.0	0.0	0.0	0.0	0.0	0.0
Co	0.0	0.0	0.0	0.0	0.0	0.0

Based on the data presented in Table 1 and 2, it is very clear that the heavy metals concentration in soil samples were relatively low when compared to the USEPA standards. In another case, the concentration of heavy metals in plant samples was significantly very low; hence comparison with USEPA standards was omitted. Manganese concentration is ranging from 55ppm to 90ppm (Graph 1a). The highest concentration was observed at S2 (Jamba puram) and the lowest concentration was observed at S3 (Thurakapalle). Nickel concentration is ranging from 40ppm to 52ppm (Graph 1b). The highest concentration was observed at S1 (Nallingayapalle) and the lowest concentration was observed at S2 (Jamba puram). Copper concentration is ranging from 43ppm to 60ppm (Graph 1c). The highest concentration was observed at S1 (Nallingayapalle) and the lowest concentration was observed at S3 (Thurakapalle). Zinc

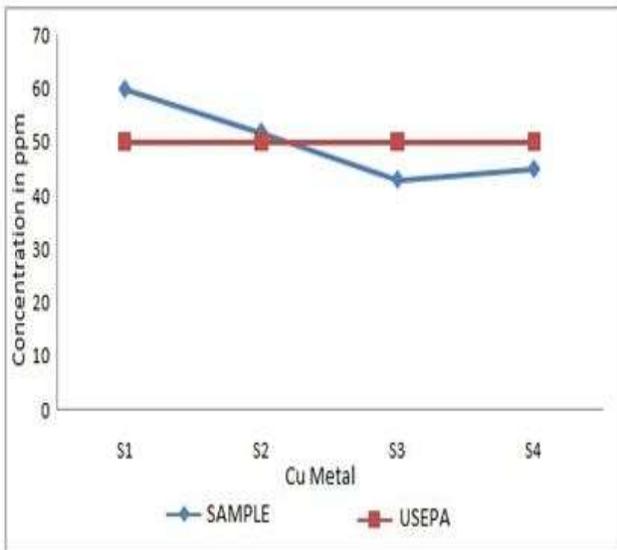
concentration is ranging from 185ppm to 223ppm (Graph 1d). The highest concentration was observed at S1 (Nallingayapalle) and the lowest concentration was observed at S3 (Thurakapalle). Arsenic concentration is ranging from 10ppm to 12ppm. The highest concentration was observed at S3 (Thurakapalle) and the lowest concentration was observed at remaining sampling locations. Selenium concentration is ranging from 5ppm to 10ppm. The highest concentration was observed at S1 (Nallingayapalle), S3 (Thurakapalle) and S4 (Appayapalli) but not detected at S2 (Jamba puram). Lead concentration is ranging from 190ppm to 321ppm (Graph 1e). The highest concentration of lead was observed at S1 (Nallingayapalle) and the lowest concentration was observed at S4 (Appayapalli) and it is important to mention that chromium and cobalt were not detected in the tested soil samples.



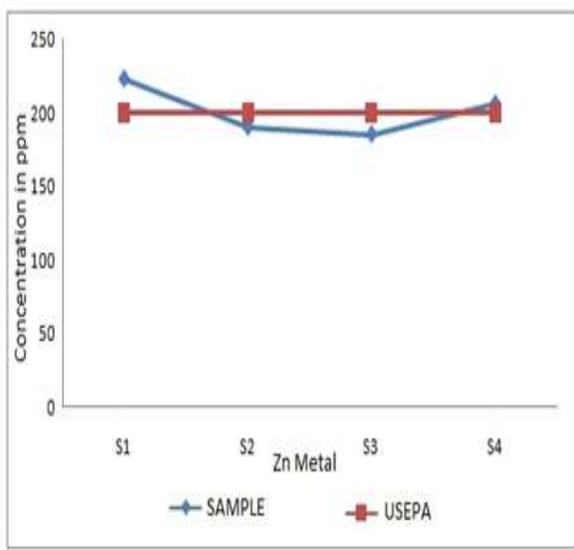
(a)



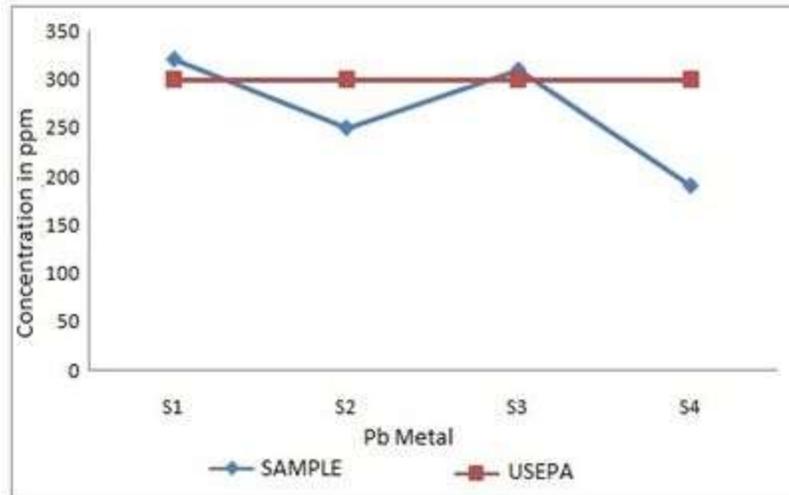
(b)



(c)



(d)



(e)

Graph 1: Comparison of levels of HMs (Mn, Ni, Cu, Zn and Pb) with USEPA limits at S1 to S4 sampling locations

CONCLUSION: In this study we thoroughly investigated the soil and plant samples to know the heavy metals concentrations of in and around Yerraguntla villages, YSR Kadap district, Andhra Pradesh, India. In the study area, variations in the pH value ranging from 7.02 to 7.26 which shows that the soil is slightly alkaline in nature. Organic Matter ranges from 1.22 to 1.54 mg/kg in the soil samples. Soil of the study area is known to be moderate for cultivation because high salinity. Generally, soils with low bulk density have favorable physical conditions (porosity and permeability) whereas those with high bulk density exhibit poor physical conditions for agriculture crops. Moreover the heavy metals concentrations in soil samples were relatively low when compared to the USEPA standards. In another case, the concentration of heavy metals was significantly very low in plant samples.

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