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ANALYSIS OF HEAVY METALS LEAD, CHROMIUM, CADMIUM AND MERCURY IN SOIL AND WATER SAMPLES OF GUNTUR DISTRICT, A.P

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Article Received: 17/09/2013	Article Revised: 28/9/2013 Article Accepted: 30/09/2013
Dr. T. Raja Rajeswari* Email:impactPOPS@gmail.com	ABSTRACT The analysis of heavy metals Lead, Chromium, Cadmium and Mercuryin water and soil samples were investigated in Piduguralla mandal of villages Brahmanapalli, Kondamodu, Nizampatnam mandal of villages Bavujipalem, Gokarnamatam, Nizampatnam Port and Pittalavanipalem mandal of villages Alluru, Manthenavaripalem, Pittalavanipalem areas in the Guntur district of Andhra Pradesh by using Electro Thermal Atomic Absorption Spectrometry. The results showed that the heavy metals concentration in soil samples are more than that of water samples in selected areas. Among these Chromium levels are high than the other in all samples. In soil samples, Lead content is high than the other samples. In Nizampatnam and Pittalavanipalem the P ^H levels are increased in the range of 7.0 – 7.3 in both water and soil samples. This increase may be due to the selected places are nearer to the coastal area and aquaculture. Electrical conductivity is also slightly increased in both soil and water samples in 2015 than in the 2014. The results indicated that the methods applied were very effective since the presence of Lead, Chromium, Cadmium and Mercury was clearly confirmed. This study has shown that Electro Thermal Atomic Absorption Spectrometry is an accurate, reliable and effective analytical method for the determination of target compounds at low concentrations in the environment.
	Spectroscopy

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INTRODUCTION

Heavy metals are present in all types of ecosystems. Their existence is mainly due to anthropogenic sources such as industrial and agricultural activities ^[1]. Waste from such activities contributes to the pollution of water bodies and soil, affecting the growth of plants and aquatic life ^[2]. A large portion of these pollutants can ultimately be traced to various consumable items such as dietary, supplemental, natural medicinal

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remedies, cosmetics, and various other commercial products ^[3]. Within the literature, the presence of heavy metals in various samples such as soil ^[4], diet ^[5] and natural medicinal products ^[6] ^[7] has frequently been reported. Long term exposure even to low concentrations of heavy metals can cause many adverse health effects and even toxicity ^[8]. Some heavy metals are essential to maintain normal human body functions at trace amounts. However, they may be dangerous or even toxic if present at higher concentrations ^[9,10]. Heavy metals such as lead (Pb), mercury (Hg), cadmium (Cd), and chromium (Cr) are substantially toxic elements known for their ability to bioaccumulate in the human body, resulting in multi-organ disruption ^[11]. The mechanism of toxicity for heavy metals can be explained by their ability to interact with nuclear proteins and DNA, causing oxidative deterioration of biological macromolecules ^[12]. Due to the metals toxicity and their adverse effects on the public health and the environment, it is essential to precisely measure their levels in soil and water samples.

Study Area

The analysis of heavy metals Lead, Chromium, Cadmium and Mercury in water and soil samples were investigated in Piduguralla mandal of villages Brahmanapalli, Kondamodu, Nizampatnam mandal of villages Bavujipalem, Gokarnamatam, Nizampatnam Port and Pittalavanipalem mandal of villages Alluru, Manthenavaripalem, Pittalavanipalem areas in the Guntur district of Andhra Pradesh. Guntur district has coastline of approximately 100km and is situated on the right bank of Krishna River which separates it from Krishna River and extends till it empties into the Bay of Bengal. It has total area 11,391 km². The geographical coordinates of Guntur district are 16^o18'N 80^o27'E. The district is a major centre for agriculture. It exports large quantities of chillies and tobacco. The water and soil samples are collected from the selected areas which were represented in the Figure 1.

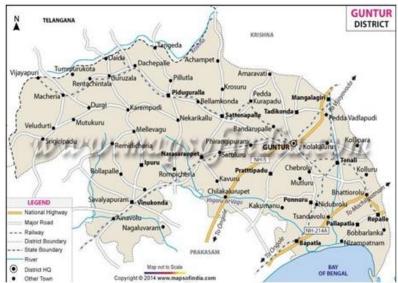


Figure 1: A Map indicating the sampling sites in Guntur district

MATERIALS AND METHODS

We analysed the presents of heavy metals in both water and soil samples in selected areas of Guntur district for two consecutive years that is May 2014 and May 2015. The parameters analysed in the both water and soil samples were heavy metals like Lead, Chromium, Cadmium, Mercury, P^H and electrical conductivity. **Soil sampling**

The soil samples are collected in three mandals of Guntur district, from each mandal three villages are selected which are polluted with heavy metals. The soil is collected by using a spade in 5.0-10.0 acres of the field in a depth of 15.0-20.0 cm, from 15.0-20.0 spots are taken in a zigzag pattern. All the lumps should be reduced by successive quartering to about half a kilogram. The samples are dried in a shade before doing the analysis. The following parameters are analysed in the soil samples using the standard procedures.

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Determination of Soil reaction or P^H

By using the potentiometer, the P^{H} of the soil samples are analysed, before doing the analysis the instrument is calibrated with P^{H} 4.0-9.2.

Determination of Electrical Conductivity

The electrical conductivity of soil samples or total dissolved salts are determined using the conductivity bridge. The instrument was calibrated with 0.01N KCl solution (Specific conductivity 1.41m mhos/cm²at 25 $^{\circ}$ C).

Water sampling

The water samples are collected from tanks, canals, bores, ponds from different depths, different spots in the selected areas in 500ml polythene bottles which are transparent. The bottles are properly marked and labelled then added 2 or 3 drops of toluene to prevent bacterial activity and stoppered tightly prior to the analysis.

Spectrophotometric determination of Lead: Extraction of Lead

500ml of digested sample is evaporated to dryness in a silica dish in a hot air oven. The residue is then ashed by ignition over a Bunsen burner in a fume cupboard. The ash is dissolved in 100ml of water containing 5ml of Conc. HCl. The solution is transferred to a separating funnel, 50ml of 20% sodium citrate is added and the mixture made alkaline by the addition of ammonia. 50ml of 10% KCN are added and the mixture cooled thoroughly. 5ml of 2% sodium diethyl dithiocarbamate is added and the mixture extracted times with ether, 25ml on each occasion. The ether extracts which are separately washed with water are transferred to a hard glass round-bottomed flask. The ether is evaporated off and the residue digested with 1ml Conc. H₂SO₄and 1ml HClO₄to destroy organic matter. The residue is diluted with water, 1ml glacial acetic acid was added, followed by 5ml ammonia sp. gr. 0.0-88.0 and the mixture diluted to 25ml by the addition of water.

Preparation of standard

To 1ml Conc. H₂SO₄ a little water, 1ml glacial acetic acid and 5ml ammonia sp. gr. 0.0-88.0 are added and the whole diluted with water to a volume of 25ml giving ammonium acetate. A known amount of Pb is added to 5ml of this mixture. To this are added 5ml of 1% KCN and 10ml of CCl₄. To this mixture added drop by drop an ammonical solution of dithizone reagent, with constant shaking until excess has been added. Too great an excess must be avoided. Sufficient excess is indicated when the CCl₄layer has reached its maximum intensity of redness and the aqueous layer is tinged brown. At this stage, the aqueous layer is removed and discarded. The CCl₄layer containing the red coloured lead complex, is shaken repeatedly with aliquots of 5ml of 1% KCN until the aqueous layers are no longer coloured. The CCl₄layer may be passed through a filter to remove droplets of water and is then ready for comparison. A range of standards may be prepared but it prefers to use a standard containing 0.0-0.02mg Pb, and to take the requisite amount of the unknown to conform to this. This standard may be obtained by using 2ml of a standard solution of lead acetate, containing 0.0-0.01mg Pb per mL.

Blank

A blank should always be done on a new set of reagents. In estimating the blank, the complete process is carried out. The blank is small and is thus difficult to estimate accurately so that the following method has been adopted. Before colorimetric estimation, 0.0-0.02mg Pb is added to the blank. This, after the development of the colour with dithizone, is compared with a standard containing 0.0-0.02mg Pb. The blank is then calculated from the difference.

Preparation of sample

The extracted Pb is contained as PbSO₄in a solution of ammoniacal ammonium acetate having a volume of 25ml. For the estimation, 5ml of the solution are taken and to this are added 5ml of 1% KCN and 10ml of CCl₄. The colour is developed.

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Estimation

The Wavelength of both Standard and sample is measured by using colorimeter and the lead is estimated in sample compare with standard.

Analytical methodology

The analysis of heavy metals is quantified by using Electro Thermal Atomic Absorption Spectroscopy (AAS). Samples are digested in Conc. HNO₃in hot condition upto 4mins. After filtration sample is ready for analysis in AAS for the quantification of total Cr/Hg/Cd and in water Chromabond NH₂columns (aminopropyl phase with a 3ml volume and 500mg of sorbent) obtained from Machery-Nagel (Duren, Germany) were used. The P^H value of the water/ soil sample was adjusted to 5.5 using acetic acid or sodium acetate and sample was aspired through the previously conditioned column. The column contents were dried under vacuum and the Cr/Hg/Cd selectively linked was eluted with nitric acid and quantification was performed by Electro Thermal Atomic Absorption Spectroscopy (ETAAS). For the detection of total Cr/Hg/Cd treated with 1% K₂S₂O₈solution and AgNO₃at 100 $^{\circ}$ C for 15min. Oxidised solution was eluted through a Chromabond column and total Cr/Hg/Cd levels was quantified by ETAAS using the same instrumental condition used for the same instrumental conditions used or the quantification of chromium, mercury and cadmium.

RESULTS AND DISCUSSIONS

The results of heavy metals shown that there are soil samples had showed more heavy metal concentrations than the water sample. Ranges of Heavy metals Pb, Cr, Cd, Hg have been studied and these slightly increase is observed. Among these Chromium levels are high than the other in all water samples. In soil samples Lead content is high than the other samples. The P^H levels are increased to 7.0-7.3 is observed in both water and soil samples of Nizampatnam and Pittalavanipalem mandals. This increase is mainly due to the selected areas are nearer to the coastal area and aquaculture. Here the electrical conductivity is also slightly increased in both water and soil samples in 2015 than the 2014. The results of heavy metals analysis in both soil and water samples along with P^H and Electrical Conductivity (EC)are represented in the tables given below.

	Dist	trict: Gu	ntur			Manda	l: Pidugu	ralla		Village: Brahmanapalli			
C N I	El			Wat	ter					So	il		
S.No	Element ppm	Sample 1		Sample 2		Sample 3		Sample 1		Sample 2		Sample 3	
		May Ma		May	May	May	May	May	May	May	May	May	May
		2014	2015	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015
1	Pb	0.06	0.68	0.06	0.0	0.0	0.0	9.52	9.709	9.606	9.97	9.64	10.1
		71	9	56	718	632	659						
2	Cr	0.0	0.07	0.07	0.0	0.0	0.0	6.41	6.808	6.201	6.46	6.07	6.48
		74	5	4	812	762	821						
3	Cd	0.00	0.0	0.00	0.0	0.0	0.0	0.67	0.74	0.705	0.83	0.44	0.58
		009	001	011	0014	00081	009				6		
4	Hg	0.00	0.00	0.0	0.0	0.0	0.0	0.80	0.91	0.835	0.88	0.91	0.92
		07	11	008	0091	097	01						
5	рН	6.76	6.81	6.8	6.9	6.7	6.8	6.85	6.98	6.74	6.84	6.88	6.89
			4	02	45	5	08						
6	EC	0.67	0.67	0.67	0.6	0.6	0.6	2.65	2.76	2.82	2.85	2.75	2.81
			7	7	86	71	92						

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	Distrie	ct: Guntur			Ν	/landal: Pi	duguralla	a		Villa	ge: Konda	modu	
				Water Soil		bil	1						
S.No	Element ppm	Sample 1			nple 2	Sample 3			Sample 1		nple 2	Sam 3	
	May M		May	May	May	May	May	May	May	May	May	May	May
		2014	2015	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015
1	Pb	0.0	0.6	0.0	0.0	0.06	0.0	9.5	9.79	9.561	9.976	9.614	10.1
		662	89	68	71	86	738	21					25
2	Cr	0.071	0.074	0.04	0.08	0.071	0.08	6.24	6.805	6.172	6.514	6.125	6.41
		8	5	5	1	4	26	7					
3	Cd	0.0	0.0	0.0	0.0	0.0	0.0	0.67	0.714	0.721	0.819	0.446	0.51
		0012	0013	0009	001	0081	009						
4	Hg	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.9	0.8	0.8	0.9	0.97
		006	007	0075	0082	0099	01	25	72	55	83	11	
5	рН	6.815	6.822	6.81	6.91	6.682	6.87	6.85	6.91	6.77	6.85	6.81	6.95
6	EC	0.65	0.67	0.69	0.70	0.67	0.69	2.74	2.76	2.84	2.86	2.69	2.81

	Distric	t: Guntui	•		Ma	ndal: Ni	zampatn	am		Villag	e: Bavu	jipalem	
				Wa	ater					So	oil		
S.No	Element	Sam	Sample 1		Sample		Sample		ple	San	nple	San	nple
	ppm			:	2		3	1	L		2	3	3
		May	May	May	May	May	May	May	May	May	May	May	May
		2014	2015	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015
1	Pb	0.061	0.68	0.07	0.08	0.06	0.07	9.29	9.65	9.68	9.76	9.64	9.96
		5	5	552		2	2	2			5		
2	Cr	0.072	0.07	0.04	0.05	0.05	0.08	6.42	6.51	6.56	6.62	6.16	6.46
			95	55	2	6	2	5			2	4	
3	Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.72	0.75	0.76	0.80	0.46	0.55
		009	01	001	01	06	081	85			4	1	
4	Hg	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.38	0.65	0.89	0.93	0.93
		046	049	051	07	01	012	5		6	541	1	6
5	рН	7.02	7.08	7.11	7.09	6.99	7.20	7.06	7.12	7.07	7.19	7.25	7.30
6	EC	0.63	0.65	0.66	0.76	0.63	0.725	2.52	2.55	2.75	2.93	2.61	2.81
		9	5					2	2		2	2	2

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	Distric	t: Guntu	r		Mar	ndal: Niz	ampatr	am		Village	: Gokarı	namatar	n
				Wa	ter					So	oil		
S.No	Element	Sam	ple 1	San	nple	San	nple	Sample		Sample		San	nple
	ppm			2	2	3	3	1	L	2			3
		May	May	May	May	May	May	May	May	May	May	May	May
		2014	2015	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015
1	Pb	0.061	0.68	0.07	0.07	0.06	0.07	9.29	9.65	9.68	9.76	9.65	9.96
		5	1	5	5	25	25	5	8	5	5	4	3
2	Cr	0.07	0.07	0.04	0.05	0.05	0.08	6.42	6.51	6.56	6.25	6.16	6.46
		35	92	55	21	64	21	5	4	8	2	24	3
3	Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.72	0.75	0.76	0.80	0.46	0.55
		01	011	001	011	07	09	5	2	6	5	41	2
4	Hg	0.00	0.00	0.00	0.00	0.0	0.0	0.26	0.38	0.63	0.89	0.93	0.93
		045	05	06	075	008	001	4	2		5	61	96
5	рН	7.20	7.18	7.08	7.05	7.08	7.11	7.18	7.17	7.20	7.23	7.02	7.30
6	EC	0.635	0.655	0.65	0.76	0.63	0.72	2.39	2.41	2.88	2.93	2.61	2.81
					85	9	5						

	District	:: Guntu	r		Mar	ıdal: Niz	ampatn	am	\ \	/illage:	Nizampa	atnam p	ort
<u> </u>				Wa	iter					S	oil		
S.No	Element ppm	Sam	Sample 1		nple 2		Sample 3		Sample 1		nple 2		nple 3
			May 2015	May 2014	May 2015								
1	Pb	0.06 65	0.68 6	0.06 17	0.07 65	0.06 31	0.06 65	9.65 2	9.78 22	9.56 8	9.64 2	9.65	9.621
2	Cr	0.07 54	0.07 2	0.06 7	0.08 35	0.07 36	0.08 25	6.25 4	6.82 4	6.16 8	6.24 6	6.16	6.29
3	Cd	0.00 008	0.00 01	0.00 011	0.00 012	0.00 008	0.00 081	0.62 4	0.73 5	0.62 4	0.71 5	0.45	0.51
4	Hg	0.00 092	0.00 1	0.00 09	0.00 091	0.00 092	0.00 092	0.62 85	0.96 2	0.47 2	0.52 8	0.91	0.93
5	рН	7.04	7.12	7.18	6.96	7.25	7.12	7.18	7.09	7.08	7.12	7.20	7.22
6	EC	0.64 8	0.68	0.67 1	0.69 6	0.69 25	0.69 95	2.49	2.58 2	2.02 55	2.21	2.62	2.89

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	Distric	t: Guntur			Ма	ndal: Pitta	lavanipale	em		١	/illage: All	luru				
				Wa	ter			Soil								
S.No	5.No Element ppm	Sample 1			Sample 2		Sample 3		Sample 1		nple 2	Sample 3				
		May 2014	May 2015	May 2014	May 2015	May 2014	May 2015	May 2014	May 2015	May 2014	May 2015	May 2014	May 2015			
1	Pb	0.067	0.68 5	0.06 5	0.07 8	0.06 3	0.06 5	9.52 5	9.79	9.66	9.92	9.6	10.1			
2	Cr	0.07	0.07 5	0.07 41	0.08 1	0.07 6	0.08 2	6.41 5	6.88	6.21	6.48	6.0	6.4			
3	Cd	0.00 0091	0.00 01	0.00 011	0.00 012	0.00 008	0.00 091	0.67 5	0.76	0.75	0.83 1	0.4	0.5			
4	Hg	0.00 08	0.00 1	0.00 09	0.00 091	0.00 096	0.00 99	0.80 7	0.96 3	0.85	0.88 4	0.9	0.96			
5	рН	7.27	7.1	7.09	7.09	7.27	7.28	7.35	7.19	7.27	7.18	7.21	7.25			
6	EC	0.67 6	0.67 9	0.67	0.68	0.67 5	0.69 5	2.6	2.7	2.2	2.8	2.7	2.82			

	District	: Guntur			Manda	l: Pittalava	nipalem			Village: N	lanthenav	varipalem					
				Wat	ter				Soil								
S.No	Element	Sam	Sample 1		Sample 1		Sample 1		ple	San	nple	Sam	ple	San	nple	Sam	nple
	ppm			2		3		1		2			3				
		May 2014	May 2015	May 2014	May 2015	May 2014	May 2015	May 2014	May 2015	May 2014	May 2015	May 2014	May 2015				
1	Pb	0.06 1	0.68	0.06 5	0.07 1	0.06 2	0.06 5	9.53	9.79	9.66	9.94	9.64 6	10.1 5				
2	Cr	0.076	0.075	0.074	0.081	0.09	0.08	6.44	6.88	6.21	6.46	6.07 1	6.48 1				
3	Cd	0.9	0.1	0.11	0.13	0.9	0 91	0.67 5	0.84	0.7	0.86	0.44 2	0.58 8				
4	Hg	0. 71	0. 11	0. 9	0. 91	0. 9	0. 16	0.811	0.96	0.83	0.88	0.91 9	0.92 2				
5	рН	6.961	6.95	7.1	7.19	7.27	7.08	6.99	6.98	7.17	7.28	7.28	7.38				
6	EC	0.676	0.679	0.67	0.68	0.674	0.695	2.61	2.79	2.81	2.81	2.7	2.81				

	Distric	t: Guntur			Ма	ndal: Pitta	alavanipale	em		Village	e: Pittalav	anipalem		
				Wa	ter			Soil						
S.No	Element ppm	Sample 1		Sample 2		Sample 3		Sample 1		Sample 2		Sample 3		
		May 2014	May 2015											
1	Pb	0.06 3	0.68 1	0.06 68	0.07 1	0.06 81	0.07 65	9.51 5	9.71 4	9.51 6	9.97 4	9.62 4	10.1	
2	Cr	0.07 62	0.07 76	0.05 41	0.08 18	0.07 25	0.08 35	6.22 5	6.82 9	6.18 1	6.52 1	6.11 4	6.44 6	
3	Cd	0.00 01	0.00 013	0.00 011	0.00 012	0.00 081	0.00 09	0.67 16	0.75 8	0.72 5	0.81	0.42 4	0.56 1	
4	Hg	0.00 068	0.00 08	0.00 078	0.00 092	0.00 097	0.00 1	0.82 15	0.98 7	0.85 4	0.87	0.91 4	0.96 5	
5	рН	7.08	7.10	7.28	7.09 2	7.17 1	7.28	7.12	7.26	7.37	7.08	7.25	7.31	
6	EC	0.68	0.67	0.62	0.68	0.67 4	0.68 5	2.74 6	2.74	2.82	2.85	2.75	2.81	

Opaluwa et al. reported that in soil samples at site A, the concentration of lead and cadmium is 0.49 mg/kg and 0.48 mg/kg and at site B, the concentration of lead and cadmium is 0.53mg/kg and 0.84 mg/kg.^[13]

S. Atal et al. have been reported that in soil samples, lead, cadmium and chromium mean concentrations are ranged from 0.459 mg/l to 0.797 mg/l, 0.205 mg/l to 1.062 mg/l and 0.074 mg/l to 2.598 mg/l. $^{[14]}$

M. Sundarrajan et al. reported that in soil samples they found maximum values for Cd (1.140 mg/l), Pb (136.2 mg/l) and Cr (316.3 mg/l) and minimum values as Cd (0.300 mg/l), Pb (5.680 mg/l) and Cr (25.02 mg/l). The average concentration of heavy metals is in the order of Cr > Pb > Cd. ^[15]

Dong Jiang et al. has been reported that in soil samples the lead and cadmium concentration is ranged from 19.91 to 837.52 mg/kg and 0.35 to 6.47 mg/kg. ^[16]

Ruqia Nazir et al. reported that the maximum permissible limit (mpl) for Cr in water is 0.1 mg/l values of Cr in all water samples the concentration ranges between 1.313 to 2.886 mg/l and in soil samples ranged between 4.123 mg/kg to 6.744 mg/kg. The mpl for Cd in water is 0.01 mg/l. whereas the concentration of Cd in soil samples ranged between 0.029mg/kg to 0.328 mg/kg. The concentration of lead in all collected water samples between 0.167 to 0.723 mg/kg and in soil samples the concentration of lead was recorded to range between 0.061 to 0.461 mg/kg.^[17]

CONCLUSION

From our analytical studies, we concluded that, there is gradual increase in water pollution from first year to second year. In Guntur district Piduguralla town and surrounding villages are more polluted heavy metals. The places Pittalavani palem and Nizampatanam Mandals have basic soils than others, may be it happened due to aquaculture. The selected areas are polluted by heavy metals due to they are located near to Bay of Bengal sea. Due to industrial effluents sea world is completed polluting day by day.

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