

**Determination of Heavy Metals (Zn,Cd,Pb,Cu) by Atomic
Absorption Spectrophotometer (AAS) Technique**

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**Determination of Heavy Metals (Zn,Cd,Pb,Cu) by Atomic Absorption
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Abstract

The current study was conducted to measure the total concentration of heavy metals (Zn,Cd,Pb,Cu) in contaminated soil in Baiji oil refinery at Salah -alden governate, Iraq . Forty one samples were collected from different area distributed in two stations . The total concentration of heavy metals in soil samples were extracted by digestion of soil with concentrated nitric acid . The AAS was used to determine the metals at specific wave length and Hallow Cathode Lamp (HCL).Metal speciation was also determined by AAS after extraction of the metal with different chemical reagents .

Keywords : Determination, Speciation and Heavy Metals ,Zn,Cd,Cu,Pb, Atomic Absorption.

تقدير تراكيز العناصر الثقيلة (الزنك والكاديوم والرصاص والنحاس) المرتبطة مع طبقات التربة
بواسطة تقنية طيف الامتصاص الذري

حسين حسن خرنوب و احمد رؤوف محمود

جامعة تكريت - كلية الصيدلة

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الخلاصة

تضمنت هذه الدراسة قياس التراكيز الكلية للعناصر الثقيلة (الزنك والكاديوم والرصاص والنحاس) في التربة الملوثة في مصفى بيجي حيث تم جمع (40) عينة من التربة وقد تم القياس باستخدام تقنية طيف الامتصاص الذري بعد الاستخلاص باستخدام حامض النتريك المركز. تم قياس تركيز العناصر المرتبطة بطبقات التربة بعد استخلاص العناصر باستخدام مواد كيميائية مختلفة ومن ثم قياس كمية العنصر المرتبطة بالطبقة

الكلمات المفتاحية: قياس، عناصر ثقيلة،الزنك، الخارصين،النحاس، الكاديوم، الطيف الذري

Introduction

During the last twenty years ago , there has been increasing interest in environmental contamination by heavy metals due to some are essential for maintenance for normal growth and development , while other are toxic^(1,2) . Heavy metals have also received special attention because they are immutable , i-e not biodegradable in biochemical cycle⁽³⁾, and so can enter food chain via plant uptake or contamination of fresh water⁽⁴⁾. Recently the association between heavy metals accumulation in man and the incidence of disease has been recognized^(5,6). The metals used in this study were Zn,Cd, Cu,Pb . The sources of these metals in soil are generated from geological origin and man activities⁽⁷⁾, therefore the soil was considered the main source of pollution to the environmental⁽⁸⁾. The sequential extraction gives good information about the chemical formula of the metal ion , bonded and free⁽⁹⁾. The metal species in ion exchangeable layer is weakly associated and can be release easily to the environmental⁽¹⁰⁾.The chemical agent was used to extract metal in ion exchangeable layer is magnesium chloride at pH =5.4 , while the rest of the metal in carbonate , Fe-Mn oxide , organic matter and residual layers can be extracted by sodium acetate (pH=5) , hydroxyl amine hydrochloride,H₂O₂, and mixture of strong acid (HCl+HNO₃ respectively⁽¹¹⁾. There are many analytical methods used for determination of Zn,Cd,Pb,Cu in environmental samples such as spectrophotometric, , inductive couple plasma, electrochemical and atomic absorption methods⁽¹²⁾. In present work flame atomic absorption spectrophometry was used due to its availability , sensitivity and reliable for use.

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Experimental part and methods

Sample area and collection of samples

The area was oil refinery in Baiji at Salah –alden governate which is fifty kilometer north of Tikrit city on west of Tigris river .Fourty samples soil were collected in plastic bags , labeled and removed to the laboratory . The samples were dried and prepare to determine total concentration of Zn,Cd,Cu,Pb .

Materials

Concentrated nitric acid, hydrogen peroxide, acetic acid, ammonium acetate, hydroxylamine hydrochloride and magnesium chloride are pure chemical from BDH company.

Atomic absorption type Germany Varian AA240FS was used

Methods

The sample was grinded in motor and sieving . Using 1mm , the sample (1gm) was digested with concentrated nitric acid at sand bath , until the dryness of the sample , then deionizer water was added , filtered and complete the filtrate to 25ml with deionizer water.

Results

The total concentration of Zn ,Cd, Cu, Pb were determined by AAS using the Air /Acetylene flame , specific Hallow Cathode Lamp, specific Wavelength and calibration curve of standard solution of each metals was run . After fitting the absorbance of the sample to the calibration curve of the metal to get the concentration of the metal , the result was multiple by 25ml and divided by one to get the result as $\mu\text{g/g}$. The results were described in Table -1-

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Table -1- Total concentration of Zn,Cd,Pb,Cu in Soil (µg/g).

	Zn	Cd	Pb	Cu	Site
	48.125	1.5625	280.5	12.15	North of St-TEL
	53.94	1.2875	254.25	10.375	
	60	1.54375	242.10	21.8	
	52.6	1.20625	93.75	16.1	
	61.8	2.31875	150.25	17.725	
	47.37	1.30625	97	15.1	
Mean	53.972	1.537	186.308	15.541	
SD	5.9543	0.4089	82.998	4.065	
	55.24	1.31875	134.91	12.725	South of St-TEL
	50.57	1.0125	107	11.05	
Mean	52.905	1.165625	120.955	11.887	
SD	3.302	0.216	19.735	1.184	
	55.075	1.43125	103.65	6.75	East of St-TEL
	53.87	1.00625	80.22	10.675	
	39.752	1.40625	73.25	14.325	
	49.825	1.33	65.25	10.775	
	62.059	1.082	109	60.625	
Mean	52.116	1.251	86.274	20.63	
SD	8.197	0.194	19.148	22.517	
	43.83	1.2125	105.75	13.75	West of St-TEL
	64.42	1.1812	194.25	14.525	
Mean	54.125	1.1968	150	14.137	
SD	14.559	0.0221	62.578	0.548	
	57.7	1.443	102.5	11.95	Random of St-TEL
	45.82	1.256	72.5	11.45	
	64.76	1	79.5	12.375	
	147.93	1.068	185.5	21.225	
	47.375	1.275	34.5	12.9	
Mean	72.717	1.208	94.9	13.98	
SD	42.753	0.1766	56.243	4.085	

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Studying the speciation of Zn,Cd,Pb,Cu in soil

Scheme -1, listed below, was selected to study the speciation of Zn,Cd,Pb,Cu in different sites at Baiji refinery soil.

Step	Surface layers	chemicals reagents and conditions
1	Exchangeable	1 g is extracted at room temp. At 8 ml of 1 M MgCl ₂ (pH 7) shaking for 1 h with centrifuge for 30min at 3000r/min, filtrate in 25ml the volume to mark de-ionized water ,measure metal by AAS.
2	Carbonate	To the step 1 residue add 8 ml of 1 M sodium acetate adjusted to pH 5 with acetic acid shake for 5 h at room temperature, filtrate as step 1.
3	Fe-Mn oxide	To the residue of step 2 add 20ml 0,04M NH ₂ OH.HCl in 25% acetic acid shaking in water bath at 95±°C for 6 h, centrifuge for 5min at 3000r/min, filtrate as step 1
4	Organic matter	To the residue of step 3 add 3 ml of 30% H ₂ O ₂ shaking and add 5ml H ₂ O ₂ heat to 85±3 °C for 2 h; add 3 ml of acidified H ₂ O ₂ , heat to 85±3°C for 2 h; finish with 5ml of 3.2M ammonium acetate in 20 % HNO ₃ .for 20ml of de-ionized water and agitate shaking for 0,5 h, centrifuge at 5min for 3000r/min, filtrate as step 1.
5	Residual	To the residue of step 4 few drop of 0.005N HNO ₃ , add 3:1 HCl and HNO ₃ 2.5 ml and 750µml in 30% H ₂ O ₂ Leaves 24h, hated at 95±3C ⁰ end drought add 2.5ml HF and 750 µml in 30% H ₂ O ₂ , hated 5 min at 95±3C ⁰ add 250 µml HCl, with 2.5 ml of de-ionized water, again hated 0.5h at 95±3C ⁰ , filtrate as step 1.

The results obtain in all steps are illustrated in Tables(2—6)

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Table -2- Speciation of Zn, Cd, Pb, Cu, in North of Station TEL

Speciation $\mu\text{g/g}$	Zn	Cd	Pb	Cu
Ion exchangeable	1.425	0.25	35.75	0.2
	3.25	0.175	134.5	0.275
	1.875	0.4	132	0.275
	3.475	0.2	12.25	0.25
	3.95	1.175	36.75	0.375
	2.825	0.225	7.75	0.175
Mean	2.8	0.4041	59.833	0.258
SD	1.235	0.0432	1.435	0.321
Carbonate	9.992	0.175	158.75	0.425
	11.737	0.075	32.05	0.325
	14.797	0.2	33.625	1.15
	9.665	0.025	32.25	0.4
	11.025	0.025	41.75	0.5
	11.94	ND	26	0.1
Mean	11.526	0.0833	54.070	0.483
SD	1.234	0.0123	1.876	0.123
Fe-Mn oxide	26.93	1.1	67.75	5.175
	27.69	1.075	36.35	4.625
	26.096	1.1	36.25	10.42
	25.4928	1.25	28	8.352
	33.225	1.175	29.5	9.275
	24.515	1.225	32	7.825
Mean	27.3248	1.1541	38.308	7.612
SD	1.765	0.675	1.654	2.876
Organic matter	3.3475	0.425	6	2.125
	4.0375	0.35	38.5	1.2
	3.8875	0.25	22.25	2.575
	3.2575	0.325	4.5	2.82
	4.38	0.325	31.25	3.025
	3.105	0.35	22.75	2.9
Mean	3.669	0.3375	20.875	2.440
SD	0.543	0.876	1.8760.8	0.876
Residual	5.97062	N.D	10.937	2.925
	7.42625	N.D	12.3	2.843
	12.3575	N.D	18.506	6
	10.8669	N.D	15.725	3.831
	9.00313	N.D	10.293	4.187
	6.7468	N.D	9.95	4.656
Mean	8.728	N.D	12.951	4.073
SD	1.765	N.D	1.876	0.765

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Table -3- Speciation of Zn, Cd, Pb, Cu, in of East of Station

Speciation $\mu\text{g/g}$	Zn	Cd	Pb	Cu
Ion exchangeable	4.65	0.25	12.25	0.6
	1.625	0.025	18.25	0.275
	2.125	0.375	5	0.05
	2.825	0.2	4	0.15
	1.7	0.3	6	0.6
Mean	2.585	0.23	9.1	0.335
SD	1.543	0.012	1.234	0.432
Carbonate	9.155	N.D	36	0.35
	6.17	N.D	33.5	0.05
	7.1425	N.D	13.75	0.7
	9.695	N.D	13.75	0.225
	10.765	0.175	31.75	1.975
Mean	8.5855	0.035	25.75	0.66
SD	0.987	0.1231	1.432	0.321
Fe-Mn oxide	28.835	1.275	13.425	3.425
	33.472	1.275	12.75	2.25
	19.892	1.35	17.5	9.125
	26.725	1.15	31.25	6.25
	28.94	0.975	27.75	34.9
Mean	27.5728	1.205	20.535	11.19
SD	2.876	0.567	1.453	0.342
Organic matter	4.1225	0.35	29.25	1.175
	4.095	0.425	7.44	2.7
	2.5075	0.175	26.75	1.5
	3.7075	0.575	4	1.2
	6.3525	0.1	33.25	11.15
Mean	4.157	0.325	20.138	3.545
SD	0.453	0.124	1.123	1.234
Residual	7.3481	N.D	11.518	2.037
	7.7137	N.D	6.6187	3.781
	6.3856	N.D	11.075	2.862
	7.1193	N.D	11.606	2.45
	15.631	N.D	10.35	12.22
Mean	8.83954	N.D	10.2335	4.67
SD	1.343	N.D	3.786	4.874

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Table -4- Speciation of Zn, Cd, Pb, Cu, in South of station TEL

Speciation $\mu\text{g/g}$	Zn	Cd	Pb	Cu
Ion exchangeable	3.425	0.35	20.25	0.2
	1.975	0.275	4.75	0.8
Mean	2.7	0.3125	12.5	0.5
SD	1.025	0.053	10.96	0.424
Carbonate	12.227	0.025	35.75	0.425
	13.37	0.1	37.5	1.2
Mean	12.798	0.0625	36.625	0.812
SD	0.808	0.053	1.237	0.548
Fe-Mn oxide	29.39	1.075	39.5	6.875
	27.192	0.975	11	3.65
Mean	28.291	1.025	25.25	5.262
SD	1.554	0.07	20.15	2.28
Organic matter	3.275	0.325	27	1.725
	4.03	0.275	37	2.125
Mean	3.6525	0.3	32	1.925
SD	0.533	0.035	7.071	0.282
Residual	6.285	N.D	11.687	3.068
	5.006	N.D	16.65	2.268
Mean	5.6455	N.D	14.1685	2.668
SD	0.904	N.D	3.509	0.565

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Table -5- Speciation of Zn, Cd, Pb, Cu, in West of station TEL

Speciation $\mu\text{g/g}$	Zn	Cd	Pb	Cu
Ion exchangeable	2.175	0.175	12.5	0.225
	2.725	0.125	24.25	0.15
Mean	2.45	0.15	18.375	0.187
SD	0.388	0.0353	8.308	0.053
Carbonate	7.6725	0.075	31.25	0.15
	7.175	0.125	48	0.275
Mean	7.42375	0.1	39.625	0.2125
SD	0.351	0.035	11.844	0.088
Fe-Mn oxide	18.552	1.25	29	4.075
	40.786	1.125	94.25	6.225
Mean	29.669	1.1875	61.625	5.15
SD	15.721	0.088	46.138	1.523
Organic matter	2.925	0.225	30.75	2.9
	5.845	0.225	9	3.175
Mean	4.385	0.225	19.875	3.037
SD	2.064	0	15.37	0.194
Residual	12.243	N.D	2.8	6.813
	6.6756	N.D	17.743	4.25
Mean	9.4593	N.D	10.271	5.531
SD	3.936	N.D	10.566	1.812

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Table -6- Speciation of Zn, Cd, Pb, Cu, in of Random station TEL

Speciation µg/	Zn	Cd	Pb	Cu
Ion exchangeable	2	0.2	4.75	0.12
	1.375	0.15	1.75	0.132
	1.775	0.15	1.75	0.025
	6.825	0.225	11	0.775
	4.425	0.225	1.25	0.525
Mean	3.28	0.19	4.1	0.315
SD	2.313	0.037	4.098	0.32
Carbonate	8.177	0.025	21.75	0.15
	6.412	N.D	20.75	0.375
	10.715	N.D	41	0.3
	36.417	N.D	61	0.35
	11.027	N.D	7.25	1.125
Mean	14.549	0.005	30.35	0.46
SD	12.37	0.0089	20.93	0.381
Fe-Mn oxide	32.554	1.3	31	4.55
	24.302	1.325	33.5	4.15
	37.207	1	14.5	4.2
	69.262	1.075	60	7.65
	17.747	1.025	7.5	5.275
Mean	36.214	1.145	29.3	5.165
SD	19.934	0.162	20.354	1.46
Organic matter	4.775	0.325	32.5	1.6
	3.692	0.325	4.5	2.25
	4.987	0.325	7.75	3.328
	30.337	0.275	38	5.675
	7.357	0.3	3.75	1.575
Mean	10.229	0.31	17.3	2.885
SD	11.319	0.039	16.569	1.713
Residual	10.843	N.D	13.237	3.337
	8.331	N.D	11.918	3.006
	11.142	N.D	12.781	3.6
	4.881	N.D	16.168	6.231
	5.7043	N.D	13.568	3.7
Mean	8.1806	N.D	13.534	3.975
SD	2.868	N.D	1.597	1.289

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Discussion

The results in Table -1- indicate that all sites of the station TEL are contaminated with lead in all surface of layers of soil as showing in Figure-1-

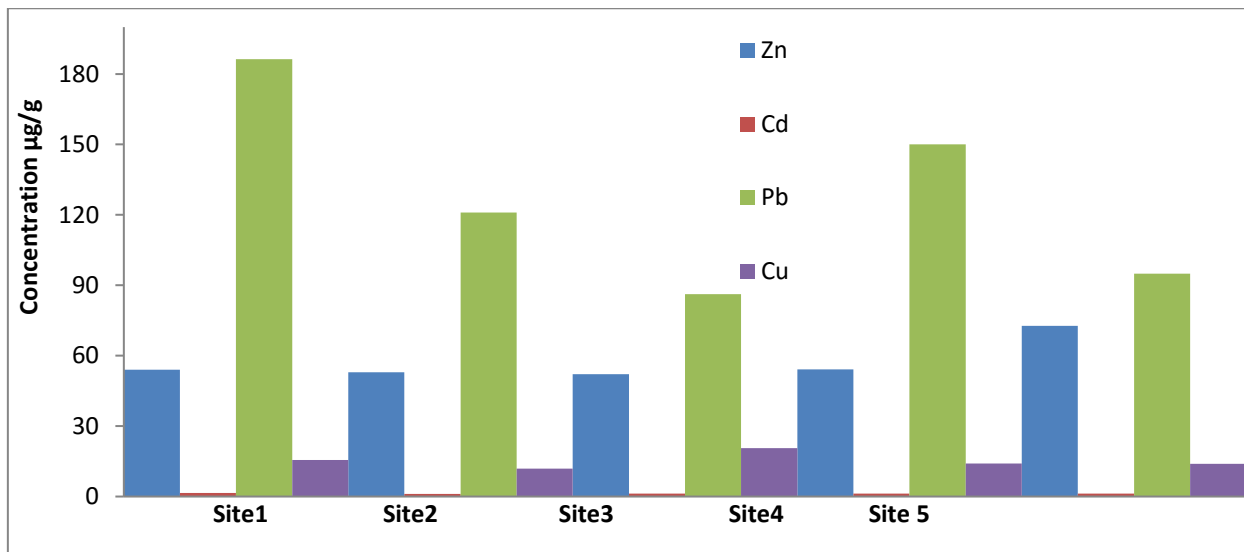


Figure -1- Distribution of Total Concentration of Zn, Cd ,Cu and Pb in Soil

Speciation of Zn, Cd, Cu,Pb in Baiji Refinery Soil

1. Zinc metal exists in all sites in following order(Figure-2-)

Fe-Mn oxide > carbonate >residual >organic matter > ion-exchangeable .

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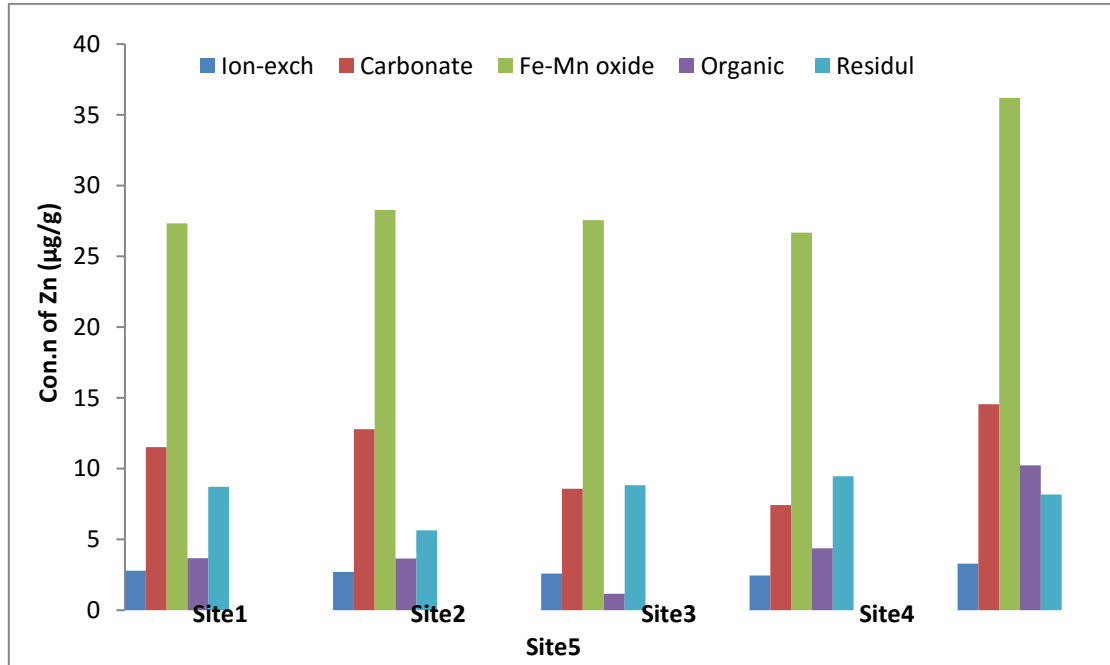


Figure-2- Speciation of Zinc in Soil

2. Cadmium metal present in all sites of the soil in the following order(Figure-3-)
 Fe-Mn oxide >organic matter>ion-exchangeable > carbonate >residual

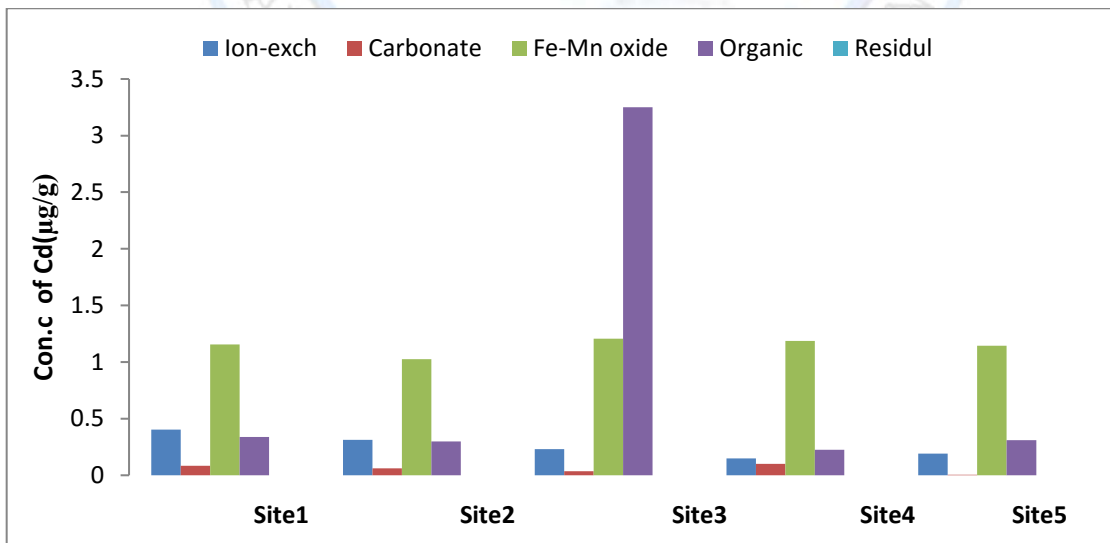


Figure-3- Speciation of Cadmium in Soil

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3. Copper exists in all sites in the layer as following (Figure-4-)

Fe-Mn oxide >Residual>organic matter >carbonate >ion-exchangeable .

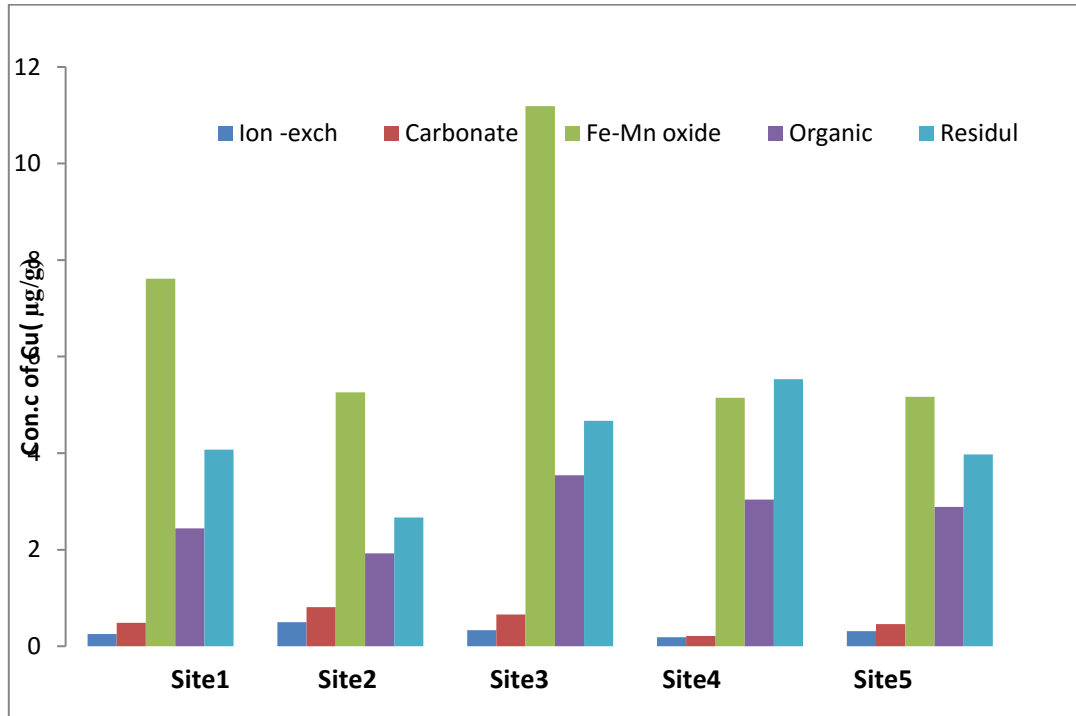


Figure-4- Speciation of Copper in Soil

4. speciation of lead as following order(Figure-5-)

carbonate > Fe-Mn oxide >Ion-exchangeable > organic matter >residual.

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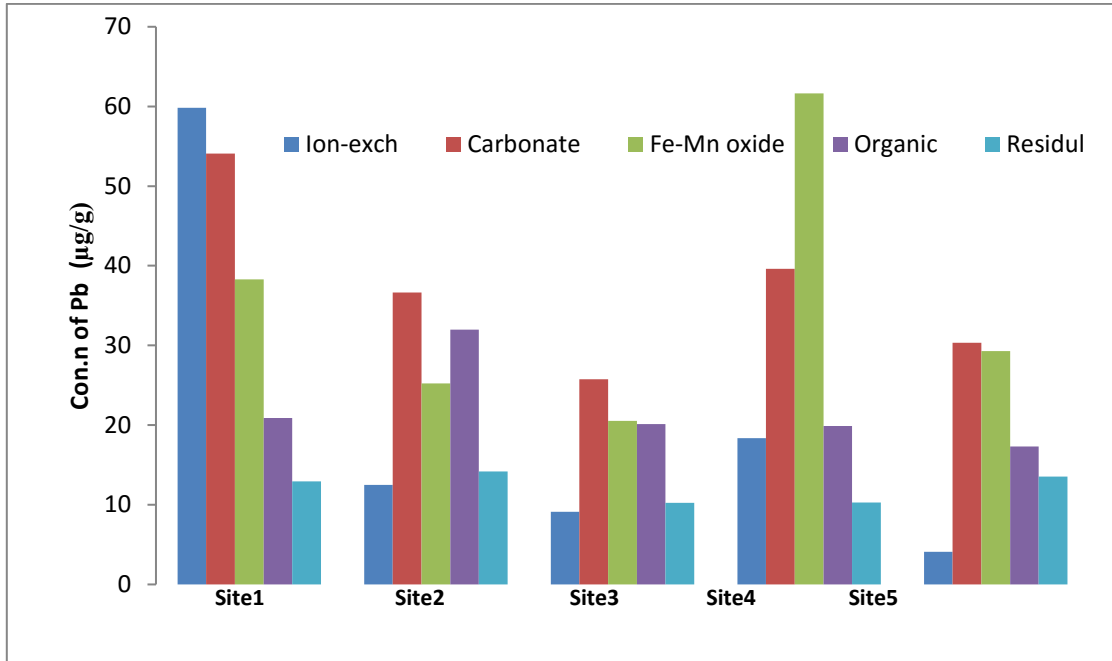


Figure-5- Speciation of Lead in Soil

The results mentioned previously mean that lead metal is easily available to be taken up by plants and other biota while Cd, Zn, Cu are less available to biota, this fact explains that lead is more toxic than Cd, Zn, Cu. The analytical parameters for the determination of Zn, Cd, Cu, Pb in Baiji soil were illustrated in Table-7-, the results show low detection limits for each metal which indicate the method is sensitive enough to determine the pollution of metal in soil.

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Table-7- The Analytical Parameters for Determination of Zn,Cd,Cu,Pb in Soil

Metals	Zn	Cd	Pb	Cu
λ max(nm)	213.9	228.8	217	324.8
Regression line	$Y=0.199x+0.0097$	$Y=0.294x+0.0036$	$Y=0.0403x+0.0069$	$Y=0.1005x-0.0009$
Standard deviation	0.0003	0.0004	0.0005	0.0004
Correlation coefficient R^2	0.997	0.997	0.998	0.998
Limit of detection ($\mu\text{g/ml}$)	0.013	0.006	0.033	0.012
Limit of quantity ($\mu\text{g/ml}$)	0.003	0.012	0.110	0.041
Total concentration($\mu\text{g/g}$)	58.103	1.312	128.281	15.917
Flame	Air/Acetylene	Air/Acetylene	Air/Acetylene	Air/Acetylene

The speciation study was carried out using Tessier scheme by sequential extraction the chemical formula of metal present the layers , ion – exchangeable , carbonate , Fe-Mn oxide , organic matter and residual . The metal species was also determined by AAS (Table-8-). The results which are listed below showed that the area of the study was contaminated with lead metal due to addition of tetraethyl lead(TEL) to petrol as anti-knock agent and to increase octane number of fuel .

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Table-8- Speciation of Zn,Cd,Cu,Pb in Baiji Soil Sample

Metals concentration (µg/g)	Zn	Cd	Pb	Cu
Ion – exchangeable	2.820	0.272	24.337	0.308
Organic matter	5.501	0.372	20.809	3.836
Residual	8.834	N.D	12.721	4.203
Carbonate	11.624	0.051	37.871	0.527
Fe-Mn oxide	29.940	1.152	32.638	7.413

The results obtained in this study was compared with other workers⁽¹³⁻¹⁹⁾ as showing in Table (9). The results shows that AAS is useful technique for determination of heavy metals in soil as comparing with other analytical techniques .

Table (9) Comparison Between Present Results with Results of Other Workers for Soil Analysis Using Different Analytical Techniques

Technique	Total concentration µg/g				Ref
	Zn	Cd	Pb	Cu	
DPASV	---	0.62	12.24	18.36	13
ICP-OES	103	----	----	----	14
XRF	11.33	3.03	23.79	10.1	15
ICP/OES	0.03	0.068	0.037	1.27	16
ICP	53.93	---	18	111.0	17
ICP/MS	9.8ng/ml	0.89	22.0	20	18
AAS	25.06	9.11	14.13	22.14	19
A AAS AAS	8.103	1.312	12.281	15.917	Present Work

Conclusion

The results obtained in this work proved that measurement of total concentration of metal does not consider as pollution index while determination the concentration of metal speciation indicate the pollution index . The recent study was also conclude that all the sites of the soil in Baiji refinery are contaminated with Pb,Cd,Zn,Cu due to close these sites to the station of tetraethyl lead (TEL). The metals mentioned before have the ability to accumulated in the

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environment and effect on people working in and out the sites , therefore precaution must be taken to reduce the risk of these metal on public health .

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