Sudan University of Science and Technology

College of Graduate Studies

Assessment of Common Heavy Metal Pollution in Topsoils Along Major Roadside Areas due to Traffic Activity in Khartoum State -Sudan

تقدير التلوث الشائع بالفلزات الثقيلة فى الطبقة العليا للتربة على طول مساحات جوانب الطرق الرئيسية والناتجه من نشاط الحركة المرورية فى ولاية الخرطوم- السودان

By

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بسم الله الرحمن الرحيم

قال تعالى : (قُلْ هَلْ يَسْتَوِي الَّذِينَ يَعْلَمُونَ وَالَّذِينَ لَا يَعْلَمُونَ ۗ إِنَّمَا يَتَذَكَّرُ أُولُو الْأَلْبَابِ)

صدق الله العظيم

سوره الزمر الايه (9)

Dedication

This work is dedicated to my colleagues for making everything worthwhile and for their continuous support, my family for the love and encouragement, my teachers who taught us the meaning and value of education and scientific research, my friends and everyone who helped me , to complete this work.

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Abstract

This study was carried out to investigate the accumulative levels of Pb, Cr, Cd, Ni and Cu in roadside topsoil of three major streets in Khartoum State and the relation between the concentration of these metals and soil chemical properties. The collected roadsides topsoil samples were prepared with an improved closed wet digestion system and the heavy metals concentrations in the extracts were determined using flame atomic absorption spectrometry. The mean concentration ranges of metals (µg /g) were (17.74-536.65) for Pb, (less than 0.10-0.63) for Cd, (43.82-283.6) for Cr, (4.54-33.72) for Ni, and (7.42-23.03) for Cu. The method of determination used was evaluated using a certified reference material (IAEA soil-7). The recovery values were found to be (106.20, 118.64, 102.31, 91.80 and 93.54) % for Pb, Cd, Cr, Ni and Cu respectively. The accuracy was within 95% confidence interval levels for all the heavy metals determinations and the calibration curves correlation coefficients of linearity were better than 0.999. Significant correlations were found between the metals contents and soil chemical properties specifically organic matter contents and to some extent total dissolved solids and roadside soils texture as all soils samples showed moderately alkaline nature that ranged between 7.58 and 8.2 pH unit. The percentage of total organic matter and total dissolved solids in (ppm) were determined, determinations were within 0.0-9.40 % of RSD % of the mean values. The extend of heavy metals contamination was assessed, and the results inference was that there is a considerable level of contamination with Pb and Cr while low to no contamination with Cd, Cu and Ni on these roadside soils.

المستخلص

اجريت هذه الدراسه للتحقق من مستويات تراكم الرصاص والكروم والكادميوم والنيكل و النحاس فى طبقه التربه السطحيه نتيجه للانبعاثات من السيارات على جوانب ثلاث طرق اسفلتيه ريئسيه فى ولايه الخرطوم والعلاقه بين تراكيز هذه العناصر والخواص الكيميائيه للتربه. تم جمع العينات من جوانب الطرق الاسفلتيه و عولجت بطريقه محسنة للهضم الرطب المغلق حيث تم تحديد تراكيز العناصر الثقيلة بمطيافيه الامتصاص الذرى اللهبى. كان المدى المتوسط للتراكيز بالميكروجرام/الجرام 536.65-17.74 للرصاص, وأقل من 0.63-0.10 للكادميوم 283.6-43.82 للكروم, و4.54 -33.72 للنيكل و 23.03-7.42 للنحاس. تم تقييم طريقة تقدير العناصر باستخدام عينه تربه مرجعيه معتمدة (IAEA-7). وكانت كفاءة الاسترجاع 106.20، 118.64، 102.31 ، 91.80 و93.54 % للرصاص, الكادميوم ,الكروم , النيكل والنحاس علي التوالي. وكانت مستويات حد الثقه في حدود 95 % لكل الفلزات الثقيله المقاسه كما كانت معاملات الارتباط للمنحنيات القياسيه اكبر من 0.999. تم العثور على علاقة ارتباط كبير بين مستويات تركيز المعادن والخواص الكيمائية للتربة وعلى وجه التحديد محتوي المادة العضوية و بدرجة أقل المواد الصلبة الذائبة الكلية وتوزيع حجم حبيبات التربة على جوانب تلك الطرق المسفلته. إذ أن كل عينات التربة أظهرت طبيعة قلوية معتدلة تراوحت بين 7.58 و 8.20 وحدة رقم هيدروجيني, كما تم تحديد النسبة المئوية لمحتوي المادة العضوية والمواد الصلبة الذائبة الكلية (جزء في الجزء في المليون) وكانت تقديرات النتائج في المدي ما بين 0.0- 9.4 بالانحراف المعياري النسبي من القيم المتوسطة. وجري تقييم التلوث بالمعادن الثقيله حيث أشارت النتائج ان هناك مستوي كبير من التلوث بالرصاص والكروم بينما كان هناك تلوث بدرجة اقل او عدم وجود تلوث بكل من الكادميوم والنحاس والنيكل في هذه الترب السطحيه علي جوانب الطرق المسفلته التي تم دراستها.

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List of abbreviations

FAAS	Flame Atomic Absorption spectrometry
GFAAS	Graphite Furnace Atomic Absorption spectrometry
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrophotometry
ICP-MS	Inductively Coupled Plasma Mass spectrometry
CRM	Certified Reference Material
EPA	Environmental protection Agency of United States
EEAE	European environment agency
OC	Organic Carbon
OMC	Organic Matter Content
EC	Electrical Conductivity
PSA	Particle Size Analysis
ppm	Parts Per million
ppb	Parts Per billion
RSD	Relative Standard Deviation
SOM	Solid Organic Matter
DOM	Dissolved Organic Matter
Has	Humic Acids
SHMP	Sodium Hexa Meta Phosphate
FA	Fulvic Acid

CEC	Cation Exchange Capacity
TDS	Total Dissolved Solids
C	Celsius
g/L	gram / Liter
h	hour
s	second
mg	milligram
Kg	Kilogram
dS/m	deciseimen per meter
mS /C	milliseimen per centimeter

Chapter one

1. Introduction and literature review

1.1. Introduction

It has been widely accepted that soil plays a key role in sustaining life in earth̓s ecosystems. It consist of a heterogeneous media comprised of decomposed rock fragments, clay minerals, oxides of Fe, Al, and Mn, organic materials, organo-metallic complexes, and soil solutions. However soil is also a transmitter of many pollutants including potentially toxic metals into the atmosphere, biosphere and water resources (Chengo Katana et al, 2013).

The role of trace metals in the soil is increasingly becoming an issue of global concern at private and governmental levels, especially as soil constitutes a crucial component of rural and urban environment (Godwin et al, 2012) and because traffic emissions from vehicles have been identified to introduce a number of toxic metals into the atmosphere which are latter deposited on roadsides, so topsoils of roadside have become an increasingly important medium for assessing an anthropogenic pollutant levels in the urban environment (Godwin et al, 2012).

Heavy metals in soil exist in several different forms and are associated with a range of other components (Tack and verloon, 1995). Because of their non-biodegradable nature (Sharma et al, 2007), the accumulation of metals in soil particularly Pb, Cd, Cu, Ni, Cr, and Zn is of concern (Chengo katana et al, 2013). Heavy metals emanating from anthropogenic sources are more dangerous because of their instability and solubility leading to high bioavailability (Chengo Katana et al, 2013).Traffic activities are one of the major sources leading to heavy metal contamination in roadside soils due to their long-term accumulation (Fan Zhang et al, 2012).Many researchers confirmed the fact that automobiles are major source of the presence of these metals in the roadside environment (Godwin et al, 2012). Heavy metals can accumulate in the topsoil from atmospheric deposition by sedimentation, impaction, and interception and therefore top and roadside soils in urban areas are indicators of heavy metal contamination from atmospheric deposition (Hakan and A .Murat, 2006). Total elemental contents and soil chemical properties can provide some information on the mobility, bioavailability and pathways of the elements of interest, and these properties of the heavy metals depend heavily on their physical and chemical forms. Also sequential extraction, although operationally defined can give information about the association of heavy metals with geochemical phases of soil, hence help to reveal the distribution of heavy metals infractions and assess the mobility and toxicity of metals in soils(Anxiang Lu et al, 2005).

1.1.2. Statement of the problem

Traffic activities are one of the major sources leading to heavy metal contamination in roadside soils due to their long term accumulation (Fan Zhang et al, 2012). Since Khartoum is relatively crowded state with heavy traffic on all its major streets (Salah et al, 2011) it is pruned to roadside soils pollution with heavy metals, these heavy metals are found in fuel, lubricating oil, fuel tanks, engines, tires, catalytic converters, brake pads and other vehicle components as well as in road surface materials (Z. Xiong ,1998and fan Zhang et al 2012).

Most observational studies on the concentrations of heavy metals in roadside soils were focused on Cu, Zn, Cd and Pb; some researchers extended the monitored metals to Cr, Ni, and As (Xuedong Yan el al, 2012).

The total heavy metal contents can indicate the extent of contamination, and by comparing these contents with the important soil properties it would be an accurate indication of the toxicity (Abdolhossein et al, 2012).The knowledge of the interactions of metals with the different soil phases and components is of major interest to assess the connections with other biotic and abiotic elements of the environment, so related soil parameters relative to their heavy metals contents is more useful assessment of contamination level (M. A. Ashraf et al, 2012). And it virtually gives information about the physio-chemical forms and species of these heavy metals in roadside soils to determine their mobility, pathways, and bioavailability (Serife et al, 2003). One of the accepted methods to determine soil pollution with heavy metals is to compare a background reference unpolluted soil sample from the same studied zone with a proposed contaminated ones (K.B. Mmolawa et al, 2011).Usually the samples are prepared by applying the wet digestion methods preferably with a closed system extraction (Somentha Mirta, 2003)In this study a revised and optimized wet digestion procedure was used in order to decompose the hard species or strong binding forms like silicates in roadside soil materials. The method has a high level of accuracy, and sufficiently reproducible for environmental monitoring purposes and suitable for hygienic and soil laboratories (Maria et al, 2006).

Heavy metals in soil samples extracts can be measured by highly sensitive spectroscopic techniques such as atomic absorption spectroscopy e.g. Flame atomic absorption spectroscopy (FAAS) or Graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma ICP spectrometry e.g.(ICP) atomic emission spectrophotometry (ICP-AES) and ICP mass spectrometry(ICP-MS) (Binggan Wei and Linsheng Yang,2010) (John .R, 2003).

1.1.3. Research Hypotheses

The contents of Pb, Cr, Cd, Ni, and Cu on the three major streets roadside topsoils are higher than the background soil contents due to vehicles emissions.

The proposed wet digestion method with its closed extraction system is more optimized and can give high accuracy and recovery for metals determinations.

The contents of these heavy metals have a significant relation to its physiochemical forms and phases and soil properties such as pH, electric conductivity (EC) and total dissolved solids(TDS), Organic matter contents(OMC) and sand , clay and silt ratios .

1.1.4. Justification of the study (Rationale)

Despite the fact that traffic related metal emissions were extensively studied in the developed countries, there are still essential gaps of knowledge. To be able to address the environmental risk, more toxicological studies on heavy metals as well as their relation with the soil properties which contain different metal species, are needed.

Also very few studies in this area have been done in developing countries, and the data on pollutant metal concentrations and distributions are extremely scarce(E.S. Abechi et al,2010). On the other hand there is strong evidence that soils is an important pathway causing exposure of people to metals that may reach toxic levels (Hakan Arslan et al, 2006).Heavy metals in soil may be washed away by rain and road runoff and eventually get into adjacent river systems, and whether they are in soil or water they may accumulate in plants, animals or humans bodies and thus constitute a threat to public health (Fan Zhang et al, 2012). With rapid industrialization and urbanization in Khartoum state and during the last few years the numbers of vehicles, mostly operated by gasoline and diesel fuel, have widely increased, leading to increase traffic density and vehicles emissions. The increment of traffic activities substantially contribute to accumulation of heavy metals discharged by vehicles in roadside soils by time. Therefore this study is initiated to assess the level of contamination on surface roadside soil by some important heavy metals along major three old and busy roads represent the three main cities in Greater Khartoum state.

However the determination of chemical species is difficult and sometimes is impossible. Therefore, the use of informative soil chemical properties which is related to heavy metals concentrations provides an important tool for the determination of the different chemical forms or ways of binding between trace metals and soil components (Erika et al, 2005).

1.1.5. Objectives

- To determine common heavy metal contents Pb, Cr, Cd, Cu, Ni which are expected to constitute a significant contaminants that originate from traffic activity and vehicles emissions on roadside soils in Khartoum state.
- To evaluate the accuracy of the used procedure for the determination of heavy metal contents in soil samples by optimized closed system wet digestion method for complete extraction efficiency followed by more sensitive conditions of instrumental atomic absorption spectrometry measurement.
- To determine the relationship between the studied heavy metals concentrations and roadside topsoil related chemical properties.

1.2. Literature review

1.2.1. Sources of heavy metals contamination in roadside soils

Heavy metals are found in fuels, fuel tanks, engines, Tires, brake pads (linings),catalytic converters and other vehicle components as well as in road surface materials (Xuedong yan et al , 2012).

The mechanism of heavy metal emission from vehicles consist fuel consumption, engine oil consumption, tire wear, brake wear, and road abrasion. Engine oil consumption is responsible for the largest emission for Cd, tire wear contributes the most important emission for Zn, and brake wear is the most important source of emissions for Cu and Pb. Though the use of unleaded gasoline which has caused a subsequent reduction in fuel emissions of Pb, but it may still occur in exhaust gas and come from worn metal alloys in the engine. Bitumen and mineral filler materials in asphalt road surfaces contain different heavy metal species, including Cu, Zn, Cd, and Pb. Heavy metals can be transported into the roadside soils by atmospheric precipitation or roadside runoff (Fan Zhang et al, 2012).

Nickel emission also results from nickel added in gasoline and atmospheric abrasion of nickel-containing parts of automobiles (Hakan Arslan et al, 2006). Cd emission is mainly from the lubricating oil consumption and tire wear (Xuedong Yan, 2012).

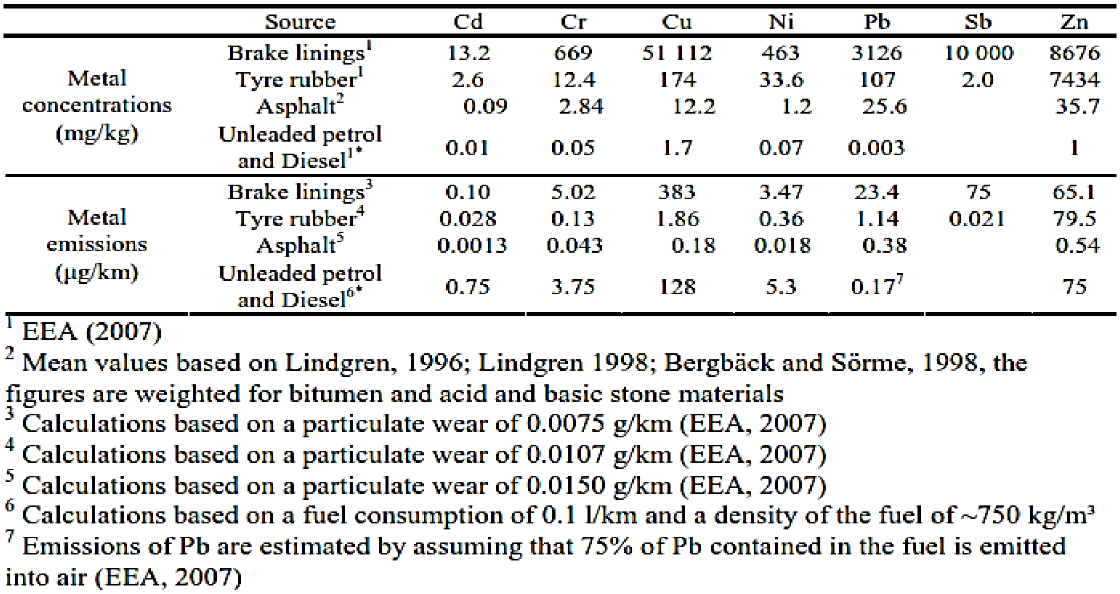
Although emissions of lead compounds into the environment has been considerably reduced by the use of unleaded fuel in vehicles since 1980s (Cory .D et al, 2011), Lead contribution has predominantly been a result of fuel combustion because it is prevalent in petrol, thus Pb particulates comes from the exhaust gas and worn metal alloys in the engine (Xuedong yan, 2012). Having been used as additive to fuel during decades in order to prevent uncontrolled combustion, which may reduce power and engine efficiency and might damage the engine, Lead has been subject for an extensive number of studies, Lenner and karlsson 1998 proposed that the discharge of lead through combustion is between 1.4 and 2.4 mg/vehicle-km depending on type of catalytic converter used. Regarding cars without catalytic converters, it was estimated that the lead emission is 16 mg/vehicle-km. Completion of data shows that between 0.1and 0.26 g tire wear is emitted per car per kilometer, and approximately 1.8%, 1% and 0.08% are Zn, Cu and Pb respectively (Liselott Petersson, 2005). Of course the proportions of components that make up tires differ with different brands, however the degree of emission is not only dependent on the tire composition, but also on the age of tires, weather and road conditions, way of driving, play a significant roles. Brake dusts consist particularly of copper as well as traces other metals. Average concentrations of metals in braking pads have been estimated to 105 mg/g for Cu whereas concentration of Pb is roughly 14mg/g and corresponding figure for Zn is 20 mg/g. Copper discharge produced from braking systems is on the order of 75 mg/vehicle-km, particles released from the brake systems are rather small, about 86% of the emission consisted of particle size smaller than 10 µm (Liselott Petersson, 2005). Traffic composition also contributes significantly to the pollution levels because emission rate varies for different type of vehicles (Niirjar et al, 2002). Hence, the same amount of traffic volume with different vehicular composition produces different amounts of pollutants. Speed limits also affect the amount of pollution (Baldasano et al, 2010), one way to reduce excessive fuel consumption and vehicular emissions is to optimize signal timings to reduce traffic congestion, delay and stops (Aleksandar et al, 2009). As the road width increases, the maneuverability to movement of the vehicles will be increased which results in the reduction of pollutants. Medians reduce the obstruction caused by the opposing vehicles, which results in the reduction of number of accelerations and decelerations. Hence the fuel consumption will be minimized consequently reducing the emission levels. The older vehicles will emit more pollutant than newer ones if they are not maintained properly .Vehicle with 4 -stroke engine would produce lesser emissions than 2-stroke engine. Similarly vehicles with catalytic converter will emit fewer pollutants (Niirjar et al, 2002).

Monitoring studies have been conducted in many cities and regions to investigate the roadside heavy metal contamination. It was found that roadside heavy metal contamination is influenced by multiple factors including traffic properties, highway characteristics, roadside terrain, roadside distance, wind direction (Fan Zhang, 2012).

Traffic junction and cross roads records higher levels of lead and also the sites with a slow moving vehicles as a result of heavy traffic jam may account for the high level of lead (E .S. Abechi et al, 2003).

generally the longer the highway usage history, the higher the concentration in the roadside soil, because it is positively related to traffic volume, normally the heavy metal content in roadside soils has a belt –shaped distribution in terms of distance to road edge, decreasing exponentially with distance from road. Compared to the background nature value of heavy metal contents, the influential space of traffic pollution can be up to 50 m far from road but within 100 m, in addition most of the deposited metal particles remain in the 0-5 cm of the road surface soil depth (Fan Zhang et al, 2012).

Table (1): Metal emissions from traffic related sources in Stockholm 1998 and 2005 (kg/year) (David, 2008)



	Source	Cd	Cr	Cu	Ni	Pb	Sb	Zn
Metal concentrations (mg/kg)	Brake linings[1]	13.2	669	51 112	463	3126	10 000	8676
	Tyre rubber[1]	2.6	12.4	174	33.6	107	2.0	7434
	Asphalt[2]	0.09	2.84	12.2	1.2	25.6		35.7
	Unleaded petrol and Diesel[1*]	0.01	0.05	1.7	0.07	0.003		1
Metal emissions (µg/km)	Brake linings[3]	0.10	5.02	383	3.47	23.4	75	65.1
	Tyre rubber[4]	0.028	0.13	1.86	0.36	1.14	0.021	79.5
	Asphalt[5]	0.0013	0.043	0.18	0.018	0.38		0.54
	Unleaded petrol and Diesel[6*]	0.75	3.75	128	5.3	0.17[7]		75

[1] EEA (2007)

[2] Mean values based on Lindgren, 1996; Lindgren 1998; Bergbäck and Sörme, 1998, the figures are weighted for bitumen and acid and basic stone materials

[3] Calculations based on a particulate wear of 0.0075 g/km (EEA, 2007)

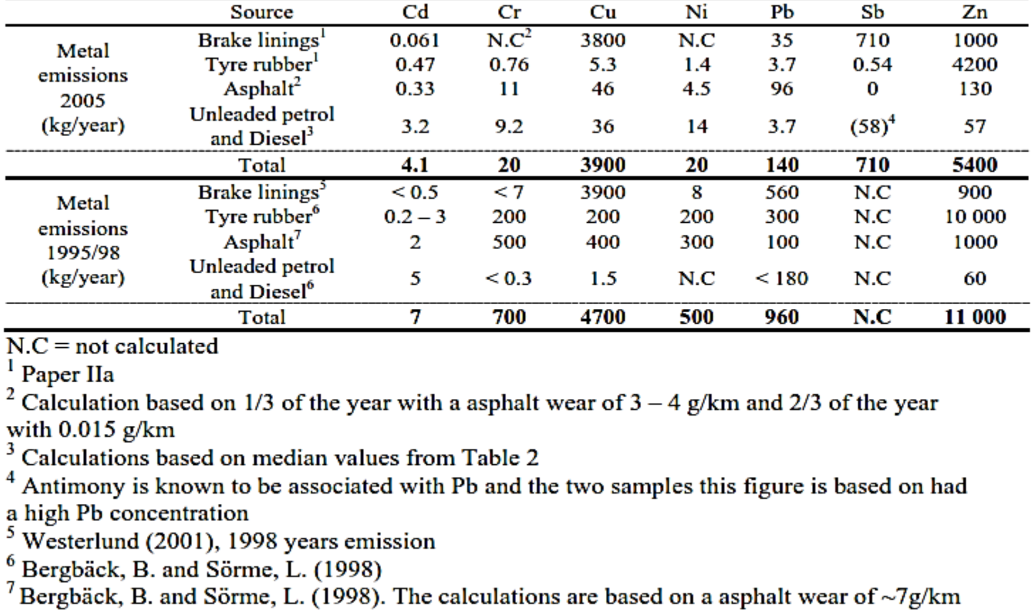
[4] Calculations based on a particulate wear of 0.0107 g/km (EEA, 2007)

[5] Calculations based on a particulate wear of 0.0150 g/km (EEA, 2007)

[6] Calculations based on a fuel consumption of 0.1 l/km and a density of the fuel of ~750 kg/m³

[7] Emissions of Pb are estimated by assuming that 75% of Pb contained in the fuel is emitted into air (EEA, 2007)

Table (2): sources of heavy metals in Stockholm by traffic activity 1995-1998 (David, 2008)



	Source	Cd	Cr	Cu	Ni	Pb	Sb	Zn
Metal emissions 2005 (kg/year)	Brake linings[1]	0.061	N.C[2]	3800	N.C	35	710	1000
	Tyre rubber[1]	0.47	0.76	5.3	1.4	3.7	0.54	4200
	Asphalt[2]	0.33	11	46	4.5	96	0	130
	Unleaded petrol and Diesel[3]	3.2	9.2	36	14	3.7	(58)[4]	57
	Total	**4.1**	**20**	**3900**	**20**	**140**	**710**	**5400**
Metal emissions 1995/98 (kg/year)	Brake linings[5]	< 0.5	< 7	3900	8	560	N.C	900
	Tyre rubber[6]	0.2 – 3	200	200	200	300	N.C	10 000
	Asphalt[7]	2	500	400	300	100	N.C	1000
	Unleaded petrol and Diesel[6]	5	< 0.3	1.5	N.C	< 180	N.C	60
	Total	**7**	**700**	**4700**	**500**	**960**	**N.C**	**11 000**

N.C = not calculated

[1] Paper IIa

[2] Calculation based on 1/3 of the year with a asphalt wear of 3 – 4 g/km and 2/3 of the year with 0.015 g/km

[3] Calculations based on median values from Table 2

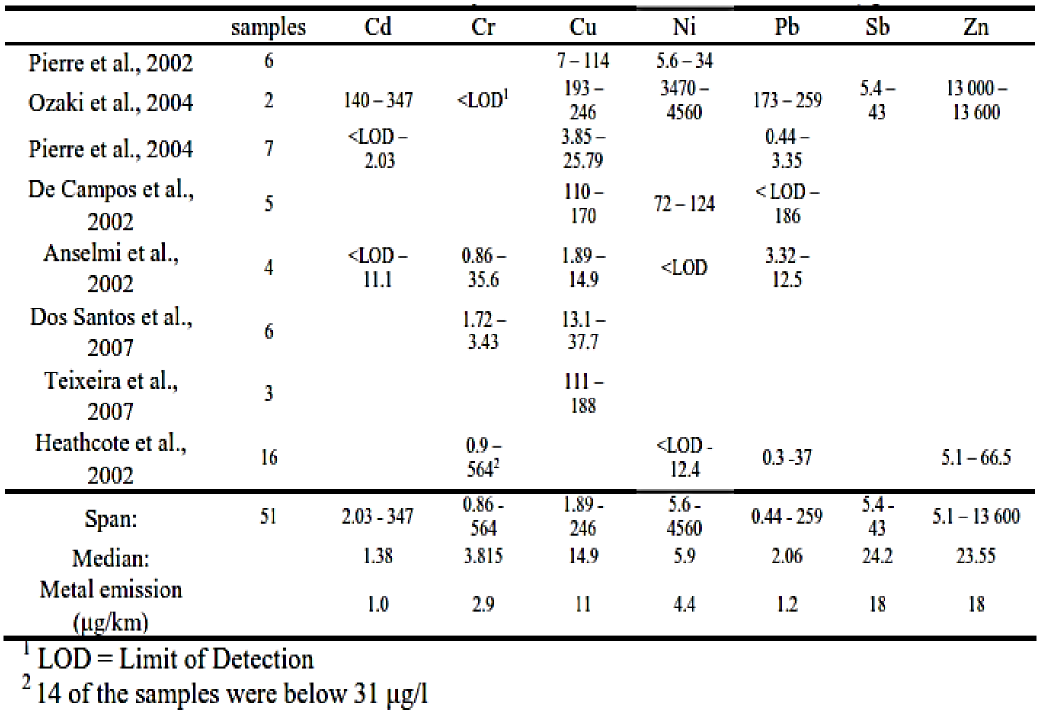
[4] Antimony is known to be associated with Pb and the two samples this figure is based on had a high Pb concentration

[5] Westerlund (2001), 1998 years emission

[6] Bergbäck, B. and Sörme, L. (1998)

[7] Bergbäck, B. and Sörme, L. (1998). The calculations are based on a asphalt wear of ~7g/km

Table (3): heavy metals roadside soils in literature (kg/year) (David , 2008)



	samples	Cd	Cr	Cu	Ni	Pb	Sb	Zn
Pierre et al., 2002	6			7 – 114	5.6 – 34			
Ozaki et al., 2004	2	140 – 347	<LOD[1]	193 – 246	3470 – 4560	173 – 259	5.4 – 43	13 000 – 13 600
Pierre et al., 2004	7	<LOD – 2.03		3.85 – 25.79		0.44 – 3.35		
De Campos et al., 2002	5			110 – 170	72 – 124	< LOD – 186		
Anselmi et al., 2002	4	<LOD – 11.1	0.86 – 35.6	1.89 – 14.9	<LOD	3.32 – 12.5		
Dos Santos et al., 2007	6		1.72 – 3.43	13.1 – 37.7				
Teixeira et al., 2007	3			111 – 188				
Heathcote et al., 2002	16		0.9 – 564[2]		<LOD - 12.4	0.3 -37		5.1 – 66.5
Span:	51	2.03 - 347	0.86 - 564	1.89 - 246	5.6 - 4560	0.44 - 259	5.4 - 43	5.1 – 13 600
Median:		1.38	3.815	14.9	5.9	2.06	24.2	23.55
Metal emission (µg/km)		1.0	2.9	11	4.4	1.2	18	18

[1] LOD = Limit of Detection

[2] 14 of the samples were below 31 µg/l

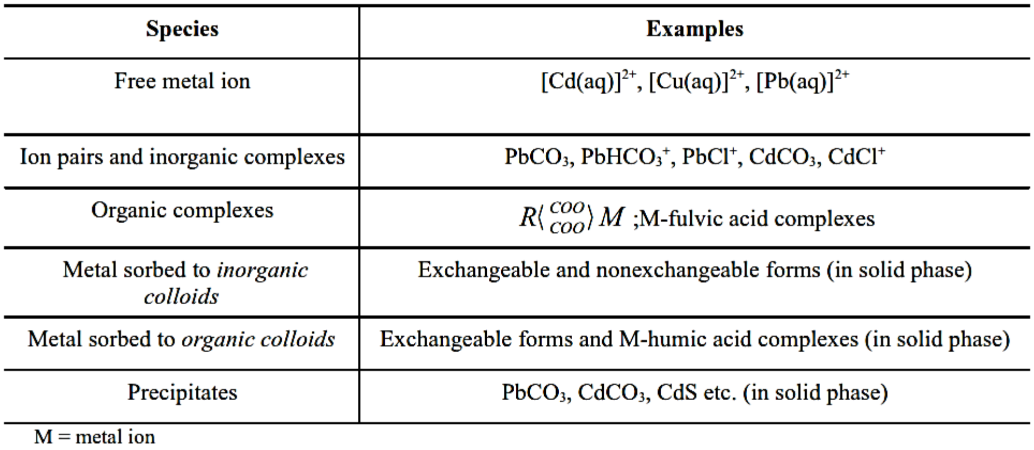
1.2.2. Behavior of heavy metals in soils

The overall behavior of heavy metals in soil is said to be governed largely by their sorption and desorption reactions with different soil constituents, especially clay components. The chemical behavior of heavy metal in soils is controlled by number of processes including metal cation release from contamination source materials, cation exchange and specific adsorption into surfaces of minerals and soil organic matter, and precipitation of secondary minerals (Issa, 2008).

The relative importance of these processes depends on soil composition and pH. In general cation exchange reactions and complexation to organics matter are most important in acidic soil, while specific adsorption and precipitation become more important at near-neutral to alkaline pH values (Issa, 2008). Elghawi et al studied the trace metal concentrations in some Libyan soils and found that the concentrations in clay surface soil are higher than in sandy soil (Elghawi et al, 2007).

Multiphase equilibria must be considered when defining metal behavior in soils as in figur1. Metals in the soil solution are subjected to mass transfer out of the system by leaching to ground water, plant uptake, or volatilization. At the same time metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution at any given time is governed by a number of interrelated processes including inorganic and organic complexation, oxidation-reduction reactions, precipitation-dissolution reactions and adsorption-desorption reactions. The ability to predict the concentration of a given metal in the solution depends on the accuracy with which the multiphase equilibria can be determined or calculated (EPA, 1992).

Table (4): Chemical species of heavy metals in soil with respect to solubility (Issa, 2008)



Species	Examples
Free metal ion	$[Cd(aq)]^{2+}$, $[Cu(aq)]^{2+}$, $[Pb(aq)]^{2+}$
Ion pairs and inorganic complexes	$PbCO_3$, $PbHCO_3^+$, $PbCl^+$, $CdCO_3$, $CdCl^+$
Organic complexes	$R\langle\begin{smallmatrix}COO\\COO\end{smallmatrix}\rangle M$;M-fulvic acid complexes
Metal sorbed to *inorganic colloids*	Exchangeable and nonexchangeable forms (in solid phase)
Metal sorbed to *organic colloids*	Exchangeable forms and M-humic acid complexes (in solid phase)
Precipitates	$PbCO_3$, $CdCO_3$, CdS etc. (in solid phase)

M = metal ion

Most studies of the behavior of metals in soils have been carried out under equilibrium conditions. Equilibrium data indicate which reaction is likely to occur under prescribed conditions. In the soil solution chemistry, metals exist in the soil solution as either free (uncomplexed) metal ions e.g. ., Cd^{+2}, Zn^{+2}, Cr^{+3}, or in various soluble complexes with inorganic and organic ligands e.g. ., $CdSO_4^0$, $ZnCl^+$, $CdCl_3^-$,or associated with mobile inorganic and organic colloidal material . The total concentration of a metal Me_Tin the soil solution is the sum of a free ion concentration $[Me^{+z}]$, the concentration of soluble organic and inorganic metal complexes , and the concentration of metals associated with mobile colloidal material [EPA ,1992].

Metals will form soluble complexes with inorganic and organic ligands. Common inorganic ligands are SO_4^{-2}, Cl^-, OH^-, PO_4^{-3},NO_3^- and CO_3^-. Soil organic ligands include low molecular weight aliphatic, aromatic, and amino acids and soluble constituents of fulvic acids. The presence of complex species in the soil solution can significantly affect the transport of metals through the soil matrix relative to the free metal ion. With complexation the resulting metal species may be charged or electrically neutral and the metal complex may be only weakly adsorbed or more strongly adsorbed to soil surfaces relative to the free metal ion. So soil properties not only affect mobility of metals but also the bioavailability and toxicity of the metal. The free metal ion is in general the most bioavailable and toxic form of the metal. Several metals of environmental concern exist in soils in more than one oxidation state , for example hexavalent Cr is relatively mobile in soils, being only weakly sorbed by soils, it is extremely toxic and a known carcinogen.

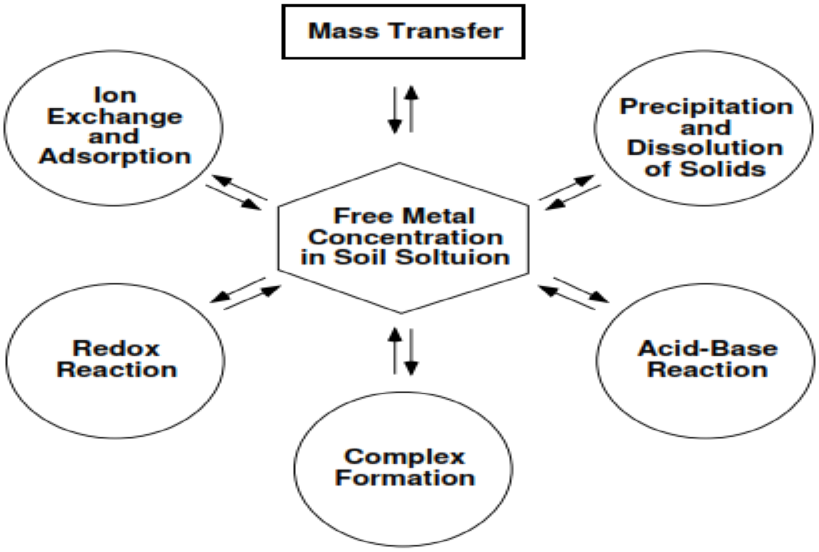


Figure (1): Principle controls on free trace metal concentrations in soils solution (EPA , 1992).

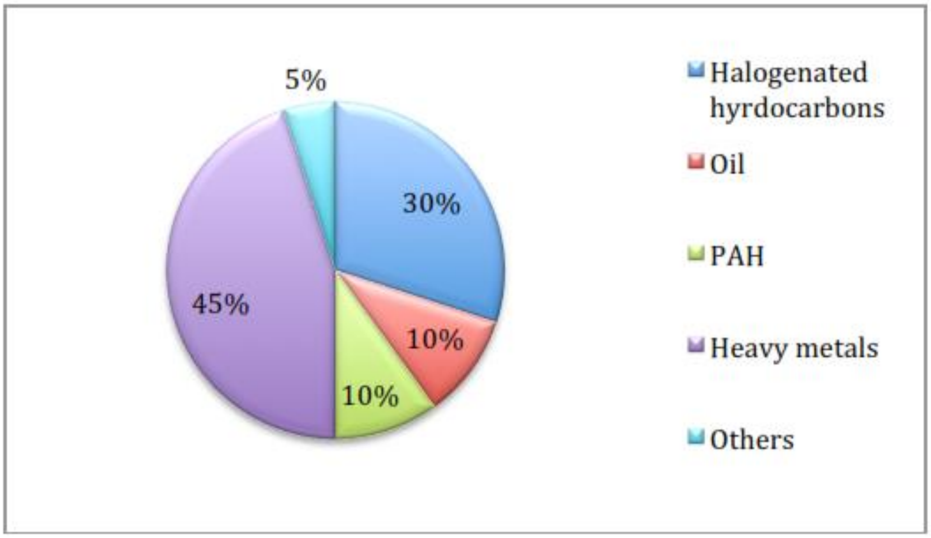


Figure (2): Distribution of common contaminants in Sweden 2005) (Qianyu Li, 2012)

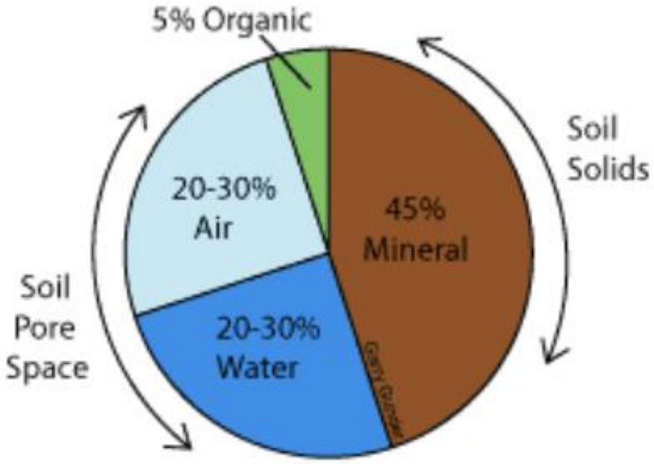


Figure (3): Natural soil composition (Commission of the European Communities, 2006) (Qianyu Li, 2012).

On the other hand trivalent Cr is relatively immobile in soil, being strongly sorbed by soils and readily forming insoluble precipitates and it is of low toxicity (EPA, 1992).

1.2.3. Solubility and mobility of heavy metals in soils

Many predictive methods based on solution and solid phase chemistry. The mobility and toxicity depends on the physicochemical properties of metals, their ions, and their compounds (vanloon and Duffy, 2010).

Distribution of heavy metals between soil and solute is the key for evaluating the environment impact of the metals, there are many factors influencing solubility and mobility of heavy metals in soils (T. Sherene, 2010).

Factors affecting adsorption and precipitation reactions are discussed below.

1.2.3.1. pH

The pH of the soil solution maintained at neutral to slightly alkaline condition showed low mobility of all heavy metals, to increase the mobility of heavy metals, the pH of the soil solution should be lowered, and the solubility of lead increase as the pH is adjusted from 6 to 3. At near neutral pH the activity of Pb^{+2} showed no clear relationship and small but significant increase resulting from changing organic matter content to pH because at near neutral pH range, higher soil organic matter (SOM) increases the dissolved organic matter (DOM), thereby promoting the formation of organo lead complexes and increasing Pb solubility (Sebastien et al, 1998). In acid solution a main value of 44% of the fractional sum of Cd is associated with the exchangeable form, thereby enhances its mobility. There is about 10 times the amount of Zn on exchange sites where the soil pH > 5.6,23% of Cd is found in exchangeable form, implying that metal is relatively very mobile.

In general, sorption increases with increasing pH. That is the lower the pH value the more metal can be found in solution and thus more metal is mobilized. When pH falls to below 5, mobility is enhanced as a result of the increased proton concentration. At pH values above 7, some heavy metals tend to form hydroxyl-complexes which will increase the solubility of the metal in question. Adsorption is greater at pH 6.5 than at pH 4.5. The adsorption of chromate did not change as significantly as other metals with pH changes. This is due to its oxyanion character in oxidizing condition, and the adsorption mechanisms are very different compared to that of positively charged metals. These results confirm that adsorption for most metal cations increases as pH increases (T. Sherene, 2010).

The pH of the soil-residual system is often the most important chemical property governing sorption and precipitation of heavy metals (Ibrahim Issa, 2008).

1.2.3.2. Organic matter

Soil organic matter is a key for sorbing phase for metals. It consist of :living organisms, soluble biochemical's (amino acids, proteins, carbohydrates, organic acids, polysaccharides, lignine.etc) and insoluble humic substances (Cory D. Lancaster, 2011)

The dissolution of humic acid (HA) at higher pH is responsible for dissolution of Cu and Pb from soil. Organic matter is important for the retention of metals by soil solids, thus decreasing mobility and bioavailability. However because of the complexation of metals by soluble OM, the addition of OM can result in release of metals from solid to the soil solution. The increase of the solubility of the copper, Nickel and lead show a strong positive relationship to the solubility of organic matter. This indicates that solution phase speciation reactions with organic matter dominate the partition of these metals at higher pH (D.J. Ashworth et al, 2008), because under high pH, the DOM increases as a result of the solubility of the non dissolved organic matter (HA) (K. kalbitz and R. Wennrich, 1998).

At alkaline range, most dissolved heavy metals are present as metal soluble organic ligands complexes. Cd can move readily in sandy loam soils, but OM in the surface layer will act as a sink for Cd and will reduce the rate of movement (Estelle et al, 2012). For Cu, in particular OM both solid and dissolved can affect its mobility substantially. The concentration of the DOM is partly controlled by Ca sorption, Ca can act as a bridge between negatively charged DOM and negatively charged soil particles both clay mineral and oxides. The heterogeneity of sorption sites is larges for natural solid OM than for dissolved purified HA (Temming Hoff et al, 1998). Complexation of metals by organic ligands play an important role in controlling metal solubility. Metal-ligand complex stability generally decreases with a reduction in pH, reflecting the role of $RCOO^-$ in metal complexation, the ligands include low molecular weight organic acids : oxalic, citric, formic, acetic, malic, succinic, malonic, maleic, lactic, aconitic, and fumeric acids have been identified in soil system. The highest amount of Cd is released by malate and the least by acetate.

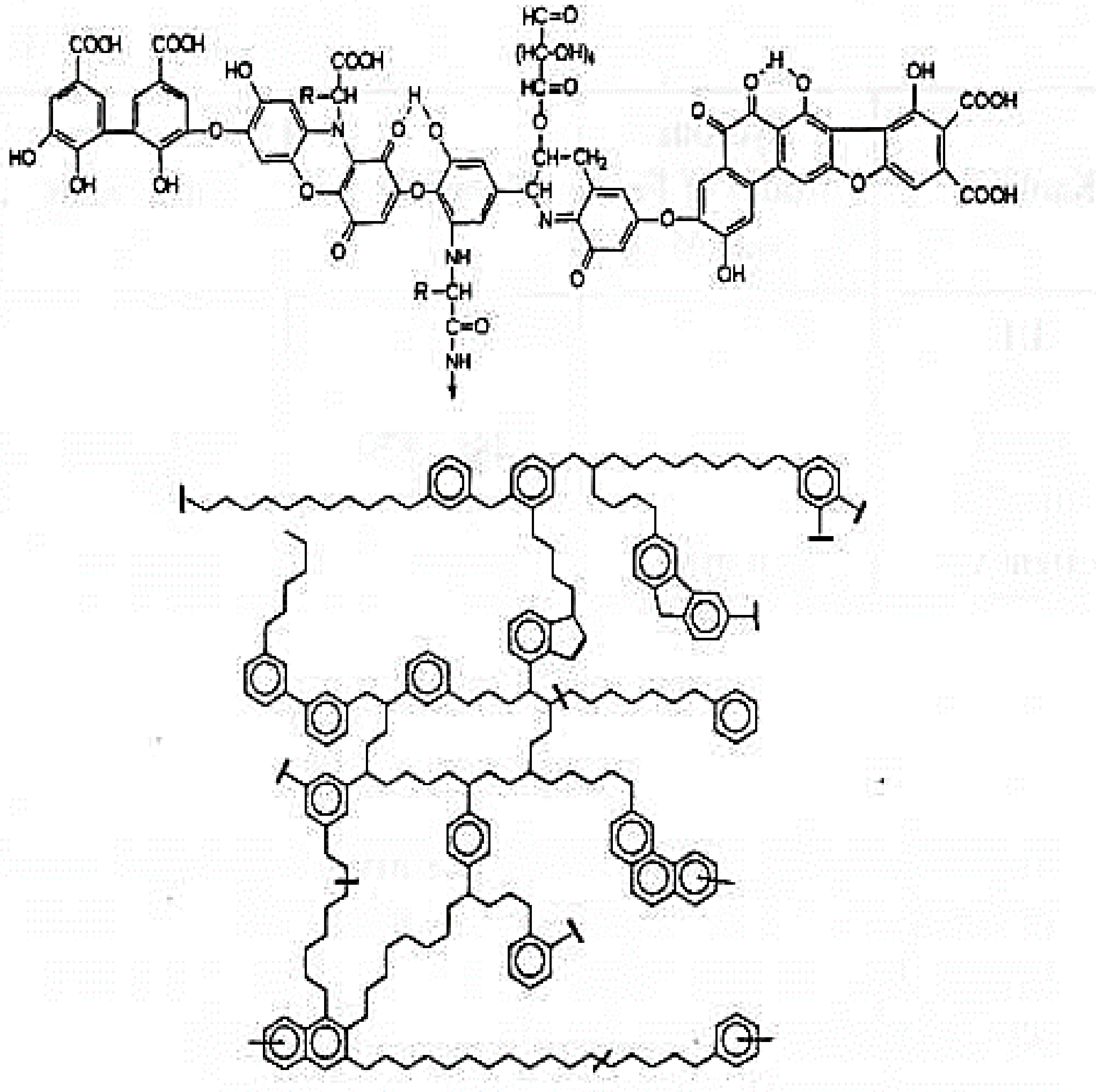


Fig (4): Model structures of humic acids according to Dube (Dube et al, 2001)

1.2.3.3. Ionic strength

The amount of metals adsorbed decreases with increasing ionic strength for minerals with permanent surface charge density (Boekhold et al, 1993). The reactions take place on the negative surface of colloids. For these surfaces the reduction of ionic strength makes the surface electric potential more negative, and thus ion adsorption is greater (Casagrande et al, 2005).

In high electrolyte concentration, it is also necessary to take into account the competition of Zn and the Ca present in the soil. The more negative electropotential of the surface soil layer explains the greater Zn adsorption at the surface for all pH and ionic strength values, as the surface soil layer presented more negative charges than the subsurface for a same pH values. It is finally concluded that, there is a pronounced increase of Zn adsorption with pH elevation and a reduction of ionic strength of background electrolyte. Results show that metal ion is more strongly adsorbed at lower ionic strengths while any increases in electrolyte concentration produce a decrease in metal adsorption (Casagrande et al, 2005).

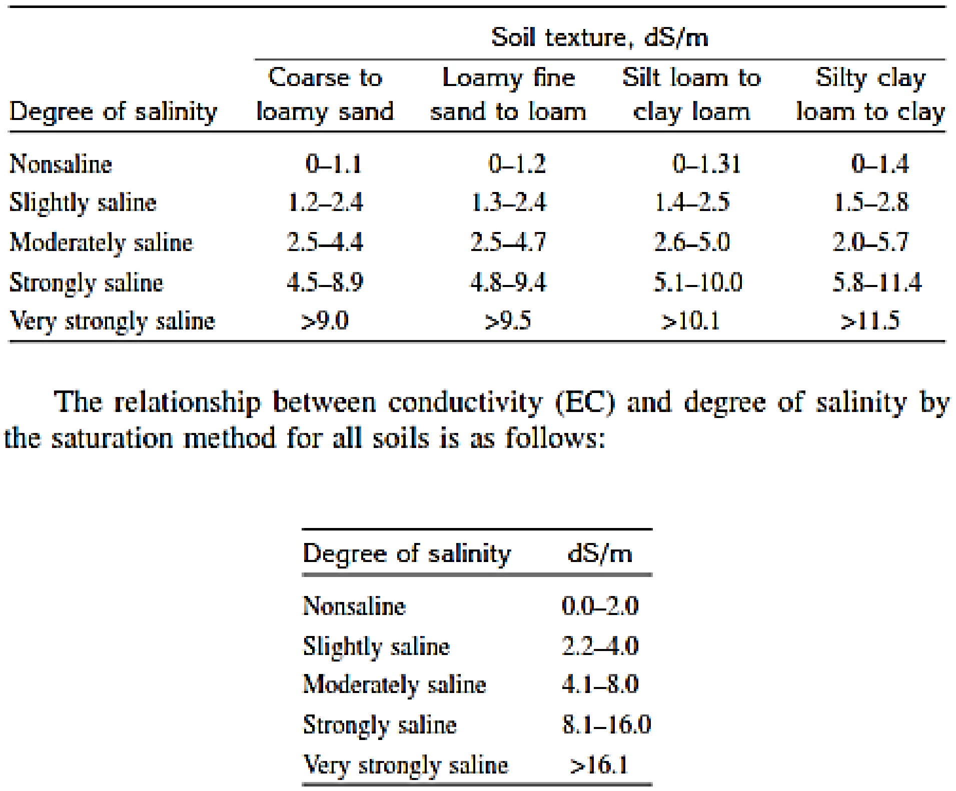
Adsorption is in relation with the cation exchange capacity (CEC) which obviously could be expected to influence the process, at each value of ionic strengths. It decreases metal sorption because of the competition by other cations for adsorption sites. The soil with higher ionic strength may have more risk of metal leaching from sewage sludge disposal than soil with lower ionic strength (T. Sherene, 2010).

1.2.3.4. Soil Texture

Soil texture plays an important role in mobility of metals in soil. Texture reflects the particle size distribution of the soil and thus the content of fine particles like oxides and clay. These compounds are important adsorption media for heavy metals in soils, with ranking in terms of adsorption clay> silt> sand (J.S. Rieuwerts et al, 2015). Thus clay soil retains high amount of metals when compared to sandy soil. The fine textured soils contain higher amounts of Pb (3889 mg kg^{-1}) and coarse textured soils contains (530 mg kg^{-1}) lower amount of Pb. The metal content of top and middle layer of soil is comparatively higher than bottom layer of soil (T.sherene, 2010).

Clays adsorb metal ions through both ion exchangeable and specific adsorption, it occur through the adsorption of (OH^{-}) ions followed by attachment of the metal ion to the clay either by bonding to the adsorbed (OH^{-}) or to sites created by proton removal. Clay along with O.M is the dominant soil constituent influencing the adsorption of p.b (J. S. Rieuwerts et al, 2015).Various clay minerals affect metal solubility by substantial differences, for example low concentration of Cd and Zn are adsorbed more strongly by kaolinite than montmorillonite possibly due to higher proportion of weakly acidic edge sites in the kaolonite surfaces, it found that adsorption is stronger for Cd than Zn due to the electrostatic attraction by permanent charge sites at the clay surface which is higher for Cd due to its larger ionic radius (Garcia-Miragaya et al, 1986). The selectivity of lillite for Pb is approximately 30 times that for montmorillonite (Hildebrand and Blum, 1974).

Table (5): Classification of Soils categories according to the USDA system (J.Benton Jones ,2001)·



	Soil texture, dS/m			
Degree of salinity	Coarse to loamy sand	Loamy fine sand to loam	Silt loam to clay loam	Silty clay loam to clay
Nonsaline	0–1.1	0–1.2	0–1.31	0–1.4
Slightly saline	1.2–2.4	1.3–2.4	1.4–2.5	1.5–2.8
Moderately saline	2.5–4.4	2.5–4.7	2.6–5.0	2.0–5.7
Strongly saline	4.5–8.9	4.8–9.4	5.1–10.0	5.8–11.4
Very strongly saline	>9.0	>9.5	>10.1	>11.5

The relationship between conductivity (EC) and degree of salinity by the saturation method for all soils is as follows:

Degree of salinity	dS/m
Nonsaline	0.0–2.0
Slightly saline	2.2–4.0
Moderately saline	4.1–8.0
Strongly saline	8.1–16.0
Very strongly saline	>16.1

1.2.3.5. Pore Structure

Soil texture and structure as evaluated by bulk density i.e. the solution flux. This plays apart in diffusion of metal ions into and out of soil aggregates in such a way be predicted with greater accuracy by having some knowledge of flow velocities. They also stated that flux is least effective for Ni. The downward migration rate of Ni is 0.83±0.72 cm year^{-1} and is well correlated with high soil macro porosity. Colloids with high surface charge and soils with greater macroporosity contributed more Pb mobility and transport

(T. Sherene, 2010). Cation adsorption by expandable clay such as vermiculite and scmectite occurs largely in inter-layer spaces compared to the relatively inactive planar surfaces, however in non-expandable phyllosilicates such as kaolinite and serpentine, penetration of water and cations between the layers is difficult and their cation exchange capacities are consequently lower (J.S. Rieuwerts et al, 2015).

1.2.3.6. Temperature

Several chemical reactions are temperature dependant in the way that they proceed at a metal concentration in plant grown on amended soil. When the temperature raises the metal activity in ion soil solution as well as that of the plant roots may be more active and has faster absorption rates. Considerable enrichment of heavy metals in the sub micron range occurs during evaporization of heavy metals in the high temperature environment and the subsequent condensation in lower temperature regions of the systems (Yu-Ling et al, 1998).

Thermal treatment of Pb^{+2} doped alumina powders could be effective in reducing the leaching level of Pb from the alumina matrix by H_2SO_4-HNO_3 in deionized water. The results of the sequential extraction of the thermally treated Pb^{+2} doped alumina powder show that as the treatment duration and temperature increased the percentage of Pb that is bound to the carbonates decrease with a concomitant increase of residual Pb.

Sheaffer et al reported that, higher soil temperature enhances the degradation of soil organic matter, thereby releasing organic acids which increase the solubility of heavy metals in soils thereby the mobility and availability increase (T. Sherene, 2010).

1.2.3.7. Index of cations and anions

The anion which can contribute in reducing heavy metal adsorption by the possible formation of negatively charged or neutral species like: MCl_2, MCl_3^-,MCl_4^-. In particular Cd is known to form relatively Cl^-complexes, which greatly influences the mobility of metals in soils. This fact is of particular importance since the ability of chloride–ions to maintain relatively high concentration of heavy metals in soil solution may produce favourable condition for a faster leaching of metals in the soil profile according to the soil texture (A. Dube et al, 2001). The amount of Cr desorbed varied with both the cationic charge and with depth of soil sample. In the surface soils the desorbed Cr decreased with increasing cationic charge ($H_2O>Na^+>Ca^{++}$) while the reversed trend ($Ca^{++}>Na^+>H_2O$) was observed in the subsurface soils. Highest Cr is released in the presence of phosphate solutions and least when Cl^- solution used as electrolyte (Avudianayagam et al, 2001).

On the other hand the lessened adsorption capacity of soils with respect to heavy metals due to the high concentration of salts could increase the availability of these contaminants. Also Cl^- ion has an important factor that enhancing Pb and Ni mobility in soil. Mobilization of Pb in contaminated roadside soils is suspected because chlorides are known to complex and stabilizing many heavy metals like Pb and Ni (yujun et al, 1999). Lead may also form complexes more readily with NO_3^- rather than Cl^-.This might be due to the ionic competition between Pb hydroxide species and Cl^- or NO_3^-

(Smolders et al, 1998).

1.2.3.8. Competing ions

Competing ions can have a marked effect on ion sorption by soils. The presence of Pb reduces significantly the adsorption maximum of cadmium on soils. There is a positive correlation exist between Mn and Ni, Ni and Cu, Ni and Fe, Pb and Cu, Pb and Fe, Pb and Mn, in soils. The presence and competitiveness of Cr (III) in a multiple ion mix will greatly reduce the amount of Pb^{2+}sorbed thereby drastically increasing their mobility and potential for transport to ground water. The stability constant for the Pb^{2+}-FA (Fulvic acid) complexes decrease with increasing concentrations of trace metals such as $Cu^{2+}$and Mn^{2+},andNi^{2+}-FA by Ca^{2+} and Mg^{2+}. This might be due to the polyelectrolyte effect (T. Sherene, 2010).

$Ni^{2+}$and Co^{2+} compete equally with Ca^{2+} only at very low solution activities. The Ni^{2+} adsorption competes by an equal Ca^{2+} desorption indicating that Ni^{2+}ions are retained at sites previously occupied by Ca^{2+}. The Ni^{2+} sorption has no effect on Cu^{2+} adsorption by reducing a Mn ion Creating an adsorption site. The Ni^{2+} should compete with Co^{2+} (but not Co^{3+}) for site occupation and Co^{2+} sorption should be decreased by increasing Ni^{2+} activity (Harter et al, 1992).

1.2.4. Fate of heavy metal in soil and environment

Migration of metals in the soil is influenced by physical and chemical characteristics of each specific metal and by several structural factors and the most significant ones are soil type, total organic content, Redox potential and pH.

In soil metals are found in one or more of several pools of the soil as described by Shuman 1991 (Issa, 2008).

1. Dissolved in the soil solution.
2. Occupying exchange sites in inorganic soil constituents.
3. Specifically adsorbed in inorganic soil constituents.
4. Associated with insoluble soil organic matter.
5. Precipitated as pure mixed solid.
6. Present in the structure of secondary minerals. and
7. In the structure of primary minerals.

As storm water leaves the pavement edge of the roadsides as overland flow aqueous phase and particulate bound metals contaminants introduced to the roadside environment are subjected to complex and dynamic functions of sediment transport, filtration and adsorption into soil matrices and existing vegetation. Hydraulically sediment transport and erosive potential is a function of runoff velocity which is a function of precipitation intensity, roadside slope, and surface roughness is dominated by the fraction of bare ground and litter cover. Once metal laden particulates are deposited, they can be subjected to both overland flow and when vegetation is minimal, raindrop erosive forces, both of which will transport particulates further down-slope. Erosive capacity of overland flow is a function of velocity and existing sediment load. Overland flow carrying a maximum sediment load has erosive ability, while sediment free overland flow of the same velocity can use considerably more erosion. Varying only sediment load introduced overland flow will result in constant down-slope sediment delivery. Bare soils are also subject to particulate dislodgment and scouring by kinetic energy of rain drops (Lancaster and Beutel, 2011). This process increases particulate availability to the transport mechanisms of overland flow.

Once related by the soil matrix either through deposition via overland flow of particulate bound metals or adsorption of aqueous phase metals following infiltration, metals are susceptible to various transport or leaching mechanisms. Transport of metals through soil enormously complex. Adsorption/desorption kinetic processes are very dynamic and while metal species are largely immobile once they adsorbed into the soil matrix, they are susceptible to some mobilization under certain conditions as described above (Karthanathsis et al, 2014). Metal species in roadside soil deposited over the past century have not has sufficient time to migrate far as there is a little evidence in the literature of metals migrating beyond depths of 1 m. One study found that ˜ 8% of the metals were removed in the runoff, 6% were removed via atmospheric deposition to environments with 50 m of the road way, and the remaining ˜ 86% were distributed away from the transportation corridor. If runoff contain about 8% of transportation generated metals then natural dispersion of this storm water roughly doubles the metal load to roadside environments (adding to the˜6% of metals deposited via atmospheric deposition) (Lancaster and Beutel, 2011).

Soluble lead added to the soil reacts with clays, phosphates, sulfates, and carbonates, hydroxide and organic matter, such that lead solubility is greatly reduced. At pH values above 6 lead is either adsorbed on clay surfaces or form lead carbonate. Of all the trace metals listed in table (6) lead retained by soil and soil constituents to the greatest extent under the conditions of these studies, have demonstrated decrease sorption of lead in the presence of complexing ligands and competing cations. Lead has strong affinity for organic ligands and the formation of such complexes may greatly increase the mobility of lead in soil (EPA,1992).

Cadmium may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide and phosphate (Dudley et al, 1991). Evidence suggests that adsorption mechanisms may be the primary source of cadmium removal from soil. The greatest percentage of the total cadmium in polluted soil is associated with the exchangeable fraction. Cadmium concentrations have been shown to be limited by cadmium carbonate in neutral and alkaline soils (Santillan-Midrano and Jurinak, 1975). As with all cationic metals the chemistry of cadmium in the soil environment is to a great extent controlled by pH, under acidic condition. Cadmium solubility increases and very little adsorption of cadmium by soil colloids, hydrous oxides and organic matter takes places, at pH values greater than 6 cadmium is adsorbed by the soil solid phase or is precipitated, and the solution concentration of cadmium are greatly reduced. Cadmium forms soluble complexes with inorganic and organic ligands. In particular Cl^- will increase cadmium mobility in soils (EPA, 1992).

Chromium exists in two possible oxidation states in soils $Cr^{(III)}$ and $Cr^{(VI)}$ forms of $Cr^{(VI)}$ in soil are CrO_4^{-2} ion (predominant at pH 6.5), $HCrO_4^-$ (predominant at pH <6.5) and a dichromate $Cr_2O_7^{-2}$(predominant at higher concentrations (>10mM) and at pH 2-6, the dichromate ion pose a greater health hazard than chromate ions , both $Cr^{(VI)}$ ions are more toxic than $Cr^{(III)}$ions, and because of the anionic nature of $Cr^{(VI)}$, its association with soil surfaces is limited to positively charged exchange sites, the number of which decreases with increasing soil pH, iron and aluminum oxide surfaces will adsorb CrO_4^{-2} at acidic and neutral pH. Concluded nonspecific adsorption of $Cr^{(VI)}$ and the presence of chloride, nitrate have little effect on $Cr^{(VI)}$ adsorption, where as sulfate and phosphate inhibited adsorption (EPA, 1992) . $BaCrO_4$ may form in soils at chromium contaminated sites. No other precipitates of hexavalent compounds of chromium have been dissolved in a pH range of (1- 9), hexavalent chromium is highly mobile in soils, and it is the only metal studied that was highly mobile in alkaline soils. $Cr^{(VI)}$ can be reduced to $Cr^{(III)}$ under normal soil pH and Redox conditions, SOM has been identified as the electron donor in this reaction and this reaction proceeds at a slow rate at environmental pH and temperatures(Bloomfield Pruden, 1980)$Cr^{(III)}$is readily adsorbed by soil, is found to be the least mobile of the relative mobility of metals in soils at pH 5, it forms hydroxyl complexes in natural water including $Cr(OH)_2^{+}$, $Cr(OH)^{+2}$, $Cr(OH)_3^{0}$and $Cr(OH)_4^{-1}$, these hydroxy species starts precipitates at pH 4.5 and complete precipitate occurs at pH 5.5(Griffin and shimp,1978).

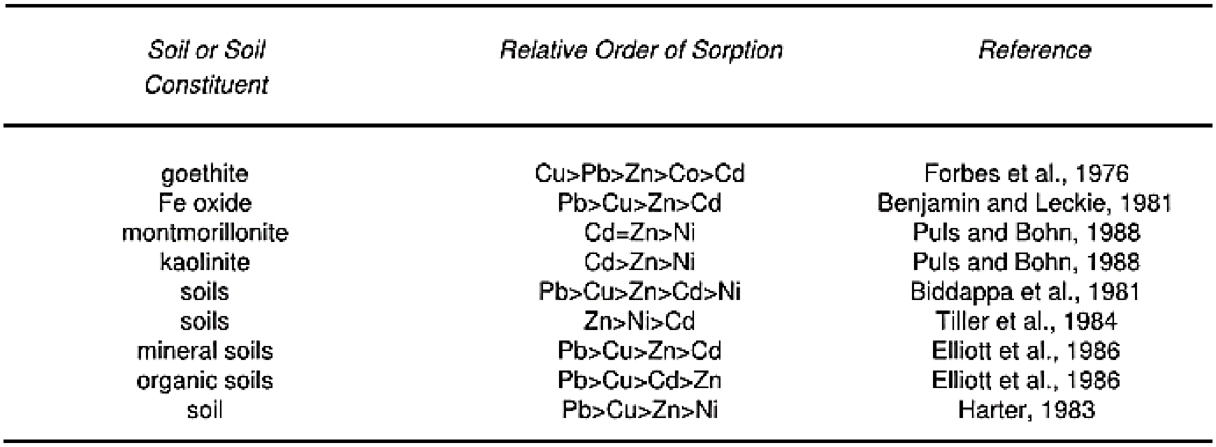
Copper is retained in soils through exchange and specific adsorption mechanisms, in the adsorption sequence Cu is adsorbed to a greater extend by soils than the other metals with the exception of lead, copper however, has a high affinity for soluble organic ligands and the formation of these complexes may greatly increase copper mobility in soils.(EPA, 1992)The O.M provides sites for Cation Exchange (CE), but its strong affinity to metals such as Cu is due to the presence of specific binders or groups that form metal complexes, these complexes occurring in great part with the fulvic and humic acids (FA and HA), the soluble one, with fulvic acid

(Estevao et al, 2004). Cu has a high affinity for soluble organic ligands and the formation of these soluble complexes may greatly increase Cu mobility in soils. (EPA, 1992)

The Nickel ionic species usually found in soil solution is Ni $(H_2O)_6^{+2}$ whose activity decrease with increasing pH. And also with the interaction with organic and inorganic compounds, forming complexes. In the solid soil fraction nickel may be found in the organic and inorganic compounds, and also in this case the PH is the main factor controlling the adsorption reactions of this metal to colloids (Estevao et al, 2004). Adsorption of Ni is less than Cu and Zn to the Fe, Al and Mn Oxides (kaolinite), but goethite and hematite are among the inorganic colloids associated to higher Ni quantities. There is a relevant affect of the organic matter on Ni adsorption. In one specific study for the OM-free soil samples the average adsorption values are 21,11,28% lower than those obtained for the original soil samples and these differences increased as pH decreased. For the pH above (6-6.5) the effect of organic matter in Ni adsorption is not significant probably because great part of the negative dependent pH charges would have the H^+ already dissociated. These complexes formation occur in great part with the fulvic and humic acids, present in the organic matter in large quantities. The insoluble combinations being associated with the humic acid and the soluble ones with the fulvic acid (Estevao et al, 2004).

Heavy metals are usually found in soil in various species as in table (6)

Table (6): Relative affinity of metals for soils and constituents (EPA, 1992)



Soil or Soil Constituent	*Relative Order of Sorption*	*Reference*
goethite	Cu>Pb>Zn>Co>Cd	Forbes et al., 1976
Fe oxide	Pb>Cu>Zn>Cd	Benjamin and Leckie, 1981
montmorillonite	Cd=Zn>Ni	Puls and Bohn, 1988
kaolinite	Cd>Zn>Ni	Puls and Bohn, 1988
soils	Pb>Cu>Zn>Cd>Ni	Biddappa et al., 1981
soils	Zn>Ni>Cd	Tiller et al., 1984
mineral soils	Pb>Cu>Zn>Cd	Elliott et al., 1986
organic soils	Pb>Cu>Cd>Zn	Elliott et al., 1986
soil	Pb>Cu>Zn>Ni	Harter, 1983

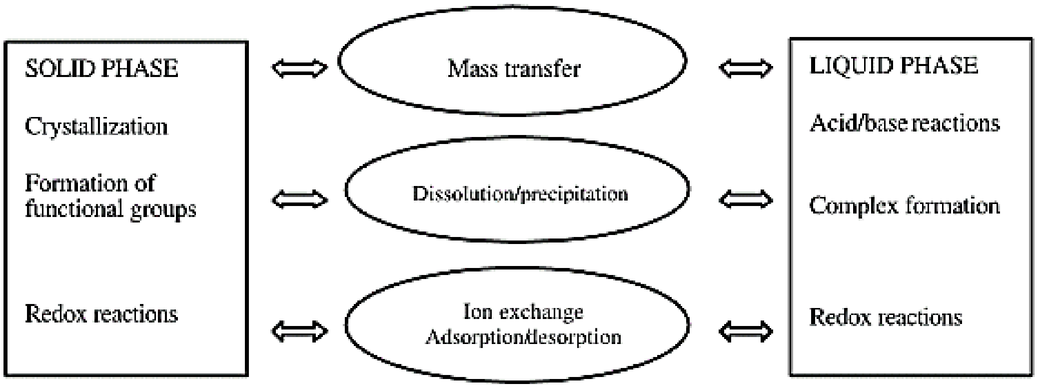


Figure (5): Types of interactions within and between solid and solution phases in soil systems (Maria et al, 2003)

1.2.5. Effects of contaminated roadside soils with heavy metals on the environment and public health

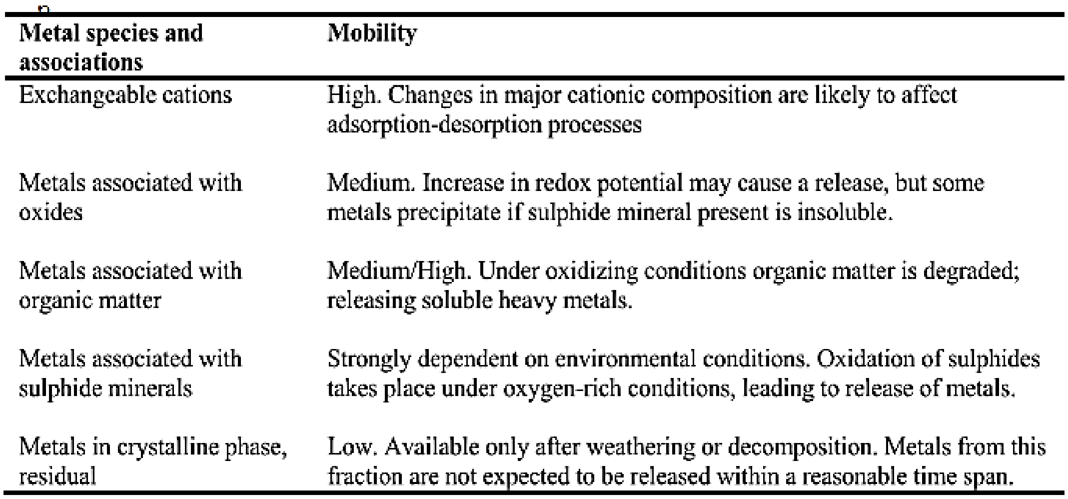
Heavy metals are typical road traffic source contaminants in the local ecological environments and thus threaten public health.

Heavy metals from roadside soils can directly harm public health by entering the body via soil and dust, dermal contact or breathing (Fan Zhang et al, 2012).

In general heavy metals with high concentrations in the environment result in health problems adversely affecting the nervous, blood forming, cardiovascular, renal and reproductive systems. The consequences of heavy metal pollution include reduced intelligence, attention deficit, and behavioral abnormality. They are toxic and are potential cofactors, initiators or promoters in many diseases including increased risk of cancer (Fan Zhang et al, 2012). At elevated levels essential and nonessential heavy metals are known to cause morphological abnormalities, reduced growth, increased mortality and antigenic effects in human, plants and animals (Godwin et al, 2012). The route of exposure to particulate dust and soil metals include inhalation of contaminated particles, direct soil ingestion (usually by children) and ingestion of food produced along the roads. The health effects of toxic metals in air and dust from road deposited dust on human is better appreciated if one consider the fact that an active person typically inhales 1000 to 2000 L of air daily (Godwin et al, 2012). Inhalation high levels can damage the lungs and ingestion will irritate the stomach (Caroline et al, 2008). Heavy metal contaminants can easily impact people residing within the vicinity of the roads via suspended dust or direct contract (Fan Zhang et al, 2012).

The metals in soil may be washed away by rain and road runoff and eventually get into adjacent river systems. It is no matter whether in soil or water, may accumulate in plants, animals or human bodies. Even extremely low doses of heavy metals may cause serious diseases in human beings (Xuedong Yan et al, 2012). Heavy metal contaminated soil affects the ecosystem when heavy metals migrate into ground water or taken up by flora and fauna (Karthanathsis et al, 2014). This can form great risk to ecosystems due to bioaccumulation and they may reach ground water via colloid –assisted and /or soil water transport. Contamination of ground water by heavy metals may pose a more directly serious and continuing health risk to humans and environment (Xin Lu, 2005).

Table (7): Metal species, associations and mobility. (Liselott Petersson, 2005)



Metal species and associations	Mobility
Exchangeable cations	High. Changes in major cationic composition are likely to affect adsorption-desorption processes
Metals associated with oxides	Medium. Increase in redox potential may cause a release, but some metals precipitate if sulphide mineral present is insoluble.
Metals associated with organic matter	Medium/High. Under oxidizing conditions organic matter is degraded; releasing soluble heavy metals.
Metals associated with sulphide minerals	Strongly dependent on environmental conditions. Oxidation of sulphides takes place under oxygen-rich conditions, leading to release of metals.
Metals in crystalline phase, residual	Low. Available only after weathering or decomposition. Metals from this fraction are not expected to be released within a reasonable time span.

1.2.6. The Chemistry of Acid Digestion

Acid digestion-whether carried under open or closed pressure digestions system are conducted with the aid of a wide variety of reagents. Aside from the various mineral acids, other reagents such as hydrogen peroxide, potassium peroxide sulfate, boric acid, and many more are also employed. The selection of the specific reagents or the preparation of reagent mixture depend on the sample composition to be digested, organic sample materials are generally decomposed into carbon dioxide with the aid of oxidizing acids primarily nitric acid and reagents (primarily hydrogen peroxide) and completely mineralized .

For inorganic matrices such as soils it is recommended to use inorganic acids such as HCl, H_3PO_4, HNO_3, $HClO_4$, HF, H_2SO_4, or their combination. These acids or extractants exhibit various peculiar properties which enable each acid to carry out specific functions during the extraction. The choice of extractants for contaminated soils analysis depends on the aim of the study, type of contaminants , properties of the extractant , experimental conditions, need to readily release extracted metal and need for minimum interference from contaminants. Extractants may be acidic or basic depending on their mode of action which depends on interacting mechanisms such as the metal ion-extractant affinity, metal ion concentration, extraction temperature, and acidity of the medium. Extractants are soil specific for example H_2SO_4does not digest samples containing Ba. HCl does not digest samples containing Ag and Pb, also As compounds forms volatile compounds with HCl.SoH_2SO_4does not used to analyze some sulphate salts. Thus it is better for total metals determination to digest soils in sealed Teflon beakers with HNO_3^-HF-$HClO_4$pure acids for complete particles decomposition and metal release.

Consideration must also be given to the possible loss during the solution process of the constituents to be determined, for trace analysis it is desirable to minimize the amounts of reagents that restrict the choices available for sample decomposition and in order to prevent the volatilization losses of low boiling point acids such as hydrofluoric acid which may be lost during the evaporation of the aqueous solution at high temperature. Also certain elements are lost partially or completely in open wet digestion methods involving halogen compounds, these include chromium as $CrOCl_2$, lead as $PbCl_4$ (Pradyot Patniak, 2004). The goal of every digestion process is therefore the complete solution of the analytes and the complete decomposition.

Acid digestion procedures are employed for the determination of elements in solids such as soils subsequent to sampling and mechanical sample preparation in order to completely transfer the analytes (targeted elements)into a clear solution so that they can be introduced into the determination step (e.g., AAS, ICP-AES) in liquid form of the soil matrix while avoiding loss or contamination of analytes.

So the advantage of the closed pressure in comparison with open digestion in a recycling device or with the traditional hot plate , lies in the significantly higher working temperatures which can be achieved(J.D.Winefordner, 2003), because regardless of the heating process used (conventional or microwave) the pressure development during closed acid digestion is a product of the acid mixtures vapor pressure at the employed temperature and the possible formation of gaseous substances (generally carbon dioxide during the digestion of organic samples). While tables provide the vapor pressure of acids , the partial pressure of the carbon dioxide can be estimated using the ideal gas equation and the sample weighed .(J.D.Winefordner, 2003).

1.2.7. Wet digestion methods and its reagents

In non oxidizing acids the electromotive force series furnishes a guide to the solution of metals, since this process simply a displacement of hydrogen by the metal, thus all metals below hydrogen displace hydrogen and dissolve in oxidizing acids with the evolution of hydrogen, but some exception to this may be found, the action of hydrochloric acid on lead, cobalt, Nickel, Cadmium and Chromium is slow and lead is insoluble in sulfuric acid owing to the formation of a surface film of lead sulfate. Therefore oxidizing acids must be used to dissolve the metals above hydrogen and the most oxidizing acids are nitric acid, hot concentrated perchloric acid and hot concentrated sulfuric acid or some mixture that yields chlorine or bromine, considerable difficulties are in countered in the dissolution of inorganic matrices such as silicates, nitrides and carbides. The selection of suitable reagents in the sample preparation technique is an important issue (Pradyot Patnaik, 2004).

1.2.7.1. Utilizing hydrochloric acid in wet digestion process

The concentrated hydrochloric acid is an excellent solvent for many metals and metals oxides it is often a better solvent for the oxides than the oxidizing acids , it dissolve the phosphates of most of the common metals although the phosphates of the niobium , tantalum , thorium and zirconium dissolve with difficulty. It decompose silicates containing a high proportion of strong or moderately strong bases but acidic silicates are not readily attacked . It has high efficiency to dissolve sulfides of antimony, bismuth, cadmium, indium, iron, lead, manganese, tin and zinc. Cobalt and nickel sulfides are partially dissolved. Addition of 30% hydrogen peroxide often assists the digestion of metals due to the release of nascent chlorine, after a period of heating in an open container, a constant boiling 6 M solution remains (boiling point 112 C^0). The low boiling point of hydrochloric acid limits it is efficiency to dissolve oxides in digestion methods.

1.2.7.2. Utilizing hydrofluoric acid in wet digestion process

The primary use of hydrofluoric acid is the decomposition of silicate rocks and minerals in which silica is not to be determined, the silicon escapes as silicon tetrafluoride, and after decomposition is complete the excess hydrofluoric acid is driven off by evaporation to fumes with perchloric acid to virtual dryness. It can dissolve niobium, tantalum and zirconium forming stable complexes, although the action is rather sometimes slow, it is an excellent solvent for the oxides and silicates of these metals which require to be heated at elevated temperatures.

1.2.7.3. Utilizing nitric acid in wet digestion process

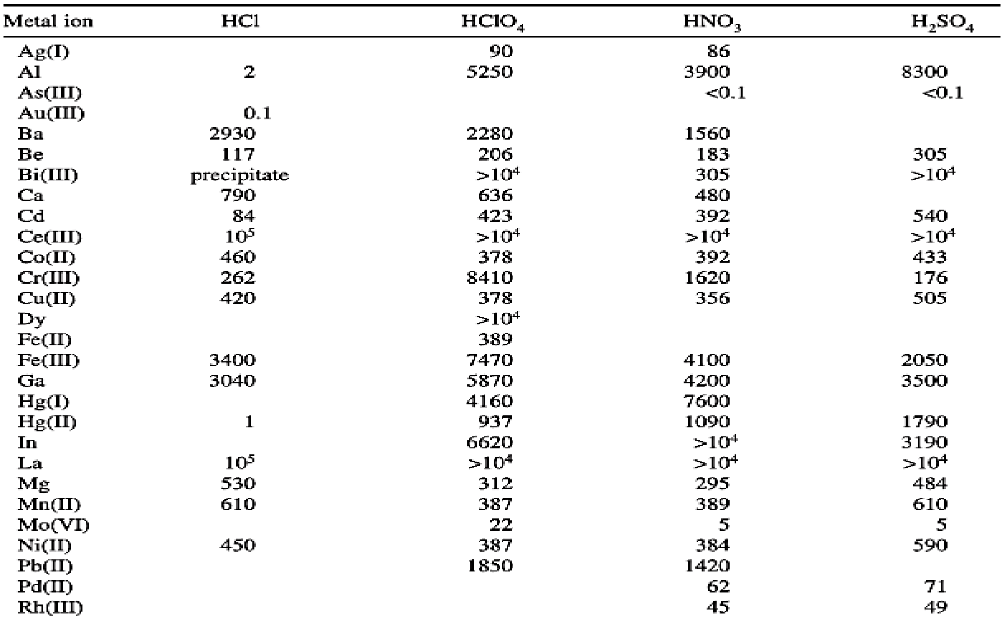
Concentrated nitric acid is an oxidizing solvent it dissolves most common metallic elements except chromium ,aluminum, gallium, indium and thorium which dissolve very slow because a protective oxide film forms, and it doesn't attack gold, hafnium, tantalum, zirconium and the metals of the platinum group (other than palladium), tin antimony and tungsten form insoluble oxides when treated with the concentrated nitric acid , also nitric acid attacks the carbides and nitrides of the vanadium and uranium, it is an excellent solvent for sulfides although the sulfides of tin and antimony form insoluble acids.

Although nitric acid is a good oxidizing agent it is usually boils away before the matrices is completely oxidized, so a mixture of nitric and hydrofluoric acids specially in a closed digestion system dissolve hafnium, niobium, tantalum and zirconium readily and it is very effective towards antimony, tin and tungsten and the carbides and nitrides of niobium, tantalum, titanium and zirconium.

1.2.7.4. Utilizing perchloric acid in digestion process

Hot concentrated perchloric acid is a potent oxidizing agent it attacks a number of ferrous salts in soils and stainless steel that are intractable to other mineral acids, oxidizing the chromium and vanadium to the hexavalent and pentavalent acids, respectively. Sulfur and sulfides are oxidized to sulfates, silica is rendered in soluble antimony and tin are converted to insoluble oxides, perchloric acid failed to dissolve niobium, tantalum, zirconium and the platinum group metals.

Table (8): partition coefficients between solids and liquid phases of metals in some acids (Pradyot patnaik, 2004).



Metal ion	HCl	$HClO_4$	HNO_3	H_2SO_4
Ag(I)		90	86	
Al	2	5250	3900	8300
As(III)			<0.1	<0.1
Au(III)	0.1			
Ba	2930	2280	1560	
Be	117	206	183	305
Bi(III)	precipitate	$>10^4$	305	$>10^4$
Ca	790	636	480	
Cd	84	423	392	540
Ce(III)	10^5	$>10^4$	$>10^4$	$>10^4$
Co(II)	460	378	392	433
Cr(III)	262	8410	1620	176
Cu(II)	420	378	356	505
Dy		$>10^4$		
Fe(II)		389		
Fe(III)	3400	7470	4100	2050
Ga	3040	5870	4200	3500
Hg(I)		4160	7600	
Hg(II)	1	937	1090	1790
In		6620	$>10^4$	3190
La	10^5	$>10^4$	$>10^4$	$>10^4$
Mg	530	312	295	484
Mn(II)	610	387	389	610
Mo(VI)		22	5	5
Ni(II)	450	387	384	590
Pb(II)		1850	1420	
Pd(II)			62	71
Rh(III)			45	49

Quarantine the completeness of digestion process to release the bonded and adsorbed heavy metals in soil sample species (Pradyot Patnaik, 2004).

1.2.8. Heavy metals determination in the digestion extracts

The small or extremely small amounts of heavy metals as contaminants in the environmental samples digestion solutions has led to ever increasing demands for the determination of these metals at trace level concentrations . The levels to be detected range from parts per million to parts per billion. In order to measure at these levels, methods of high sensitivity and selectivity are needed. They must be applicable to all categories of roadside soils samples, be accurate and reliable and preferably they should also be convenient and economical. The aim is to produce a complete decomposition with full dissolution as well as a clear solution not contain acid at a greater concentration than about 1 M since the aspiration of extremely corrosive materials into the burner of the atomic absorption spectrophotometer instrument should be avoided as far as possible .

There are several techniques for the analysis of heavy metals in trace levels, they include Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), X-Ray Fluorescence spectrometry (XRF), neutron activation analysis and electro analytical techniques. Each of the above techniques has several advantages and disadvantages in terms of (i) sample size requirement (ii) sensitivity and detection limit (iii) form of sample to be analyzed (iv) complexity of preconcentration techniques (v) quantitative application (vi) selectivity, interferences and matrix effects (Vii) number of elements that can be analyzed (viii) multi element determination (ix) preparation and use of standards (x) routine applications (xi) time, space and the cost.

Atomic absorption spectrometry combines high sensitivity, selectivity, simplicity with low cost, routine application and speed of analysis and the only criterion for sample preparation is that the metal should be in liquid solution. These characters make it one of the most popular approaches for metals analysis to the analytical chemists (S. Ahuja et al, 2006), (W.J. Price, 1979).

Atomic absorption spectrometry (AAS) measures the concentrations of ground state atoms by quantifying the absorption of spectral radiation that corresponds to allowed transitions from the ground to excited states. It measures the discrete radiation absorbed when ground state atoms are excited to higher energy levels by the absorption of a photon of energy. The radiant power of the absorbed radiation is related to the absorption coefficient of the ground state atoms using Beer lambart equation

$I_{(\lambda)} = I_{o(y)}\, 10^{-\mathbf{k}}{}_{(\lambda)}b$

Where $I_{o(y)}$is the radiant power of the incident radiation of wavelengthλ,

$I_{(\lambda)}$the radiant power of the transmitted radiation at wavelength λ, $K_{(\lambda)}$ the absorption coefficient of the ground state atoms at wavelength λ and b the path length.

This equation can be expressed in terms of absorbance $A_{(\lambda)}$

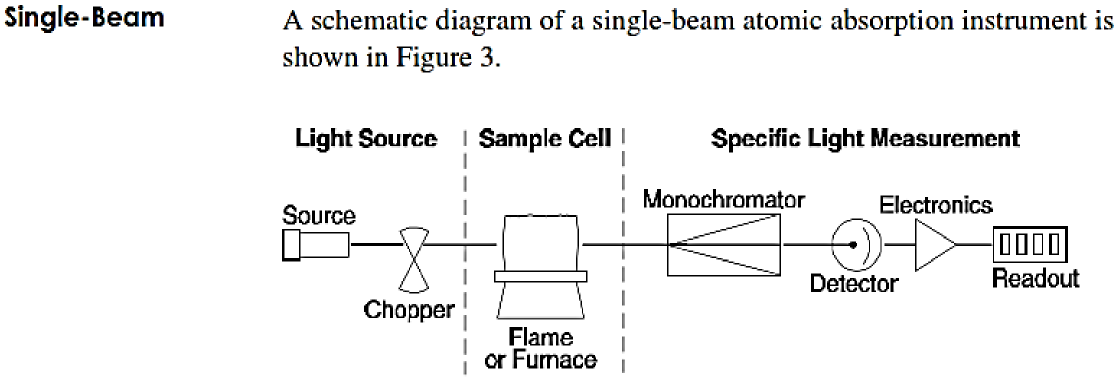
$A_{(\lambda)}=\log (I_{(\lambda)} / I_{o(\lambda)})= K_{(\lambda)}\, b$

The usual method of excitation of the ground state atoms is to use an elemental spectral source (often a hollow cathode lamp) that emits the atomic spectra of the analyte element. If the width of the emission line from the spectral source is negligible compared to the absorption line of the ground state atoms, and if it is assumed that the absorption profile is determined by Doppler broadening, then the absorption coefficient integrated over the absorption-line profile can be approximated by the absorption coefficient at the absorption peak maximum (K_{max}).

The relationship between K_{max} and the number density of ground state atoms N_0 is given by the following equation:

$$K_{\max} = (2\lambda^2/\lambda_{\mathrm{D}})(\ln 2/\Pi)^{0.5}(\Pi e^2/mc^2)N_o f$$

Where λ_D is the Doppler width of the line; λ the wavelength of the absorption maxima; e and m the charge and mass of an electron, respectively, C the velocity of light, and f the oscillator strength (average number of electrons per atom that can be excited by the incident radiation). Therefore, the absorbance is directly proportional to the concentration of atoms, provided that the absorption profile is dominated by Doppler broadening.



Single-Beam

A schematic diagram of a single-beam atomic absorption instrument is shown in Figure 3.

Figure (6): Single-Beam Atomic Absorption Spectrometer (Perkin Elmer Instrumental manual, 1996)

The light source (hallow cathode lamp or electrodeless discharge lamp) emits a spectrum specific to the element of which it is made, which is focused through the sample cell into the monochromator. The light source must be electronically modulated or mechanically chopped to differentiate between the light from the source and the emission from the sample cell. The monochromator disperses the light, and the specific wavelength of light isolated passes to the detector which is usually a photomultiplier tube, an electrical current is produced depending on the light intensity and processed by instrument electronics. The electronics will measure the amount of light attenuation in the sample cell and convert those reading to the actual sample concentration, with single beam systems, a short warm-up period is required to allow the source lamp to stabilize.

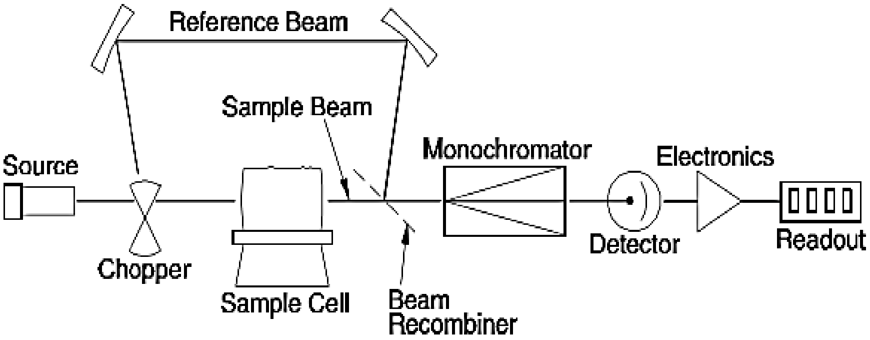


Figure (7): Double-Beam Atomic Absorption Spectrometer (Perkin Elmer Instrumental manual,

In the double beam atomic absorption spectrometry light from the source lamb is divided into sample beam, which is focused through the sample cell, and reference beam, which is directed around the sample cell. In double beam system the readout represents the ratio of the sample and reference beams thus fluctuations in source intensity do not become fluctuations in instrument readout and stability is enhanced so analysis can be performed immediately with no lamp warm-up required.

1.2.8.1. The flame atomic absorption system

The basic flame atomic absorption spectrometer figure (6,7) is that light from the source lamp generating a sharp line spectrum characteristic of the desired element passes through the flame into which the sample solution is sprayed as a fine mist. The region of the spectrum in the immediate neighbourhood of the resonance line falls on the detector, a photomultiplier, the output of which is amplified and drives a readout device .e g a meter, strip chart recorder or through a data processing to a digital display unit or printer.

The most convenient, stable and economic source of atomic vapours remains the combustion flame. Fuel oxidant mixture are now commonly used which are safe to handle and produce a range of temperature from about (2000-3000 K), also these mixtures should be combined in ratios which may be stoichiometric lean or rich (lean and rich mixtures contain less than and more than the stoichiometric quantity of fuel gas respectively). The most widely used of these fuel/oxidant mixture is air acetylene as it enables about 30 of the common metals (which include the heavy metals occurring in this chemical assessment research study). The sensitivity of some elements on the hydrogen air flame is not much inferior to their sensitivity in air acetylene (e.g. their degrees of atomization are comparable) but the presence of other substances in the sample solution may cause the formation of stable compounds and hence interferences are raised to be worse and give lower sensitivity in hydrogen-based flames.

1.2.8.2. Instrumental settings and the minimization of noise

Ideally the signal on the readout device should appear noise free and sharp, noise from various sources produces less distinct peak Values, sluggish response (damping) gives round off traces. Hence noise on the signal originates in various ways throughout an atomic absorption system and it is worthwhile to consider these individually to see how they each affect the final signal.

1.2.8.3. Flame noise

This arises from refractive index variations in the region between the hot parts of the flame and the cold surrounding atmosphere and from small variations in effective path length of the flame cell, the flame is highly dynamic system which cannot be contained within closely defined dimensional limits and the convection currents induced around it cause such variations. Flame noise always exists, it can only be minimized by good design of the burner (laminar flow burners are clearly the best), the flame compartment and chimney (a fume extraction system with too fierce a draught can cause turbulence effects within the flame compartment), and by preventing draughts from windows and doors from reaching the flame.

1.2.8.4. Nebulizer (concentration) noise

This is caused by fluctuation in the amount of the element being measured which actually reaches the flame. Nebulization is quantized process and the droplets are produced in a slightly irregular stream. The irregularities are smoothed out during the passage of the mist through the spray chamber. There is thus minimum effective size of the spray chamber, one which is too small though giving somewhat higher noise. And by whatever means the absorption signal is amplified thus noise from the nebulizer and flame will remain constant proportion of it.

1.2.8.5. Source lamp noise

The lamp discharge is a statistical mean of all the micro-scale sputtering discharges which can sometimes even be observed visually as a slight flicker, there is a minimum lamp current bellow which this effect is so great as to make the discharge unstable. The lamp current must therefore be sufficiently high to minimize this effect but not so high that broadening of the resonance lines affects the sensitivity. and any superimposed noise is therefore also amplified and recorded in the final output signal , the only exception to this is lamp noise of a frequency less than the chopping frequency in double beam spectrometer and the instrument used for roadside topsoil samples is a single beam optical design system.

1.2.8.6. Effects of slit width on the measurements

The width of the monochromatic slits has been set to the best band pass for a particular analysis, the best value is a compromise and the resolution of the monochromatic is improved up to limiting value as the slits are made narrower. So the best value depends on the following:-

(i) The wave length, if a prism monochromatic is in use. the dispersion (in mm nm^{-1}) at 220 nm can be about 10 times as great as at 400 nm and twenty times as great as 500 nm , hence slits can be considerably widened at lower wavelengths without loss of resolution but with an increase in energy falling on the detector . The Shimadzau AA-6800F spectrophotometer model which was used in our analysis on the study has a high resolution diffraction grating monochromator.

(ii) The nearness to the resonance line of other lines emitted by the source. if non-absorbing lines originating in the spectrum of the element being determined or the lamp fill -gas are included are included in the spectral bandwidth of the monochromator these will fall on the detector, and however great the absorption of the resonance line the recorded signal will never fall below their sensitivity value, there for elements with complex emission spectra (the transition and heavy metals) will require narrower slits (as in our heavy metals analysis) than those with simple spectra such as alkaline and alkaline earths .

(iii) The intensity of the resonance line. The slit width can be increased if insufficient gain is available from the electrical system to operate the instrument satisfactory. It may be regarded as a source of noiseless gain available at the cost of resolution and sensitivity., with a low intensity source there for better stability could be achieved by increasing the slit width, so that a signal with acceptable intensity falls on the photomultiplier, conversely the sensitivity (working graph slope) is best at the narrowest usable slit width. So the matching of atomic spectral and continuum lamp intensities in instruments fitted with background corrector like Shimadzu

AA-6800F, can be achieved by setting the continuum lamp energy throughput varies with the square of the slit width while the intensity is directly proportional.

On the Integration and electrical damping the degree of damping is defined by the time constant of the noise-filtering circuits, typically this may be 0.2-2 s with a meter or 1-4 s with a recorder like Shimadzu AA-6800F instrument.

The time required to make a reading is proportional to this time, if it is too long then the best very rounded off traces or irregularly drifting traces or reading may be obtained. Conditions are adjusted as before until this variation has been minimized. When actual analyses are being performed the integration time is increased to the working value which may be 4 or 10 s or thereabouts (W.J. Price, 1979) , (Shimadzu cookbook, 1997).

Procedure of graphical calibration entails drawing the calibration graph , a line or a curve of best fit through a series of points obtained by measuring the absorbance of a series of three or more standard solutions of different concentrations in advance , the range of concentrations used is chosen to close that in the samples to be analyzed , the analysis result is then obtained by calculation from the equation of the best fit line of the calibration graph, there should not have to be any particular relationship between standard concentrations but the function coefficients are better established if the standard concentration are spaced are approximately equal intervals.

In modern instruments as Shimadzau AA-6800F there are advantages of a good programme applied to avoidance of personal errors in huge computation of results, curve correction system. It uses the stray line equation which is usually the best one. it also have the ability to recalibrate on being given a new absorbance value for the top standard in order to eliminate the effects of sensitivity drift , and to correct minor errors in the automatically adjusted zero [(W.J. Price, 1979) , (Shimadzu cookbook, 1997).

1.2.9. Soils pH determination techniques

Making an accurate and consistent measurement of soil pH is not easily done, as there are a number of factors that can significantly affect the determination, the soil /solution ratio, the ionic strength of the soil solution, the type of the electrode used (combination Vs reference and glass electrodes, the position of the electrodes in the suspension and stirring of the suspension during pH measurement.

The pH of mineral soil is normally determined in a 1:1 soil -to-water mixture, some studies suggested the use of $CaCl_2$ solution for mineral soils to minimize interferences from suspension effects (due to particles suspended in the soil-solution mixture) and variable salt content. The recommendation for saline-sodic soils are related to pH values obtained with the saturated paste method, for organic soils a 1:4 soil to water mixture is recommended (Yash P. Calra et al, 1995).

The ratio of soil to water in the suspension has net effect on increasing the pH with a decrease in the soil water ratio but less than expected increase in PH with increasing soil solution ratio, it was the result of reduced dissociation of H^+ from the soil surfaces and less hydrolysis of Al that may be present. The soil suspension pH is most sensitive to differences in the soil solution salt concentration at very low soil solution salt levels. The higher pH is found due to the leaching of soluble salts out of samples. Also the leaching of soluble salts resulted in an increase in soil pH regardless of the soil/water ratio for 20 soils. In contrast, some researchers found that the addition of 0.01 mol/L Calcium chloride to the soil suspension decreased the pH by approximately 0.50 pH units from that of H_2O. Seasonal rainfall variation could therefore be expected to affect pH readings that are performed in water because soluble salts will vary among seasons. As a response to such results Rayment and Higginson 1992 recommended the use of 0.01 mol / L $CaCl_2$ 1:1 soil solution ratio for pH measurement instead of water, this method provides a more robust measurement than a water matrix and is less affected by the analytical weakness of the glass electrode systems. This provides a more consistent measurement pH on soil that may fluctuate in soluble salt content as a result of seasonal weather conditions and application of amendments. This method was chosen to our analytical roadside soil samples for pH determinations.

The device is a sensitive ion selective electrode which comprised of a glass H^+-sensing indicator electrode and a reference electrode coupled to a suitable volt- meter and equipped with a thermometer capable of measuring temperature to the nearest 0.1 C^0. A pH meter will be made up of a probe, which itself is made up of two electrodes. This probe passes electrical signals to a voltmeter which displays the reading in pH units. The glass probe has two electrodes because one is a glass sensor electrode and the other is a reference electrode. Some pH meters do have two separate probes in which case one would be the sensor electrode and the other the reference point.

Both electrodes are hollow bulbs containing a potassium chloride solution with a silver chloride wire suspended into it. The glass sensing electrode has a bulb made up of a very special glass coated with silica and metal salts. This glass sensing electrode measures the pH as the concentration of hydrogen ions (from H^+ ions activity) surrounding the tip of the thin walled glass bulb. The reference electrode has a bulb made up of a non-conductive glass or plastic to offers constant voltage output (Robert et al, 2010).

1.2.10. Soil organic matter content determination techniques

Carbon is the chief element (48-58)% in soil organic matter(SOM)there for a conversion factor of 1.724 has been proposed for the conversion of organic carbon(O.C) content to SOM content. Organic carbon can be determined by most common procedure involves reduction of potassium dichromate by O.C compounds and subsequent determination of the unreacted dichromate by oxidation reduction titration (Redox). Or the other method by loss-on-ignition technique in which the soil material is dried at 105 C^0 and then ashed at 400 C^0.The loss in weight between 105C^0 and 400 C^0 constitute the organic matter content. Although it provide sensitivity of about 0.2-0.5 % , the presence of calcium carbonate may interfere so it is not suitable for calcareous soils, or $CaCO_3$ should be removed previously (J.Benton Jones, Jr , 2001).

1.2.11. Soil moisture content determination techniques

Under natural conditions all soils contain water. The amount of

Water can be very low in air-dried soils. As a convention the total water content and dry mass of soils are measured after drying at 105C^0 (ISO 11465 1993). Thus, the water content of a soil is given as percent by weight or volume of oven-dried soil. Water which is removed at higher temperatures is not included in the definition of soil water. The soil water content can be determined with direct and indirect methods. Direct methods are more precise but time consuming. Indirect methods are mainly used for Continuous determination of water contents in the field. The most appropriate indirect method is the time Domain Reflectometry (TRD) method. The optimum water content for microbial processes is in the range of 40–60% of maximum water-holding capacity (WHC),or corresponds to the water content that is held in soil at suction pressures of (−0. 01 - −0.031) MPa (R.Margesin , F.Schinner , 2005)

1.2.12. Soil texture determination techniques

Particle size analysis (PSA) is a measurement process of the size distribution of individual particles in a soil samples. The major features of PSA are the destruction or dispersion of soil aggregates into discrete units by chemical, mechanical, or ultrasonic means and the separation of particles according to size limits by sieving and sedimentation. Dispersion of soil is accomplished by a combination of methods and those methods for dispersion can be classified as either chemical or physical. Chemical dispersion is based on the concept of particle repulsion as a result of elevation of the particle zeta potential. This process is usually accomplished by saturating the exchange complex with sodium (usually dilute alkaline solution of sodium polyphosphate). Physical methods involve separation of the individual particles by rubbing, rolling, shaking or vibrating and ultrasonic’s .Most researchers found that a combination of chemical and physical methods provides the most complete and stable dispersion (ArnoldKlute, 1986).

1.2.13. Electrical conductivity (EC) determination techniques

The determination of the electrical conductivity of the soil solution is used to classify the level of soluble salts found in the soil solution and can be assayed for its elemental content, electrical resistance is defined by the equation:-

$E = IR$

Where E is the electrical potential in Volts, I is the current in amperes and R is the resistance in ohms, electrical conductance C or the conductivity of a solution is a reciprocal of resistance.

$C = 1 / R$

C is expressed as mhos , but for convenience more commonly as millimohs which is 1/1000 mhos, because the numbers for expressing specific conductance are relatively small, it has been found convenient to express specific conductance as millimohs per centimeter (mmhos/ cm) which is equal to decisiemans per meter (dS/m) in international units.

The Specific conductance or soluble salt level of a soil can be determined Based on a water saturation extract or a1:1, 1:2 or1:5 soil/water extractions. An appropriate quantity of extractant is obtained and its specific conductivity determined (J. Benton Jones, Jr 2001) . Because saturated paste method require time and skills, fixed soil/water ratios are increasingly use, some studies have shown good correlations between EC, Mg^{+2}, K^{+1} and Cl^{-1} in 1:2 extracts versus saturation paste extracts, and between EC, Na^{+1}, Ca^{+2},

Mg^{+2} , and Cl^{-1} in 1:1 and 1:2 extracts versus saturation paste extracts (M.R. Carter and E.G. Gregorich, 2008).

A comparison study showed that, 90% of the 1:1extracts results are within ±2 Standard deviations of the mean value compared of 87% of the saturation paste extracts, and 84% of the 1:2 extracts (wolf et al, 1996), On the soil extracts for conductivity determination the chosen extraction procedure (soil/water ratio) will yield different interpretative results than another one procedure, therefore, it is important that the interpretation values chosen are appropriate to the extraction procedure employed (J. Benton Jones, Jr 2001), (M.R. Carter and E.G. Gregorich, 2008).

Specific conductance is determined using an electrical resistance (Wheatstone) bridge, commonly referred to as either a conductance or a conductivity meter. Specific conductance of a solution is the conductance that is measured at 25°C between electrodes 1 cm^3 in surface area and placed 1 cm apart thus For convenience, most cells for measuring the conductance of solutions have cell constant equivalence of unity. Most meters currently measure solutions conductivity directly.

It is not generally necessary to determine the cell constant unless there is some doubt about it. The cell constant can be determined by preparing a 0.01NKCl solution (weigh 0.7456 g potassium chloride into 500 ml in a1000-mL volumetric flask and bring to volume with water), which will give a Specific conductance reading of 1.4118 dS/m at cell constant equivalent 1 at 25°C (J. Benton Jones, Jr 2001).

An EC meter measures the concentration of all soluble salts dissolved in a solution, but does not determine which salts are present at specific concentrations. The passage of an electric current through a solution is measured via a probe with two metal prongs one centimeter apart. Electrical current flows between the two prongs, the higher the EC the easier it is for electrical current to move through the solution, thus a higher EC value. Electrical conductivity is measured in millisiemens per centimeter (mS/cm) or millimohs per centimeter (mmhos/cm). Some EC meters or combination pH/EC meters express salt concentration in total dissolved solids (TDS). This is expressed as parts per million (ppm), which is mS/cm multiplied by a converting factor 640 (Todd J et al, 2000).

Chapter two

2. Materials and methods

-Chemicals and reagents

All chemicals and reagents used were laboratory analytical grades with high purity so it didn't need another additional purification processes.

- Calcium chloride solution 0.01M prepared from $CaCl_2.2H_2O$ (97-103%) S D fine-chem limited. Mumbai. India, 0.3677g was weighed, dissolved with deionized water in a beaker, transferred to 250 ml volumetric flask; volume was made up with the use of deionized water.
- Buffer solutions 4.01, 7.0 and 10 pH for calibration points from Duksan (Duksan Pure Chemicals Co. Ltd, South Korea) traceable to INST standard reference materials.

-Potassium dichromate $K_2Cr_2O_7$ solution 1N, 60 g of the material (from Loba chemie, India) was dried at an oven at 105 C^0 for 2 hours, cooled in a desiccator and kept in well sealed dark glass bottle, 49.04 g of it was dissolved in a 500 ml beaker with distilled water, transferred to 1L volumetric flask and made up to the volume with distilled water and shaken well.

-Ferrous ammonium sulfate hexahydrate 0.5N $Fe(SO_4).(NH_4)_2SO_4.6H_2O$ wherein 196 g of the material (from central drug house (p) ltd, India) was dissolved by adding distilled water with stirring, transferred to 1L volumetric flask, 5ml of concentrated sulfuric acid were added, stirred well and made up to the volume.

-Diphenylamine indicator $NH(C_6H_5)_2$,1 g of Diphenylamine(from central drug house (p) ltd, India) was dissolved by adding 70 ml concentrated sulfuric acid in 100 ml beaker and stirred with a glass rod until it was completely solubilized and transferred to 100 ml volumetric flask, made up to volume with concentrated sulfuric acid.

- Sodium hexametaphosphate SHMP solution dispersion reagent 5%, (from S D fine-chem limited, India) aqueous solution $(NaPO_3)_6$ 50g / L).
-Reference standard solutions 1000 ppm (W/V) as Pb, Cd, Ni, Cr, Cu for each one (code ROMIL PrimAg^R-plus from Romil Pure Chemistry Ltd – Cambridge – England).

-IAEA-soil-7 Certified Reference Material (CRM) of soil sample based on dry weight for analytical method validation , obtained from the International Atomic Energy Agency- Agency's laboratories seibersdorf, A-1400 Vienna, Austria.

- Nitric acid Concentrated 70.5%, sp.gr 1.415 g / ml (Romil Pure Chemistry Ltd - Cambridge - England).

- Sulfuric acid Concentrated H_2SO_4 98%, sp.gr 1.84 g / ml (Romil Pure Chemistry Ltd -Cambridge - England).

- Phosphoric acid Concentrated 85% Wt / vol, sp.gr 1.685 g / ml (Romil Pure Chemistry Ltd- Cambridge - England).

- Hydrofluoric acid Concentrated 40% Wt/ vol, (Romil Pure Chemistry Ltd - Cambridge - England).

- Perchloric acid Concentrated 60% Wt /vol. (Romil Pure Chemistry Ltd – Cambridge – England).

-Potassium chloride KCl 0.01 N standard aqueous solution for EC meter, 0.746g of dried material (from Central drug House (P) ltd. New Delhi, India) was weighed and dissolved in small beaker, quantitatively transferred to 1L volumetric flask, and made up to the Mark with deionized water.

-Instruments and Equipments

-Instruments:-

-pH meter with combined electrode and temperature sensor (Wagtech CD-510, UK) have PH range (0.0-14.0 PH units), accuracy (±0.01 PH unit), resolution (0.01PH unit), 3 points calibration (10.0, 7.0, 4.0) USA and NIST buffers options.

-Electrical conductivity meter (Jenway 470, UK).

-Atomic absorption spectrophotometer (Shimadzau, model AA-6800F, Shimadzu Corporation - Kyoto - Japan),

- Analytical sensitive balance AX 120 from Shimadzu,

-Drying oven (memmert D91107, Schwabach, Germany) which is thermostatically controlled with forced air ventilation and capable of maintaining a temperature of 105 ± 1C^0.

-Brannan standard hydrometer (ASTM no. 152 H, Uk) with Bouyoucos scale in (g / L) from suspension.

-Laboratory electric grinder from Retsch model RS 200,

- Electric stirrer Heidoph RZR 2020, Germany.

-Orbital shaker from Edmund Buhler model KL, Germany.

-**Equipments**:-

Drying container (moisture box 25 g with lid made of waterproof material that doesn't absorb moisture for air dried soil samples), Desiccator with an active drying agent (anhydrous $CaCl_2$), Stop watch, Plungers for soil mixture sedimentation stirring, Sand bath, benzene burner, high temperature thermometer, clean and white high quality cellulose papers, Standard mercury thermometer with 1 C^0 measurement accuracy, Sedimentation cylinders with 1-L mark 36 cm from the bottom of the inside, Metals dispersing cups, Conical flasks 100 ml, precise pipette 10 ml grade A with its dispenser, measuring cylinders 10, 20 ml, water bath, volumetric flasks 100 ml grade A, small funnels and stand, Paper cups, glass rod, 50 ml polypropylene samples containers, conical flasks 50 ml, glass beakers 250 ml, Polypropylene materials of 50ml volumetric flasks, polypropylene funnels, 50 ml plastic containers of high purity polyethylene, 100 ml Teflon beakers, Teflon watch covers, bettry dishes, high quality aluminum foil, whatman filter papers No-42, Polypropylene materials of plastic shovels and scoops, self sealing polyethylene bags 5 kg capacity, 50 ml high purity polyethylene containers and sheets, 2mm laboratory soil sieve, riffle splitter (all of which were laboratories equipments).

2.1. Roadside top soils Sampling

2.1.1. Sampling Sites

Topsoil samples were collected from 12 representative sites along 3 major automobiles roads in Khartoum state, namely Sahafa Zalat street in Khartoum city, Arbaeen street in Omdurman and AL- Ma Una street in Khartoum north with coordinates (15^0 32' 42" N 32^0 32' 17") (15^0 17'38''N

32^0 28’ 56’’) (15^0 37’ 44’’ N 32^0 37’ 33’’) respectively. Four representative sites for each automobile road, tow of which are chosen as one on the beginning and the other on the end of the road, while the other sites of the study are located between them so that each road was divided into 3 semi equidistance lengths according to their traffic volume. The locations of the sites were so chosen to span a wide range of the traffic density and to give a good chemical and geological coverage on the studied area along the roads route. In Sahafa Zalat street, Algali Station was K1 sampling site, Cross 61 street was K2, station 7 is K3. The starting station of the general transport vehicles is K4. In Al Arbaeen street, after the starting point of the street by about 100m was an O1sampling site, after 2500m was O2, Abideen station was O3, before the street end by about 80 m was the O4. For Al-Ma Una street after 180 m of the starting that was N1, and after saadqishra station by 120 m was N2 and Shabia road turn was N3, then N4 was on the site where southern shambat road No11 meets on Al-Ma Una street. About 25 km away from the metropolis zone and industrial sources of contamination, and in a suburban area. Taiba Alhasanab in Jabal Awliya County was selected as a presumably uncontaminated reference site for taking the Background topsoil sample in order to judge the contamination level by the studied heavy metals in the major roads, following the method of Xiong (Z. Xiong, 1998).

The three chosen cites in this study were composed of the urban areas in Khartoum state, known by the name Triangular Capital. They feature heavy traffic activity in all its major roads (Salah et al, 2011). The land on the state is generally downgrade to the white and blue or river Nile (John Ryle et al ,2011) and there are some valleys and rills on which the rain waters are collected and flow to the rivers on the rain season such as Abuanja and

Wadisidna. Also there are some dusty storms in the month of May which might give temporary full darkness in vision due to the dust particulates, as well as floods, industrial and domestic sewage (Ahmed Alhuseen, 2014) and (Elagaba Haj Ali, Abdel-Rahman Osman, 2014). Those factors can transport and release the heavy metals from the roadside soils as soluble or particulates parts which can be in contact with human, animal, plant and aquatic marine in the local environment.

2.1.2. Preparation of plastic wares and containers

All used plastic wares and samples containers were washed well completely, firstly were rubbed with a clean laboratory brusher in a liquid soap detergent then rinsed well with hot tap water, then washed with nitric acid (1:1), and finally purged fully with the deionized water and left to dry in a clean surface and space which was free from dust and fumes.

2.1.3. Sampling procedure

12 topsoil samples were collected within 5m from the roads edges, and 0-10 cm surface layer depth at each sampling site (David et al, 2012). They were collected from the studied area during the second week of July 2015. Sampling was conducted with the use of systematic-random sampling, the studied roadsides sites were divided into 4x5 m grid in a two spots area besides the edges of the roadside sites. Then topsoil samples were groveled with the very clean -acid washed plastic shovel from the corners and middle of the grid to provide about 2.5 kg from each grid and they were introduced into a clean Al-foil wrapped from the outer side and labeled polyethylene self sealing bags. Thus the amount of each composite bulk sample is about 5 kg, they were sealed tight well and transported to the laboratory immediately

in the same day (O.J. Achadu et al, 2015) (Abdolhossein et al, 2012) (Godwin et al, 2012).

2.2. Roadside top soils samples pretreatment

The labeled bulk top soil samples were spread and demystified in a clean polyethylene plastic sheets, extraneous substances such as stones and debris were removed, then were air dried under sun light at around (28-38) C^0 for 3 days at ambient conditions with occasionally shuffle and fragmentation of the large masses, mixed entirely, sieved through 2mm mesh sieve, and finally each sample was re-homogenized before being stored in an labeled polyethylene bags at room temperature (Godwin et al, 2012).

These pretreated samples were used to determine pH, organic carbon / total organic matter contents, electrical conductivity/ total ionized dissolved solids contents and soil texture properties.

2.3. Determination of roadside soil samples pH

The used method on this study is an standard procedure for determining pH values in a soil suspension in the presence of 0.01M $CaCl_2$ to approximate a constant ionic strength for all soils regardless of past management, mineralogical composition and natural constituents levels. Hence it eliminates the interferences from suspension effects and variable salts contents, also its results are more reproducible than the other methods and one year of storage of air dried soil does not affect the pH (Conyers and Davey, 1988).

To ensure accurate measurements from the pH meter the device was calibrated before the measurements, it will need to be calibrated both before first use and its' ongoing basis. This was done by dipping the probe into a buffer solutions start from the higher one to the lower one of a known pH (4.01, 7 and 10) followed the calibration steps based on the used pH meter. Calibration solutions were never be recycled back into the fresh solution containers after the use (Todd. J et al, 2000).

2.3.1. Procedure of pH determination

After pretreatment of sample, ten grams were weighed into 50 ml paper cup, 10ml of calcium chloride solution 0.01 M was added, mixed thoroughly for 5s with glass rod , soil-$CaCl_2$ suspension was let to stand for 30 min, the mixture temperature was adapted to about 25 C^0 with the air condition, test samples were stirred with glass rod, the combined electrode of the calibrated pH meter was inserted into the sample mixture content and the soil-$CaCl_2$ suspension was swirled slightly, the pH reading was recorded immediately after 60 s to the nearest 0.1 pH unit, the electrode was removed from the suspension , rinsed with deionized water, excess water was blotted off with gentle touching of the electrode bulb with a filter paper to prevent electric charges generation (Yash Calra et al, 1995).

2.4. Determination of organic carbon (O.C) and total organic matter content (T. O .M)

In this method, potassium dichromate oxidized the organic carbon in soil matrix in acidic media then the excess amount of it was determined by oxidation back titration with the ferrous ions solution.

$$2Cr_2O_7^{2-} + 3(\text{-C-}) + 16\ H^+ \rightarrow 4Cr^{3+} + 3\ CO_2 + 8H_2O$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14\ H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7\ H_2O$$

The method is based on the widely used walkey-black procedure, however this procedure has been shown to lead to the incomplete oxidation of organic carbon and is particularly poor for digesting elemental carbon forms, Studies have shown that the recovery of organic carbon with a mean recovery been 76% as a result of the incomplete oxidation and in the absence of a side-specific correction factor, so a correction factor of 1.33 is commonly applied to the results to adjust the organic carbon recovery. The reaction is assisted by the heat generated when two volumes of H_2SO_4 are mixed with one volume of dichromate as a result of exothermic reaction (self heat source) prior to heat in a water bath. The addition of ortho phosphoric acid to the digestive mix after the sample has cooled has been used to help eliminate interferences from the ferric (Fe^{3+}) ion that may be present in the sample (Brain A. Sumacher, 2002).

2.4.1. Procedure of OC and TOM determination

The determination of organic carbon and organic matter content were conducted according to the method described by Walkey and Black with some modification (George Estefan et al, 2013) 2.5 g (for some samples 1.0g) of the pretreated top soil samples were weighed in 50 ml glass beaker, 10ml of potassium dichromate solution 1N were added, 20ml of concentrated sulfuric acid were added gradually with continuous shaking and let to set at the bench site for 10min, then heated on a water bath at 68 C^0 for 30min, cooled to room temperature and transferred to 100 ml volumetric flask, the volume was made up, then the contents were shaken well, 10ml from the clear solution was taken into a 100ml conical flask then 10ml of concentrated phosphoric acid and 3 drops of diphenylamine indicator were added and shaken the solution color was blue-violet. After that the contents were titrated against a standard solution 0.5 N of Ferrous ammonium sulfate until the color changed from blue-violet to green at the end point, titration was done on duplicate and the average volume of the titrant was taken.

TOC was calculated from the results as:-

$$\textbf{\textit{T.O.C\%}}\ \textbf{(w/w)} = \frac{(B\text{-}S)*\ 0.5*10*(12/4)*\ 1.33\ *\ 100}{1000*\ S.W}$$

-B represents titrant volume that equivalent to blank solution as titrand.

-S represents titrant volume that equivalent to sample solution as titrand.

-SW represents sample weight

-0.5 represents the concentration of $(NH_4)_2SO_4.FeSO_4.6H_2O$ solution.

-10 represents volume factor of the titrands

-(12/4) represents equivalent weight of carbon

-1.33 represents correction factor to obtain the T.O.C from the reactant carbon on the oxidation process with $K_2Cr_2O_7$ solution for soil samples.

-(1/1000**)** represents correlation factor to converts from mg to gram unit.

-***T. O.M*** **% =** T.O.C% * 1.724

-1.724 represents correlation factor to converts T.O.C % to T.O.M % of soil samples.

-RSD% = (S/mean)*100, S represents standard deviation of the values.

2.5. Determination of roadside soils electric conductivity (EC) and total dissolved solids (TDS)

2.5.1. Procedure of soils EC determination

10g of the pretreated samples were weighed into 50ml plastic container, 10ml of distilled water were added, shaken on an orbital shaker at 300 RPM for 60 min, and filtered with whatman No.42 filter paper. The clear filtrate was transferred to a 10ml test tube, the conductivity meter was calibrated with standard solution of KCl 0.01 N wherein its' reading equal 1.413 ds/m, the cell of the electrical conductivity meter was immersed in the sample solution tube and the reading was taken at the ambient room temperature. The cell was removed from the sample extract tube and washed well with distilled water and blotted off with clean tissue to be ready for the next sample extract EC estimation, the measurements were done in duplicate and the average values were taken (M.R. Carter and E .G. Gregorich, 2008)

$$\text{EC ms cm}^{-1} = \text{TDS (mg/L)} / 640$$

640 represents correlation factor that obtained via many experimental studies of the correlation between EC and TDS (640 is suitable for most alkaline soils such as our samples on this experimental study at 25 C^0). And it was used to converts EC to TDS contents.

2.6. Determination of moisture content of soil samples

Principles. Soil samples are dried at 105 ± $5C^0$ until mass constancy is reached. The differences in masses before and after drying are a measure for the water content of soils. The water content is calculated on gravimetric (*g* water/*g* soil) or on volumetric basis (cm^3water/cm^3soil). The method described below can be used for disturbed and undisturbed (sampling of soil using coring sieves) soil samples. It is a direct laboratory measurement. The Procedure described can be used for the determination of dry mass on a dry mass basis (ISO 11465 1993) (J.Benton Jones, 2001).

2.6.1. Procedure of moisture content determination

The containers with lids were dried at 105 $C^0$and then cooled with the lids closed in a desiccator for an hour, the mass (m_0) of the closed containers were determined with the sensitive analytical balance, about10g of the air dried sieved (particulates< 2 mm mesh size) pretreated soil were weighed in these containers with a stainless steel spoon. so the mass of the closed containers and soils (m_1) were determined with the accuracy of ±0.1 mg then they were dried in the drying oven at 105 C^0until constant mass is achieved, then they were cooled with the lids closed in a desiccator for 1 hour, the containers were removed from the desiccator and immediately the mass (m_2) of the closed container containing the oven dried soils were determined with the sensitive balance (R. Margesin and F.Schinner, 2005).

Calculation of the water content % (w/w) (W_{H2O}) on a dry mass basis expressed as percentage by mass to an accuracy of 0.01 % (m/m) by the following equation:

$W_{H2o\ \%} = (m_1-m_2/m_1-m_0) * 100$

- With contaminated soil samples, special measures were taken. To avoid any contact with the skin. Special measures also taken during the drying process in order to prevent contamination of the laboratory atmosphere.
- The procedures were performed as quickly as possible to prevent evaporation.

• In general decomposition of organic material can be neglected at temperatures up to $105C^0$ in these kind of less OMCs soil (<10%).

2.7. Determination of roadside soils texture

The amount of sand, silt, and clay in a soil can be determined by several different methods, although all are based on the same basic principle of varying settling velocities due to different particle size in a standing column of water (the principle of sedimentation is known as Stokes' law). This technique is frequently referred to as a "mechanical analysis." Particle separation by varying settling velocity assumes a consistent particle density (2.65 g/cm^3) for all the separates. To separate the individual soil particles adequately, the soil sample is treated with a dispersing agent (a mixture of sodium heximetaphosphate and sodium carbonate - CALGON) and vigorously mixed. Pretreatment of the soil is necessary to remove all particles greater than 2 mm in size (done by sieving), and treatment with hydrogen peroxide (H_2O_2) to oxidize (remove) the organic matter and an acid to remove carbonates may be necessary to enhance particle dispersion (Sheldrick and Wang, 1993). Once the soil sample is dispersed and vigorously mixed, passing the dispersed soil through an ASTM Number 325 (USDA system) sieve will remove all the sand. Passing the dispersed soil through an ASTM Number 80sieve will remove the fine gravel and coarse and medium sand. The particles retained on the sieves are oven-dried and further sieved for Specific particle identification and quantification. These wet sieving procedures, which remove all or a portion of the sand fractions, are not common practices unless a careful detailed textural analysis of the coarser fractions in the soil is required. The next step is to place the dispersed soil in a standing column of water (Genrich and Bremner, 1974) and, at specified time intervals, to remove a separate either by pouring or pipetting (Day, 1965; Gee and Bauder, 1986; Sheldrick and Wang, 1993) or by measuring the changing density of the column of water and dispersed soil with a hydrometer which was firstly used by Bouyoucos, 1962and Day, 1965). The hydrometer method, using the Bouyoucos hydrometer calibrated in g/L, is the most frequently used method because of its ease of operation and adequate results. In 2 h and with two hydrometer readings, the percentage of sand, silt, and clay in a dispersed soil can be determined and the textural class of the soil identified (J.Benton Jones, 2001).

The hydrometer method of silt and clay measurement relies on the effect of particle size on the differential settling velocities within a water column. By this method (using Hydrometer with Bouyoucos scale in g/L) after 40 second all sand-sized particles (0.02 mm and larger) settle out of the suspension and after 4 h, particles larger than clay (0.002 mm) settle out of the suspension.

Theoretically, the particles are assumed to be spherical having a specific density of 2.65 g/cm^3. If all other factors are constant, then the settling velocity is proportional to the square of the radius of the particle (**Stoke's Law**).

$$V = \frac{2\, r^2 \left(P_{dp} - P_{dl}\right) g}{9\, \eta}$$

Where:

-V = Velocity of fall (cm/sec).

-r= "equivalent" radius of the particle (cm).

-ρ_{dp}= Density of particle (g/cm^3), 2.65 is a usual good approximation.

-ρdl = Density of liquid (g/cm3).For water this is ~1.0 .

-g= Acceleration due to gravity (cm/sec), value at the sea level is 981cm S^{-2} .

-η= Viscosity of liquid (g/cm .sec).

In practice, the density of water and its viscosity are both affected by temperature. Therefore, we must know and make corrections for the temperature of the liquid. Greater temperatures result in reduced viscosity due to liquid expansion and a more rapid descent of falling particles (George Estefan et al, 2013).

2.7.1. Procedure of soil texture determination

42 g of air dried treated soil ((< 10 mesh sieved (2mm)) was weighed into a 250 ml beaker, and 100 ml of 5 % SHMP solution was added, stirred and let to stand overnight, then the entire contents of the beaker were transferred into a dispersion cup and it was filled two thirds full with water and placed in the electric stirrer adjusted to speed 8 with range in maximum and mixed for 3 min, the cup was removed and the entire contents were quantitatively transferred into 1000 ml cylinder and diluted to the mark with distilled water. The suspensions were allowed for a period of time to equilibrate thermally, a plunger was inserted into cylinder and the contents were agitated and shaken by dislodge sediment from the bottom using 7 strong upward strokes of plunger and finished stirring with 3 slow and smooth strokes. The Bouyoucos hydrometer is placed into the water-soil slurry. Then after 40 s of the standing, the hydrometer scale reading was measured at the upper edge of the meniscus surrounding the stem, and immediately standard mercury thermometer was placed into the column and the temperature was measured and both the hydrometer and thermometer

measured readings were recorded .Then the cylinder was left to stand undisturbed for 2 hs at that time another hydrometer and temperature readings were made.

A blank hydrometer determination R_L was conducted by taking 100 ml of the 5% SHMP dispersion solution to 1000 ml cylinder and diluted to the mark with distilled water and the hydrometer and thermometer readings were measured and recorded. The calibration value R_L is used to correct for solution viscosity and to correct the soil solution concentration (John .Benton Jones, Jr, 2001).

HR_1 is the hydrometer reading (g /L) after 40 seconds.

HR_2 is the hydrometer reading (g /L) after 2 hours.

$$(\text{Clay + silt})\ \% = \frac{((HR_1 - R_L)+((TC^0 - 19.4) * 0.36))}{\text{Dry weight}} * 100$$

$$\text{Dry weight (g)} = \frac{\text{sample weight}}{100 + MC} * 100$$

MC is the Moisture Content % (m/m)

$$\text{Clay}\ \% = \frac{((HR_2 - R_L) + (TC^0 - 19.4) * 0.36))}{\text{Dry weight}} * 100$$

Silt % = (clay + silt) % - (clay) %

Sand % = 100 - (clay + silt) %

19.4 is the hydrometer calibrated reference Celsius temperature

0.36 is a correction factor of the hydrometer reading according to temperature. Because at every 1 C^0 temperature higher than 19.4 C^0 there is a value equivalent to 0.36 hydrometer unit deviation.

2.8. Determination of heavy metals contents in roadsides topsoil samples

2.8.1. Roadsides topsoils samples preparation

The pretreated samples were allotted with riffle splitter technique (Gerlach, 2002) to obtain a representative samples of a 1 Kg of each roadside soil sample, then they were grounded with the use of electric grinder which was adjusted to give an output of 200 mesh (74 micron), then the grounded samples were sectioned with the paper cone riffle splitter technique to bring the 1Kg sample to an 8 portions each one had 125g subsamples, one of which was chosen randomly to undergo a second round of paper cone riffle splitting in order to transfer that 125g subsample into 8 subsamples, and 4 of them were composed to provide the homogenized representative sample. Then 10g of each homogenized representative samples were weighed in a pre-weighed betri dishes and dried in an oven at 105 C^0 for 5hours cooled in a desiccators and weighed. These were the prepared roadside topsoil samples which used in this study for heavy metals determination (Erika et al, 2005).

2.8.2. Procedure of improved wet digestion method for entire releasing and dissolution of heavy metals from soil samples

For total metals determination, the prepared roadsides top soil samples which mentioned above were subjected to an optimized closed system wet digestion technique, its particles size were less than 0.16mm in order to increase particles surface area to improve the acid digestion process. A mass of 0.5g was weighed in a teflon beaker, 4ml of concentrated nitric acid and 2ml of concentrated hydrofluoric acid were added and the beakers were loosely capped and left to stand overnight at room temperature for initial cold digestion (i e, digestion of organic matter). Cold digestion was found to be necessary to achieve complete digestion and dissolution of all sample constituents except silicates, hence subsequently 10ml of concentrated perchloric acid was added to the mixture, then the teflon beakers were sealed with tightly toughed teflon watch covers and heated on a sand bath at $350C^0$ for 6 hour to reflux the vapours of the acid, until complete digestion was achieved which was indicated by the non-turbid yellow- white solution appearance. Then the solution was evaporated to near dryness. The corners and walls of the beaker were washed with deionized water and filtered by whatman filter paper No-42 into 50ml standard polyethylene flask. The filter paper was washed with small volume(10ml) of 10% (V/V) nitric acid and deionized water and the volume was made up with the deionized water (Yuan et al, 2015) (Elshaikh. Z.A, 2015).

2.8.3. Instrumental conditions of FAAS for the studied heavy metals analysis

The total contents of Pb, Cd, Ni, Cu and Cr were determined in roadside top soils digestion solutions by using computerized Shimadzu AA-6800F atomic absorption spectrophotometer from Shimadzu Corporation, Kyoto, Japan., the instrument conditions were set according to Shimadzau cookbook section 2 (Shimadzu cookbook, 1997) which was adjusted to the best optimized conditions for each analyzed metal concentration for its total content determination in the soil samples and they were as follow

Table (9): Instrumental conditions for Pb analysis

Pb absorbance measurement in the standard and samples solutions	
Instrumental parameter	Optimum corresponding value
Wavelength (nm)	217
Slit width (nm)	1.0
Lamp current (m A)	10
Integration time (s)	5
Flame type	Air-acetylene
Lamp mode	BGC-D_2
Detection limit(ppm)	0.05
Sample introduction system	Pneumatic nebulizer aspiration (8ml min^{-1})
Fuel gas flow rate (L min^{-1})	2

* BGC-D_2: it means background absorption correction with the use of deuterium ultraviolet continuous spectrum lamp.

Table (10): Instrumental conditions for Cd analysis.

Cd absorbance measurement in the standard and samples solutions	
Instrumental parameter	Optimum corresponding value
Wavelength (nm)	228.8
Slit width (nm)	1.0
Lamp current (m A)	8
Integration time (s)	5
Flame type	Air-acetylene
Lamp mode	BGC-D_2

Detection limit(ppm)	0.001
Sample introduction system	Pneumatic nebulizer aspiration (8ml min^{-1})
Fuel gas flow rate (L min^{-1})	1.8

Table (11): Instrumental conditions for Cr analysis.

Cr absorbance measurement in the standard and samples solutions	
Instrumental parameter	Optimum corresponding value
Wavelength (nm)	357.9
Slit width (nm)	0.5
Lamp current (m A)	10
Integration time (s)	5
Flame type	Air-acetylene
Lamp mode	BGC-D_2
Detection limit(ppm)	0.08
Sample introduction system	Pneumatic nebulizer aspiration (8ml min^{-1})
Fuel gas flow rate (L min^{-1})	2.8

Table (12): Instrumental conditions for Ni analysis.

Ni absorbance measurement in the standard and samples solutions	
Instrumental parameter	Optimum corresponding value
Wavelength (nm)	232.0
Slit width (nm)	0.2
Lamp current (m A)	12
Integration time (s)	5
Flame type	Air-acetylene
Lamp mode	BGC-D_2

Detection limit(ppm)	0.01
Sample introduction system	Pneumatic nebulizer aspiration (8ml min^{-1})
Fuel gas flow rate (L min^{-1})	1.6

Table (13): Instrumental conditions for Cu analysis.

Cu absorbance measurement in the standard and samples solutions	
Instrumental parameter	Optimum corresponding value
Wavelength (nm)	324.8
Slit width (nm)	0.5
Lamp current (m A)	6
Integration time (s)	5
Flame type	Air-acetylene
Lamp mode	BGC-D_2
Detection limit (ppm)	0.02
Sample introduction system	Pneumatic nebulizer aspiration (8ml min^{-1})
Fuel gas flow rate (L min^{-1})	1.8

$$\text{mg /kg (metal/sample)} = \frac{\text{mg /L} * 2000}{20}$$

20000 is the conversion weight factor and 20 is the volume factor

Recovery % = observed value *100/certified value

Chapter three

3. Results and discussion

3.1. Roadside top soils samples pH determination result and discussion

Table (14): pH of soil samples

Sample ID	pH value	Temperature C^0
K1	8.12	25.4
K2	7.75	24.6
K3	7.71	24.0
K4	7.86	24.9
O1	7.86	24.8
O2	7.88	24.9
O3	7.78	24.6
O4	8.18	24.7
N1	7.58	25.0
N2	7.93	24.9
N3	8.20	25.0
N4	7.71	24.7

Various categories of soil pH may be described (George Estefan et al, 2013) as follows:-

- Strongly acid (pH < 5.0)
- Moderately to slightly acid (5.0-6.5)
- Neutral (6.5-7.5)
- Moderately alkaline (7.5-8.5), and
- Strongly alkaline (> 8.5)

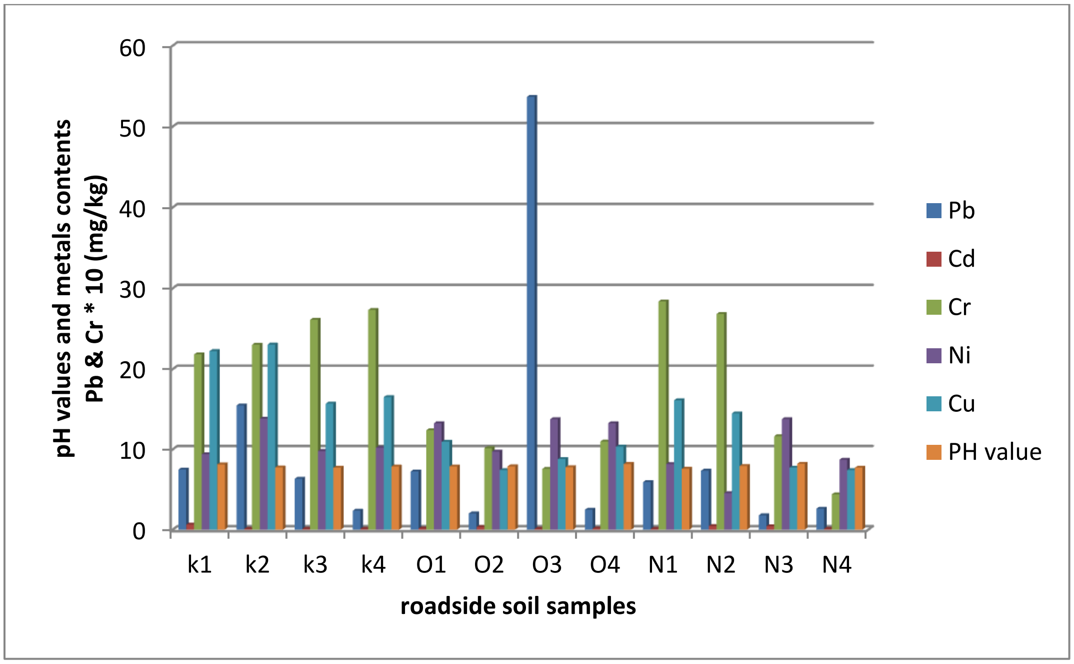


Figure (8): The relation between heavy metal concentrations and the pH values in each roadside soil site sample.

There were no significant variations between the pH values of the studied roadside soils which ranged from 7.58 -8.20 with the mean value of 7.88±01.2. This showed that the sites soils were moderately alkaline in its nature. Alkalinity is usually an inherent characteristic of soils. Metals mobility decreased with increasing pH (8 and above) and this was noticed in K1, O4 and N3 with its some higher metals concentrations, it conforms to literature data (Joseph et al, 2013) they are generally more mobile at pH<7 than at pH >7. The increase of the pH values in the studied sites can occur as the result of organic matter decomposition because mineralization and ammonification processes release OH^- ions and consume H^+. This would decrease the metal mobility and solubility in the roadside soil solution due to the formation of insoluble metal precipitates, complexes and secondary minerals and increase the accumulation rate. It retained more amounts of metals by their species via adsorption or complexation, and that is conforms to the literature values (M.C. Chuan et al, 1996) and that was appeared from the high concentrations of Pb and Cr above the background values, thus it increased the accumulation and immobility of these metals.

3.2. Roadside top soils total organic carbon (T.O.C) and total organic matter contents (T.O.M) determination results and discussion

Table (15): T.O.C % and T.O.M % (w/w) of dry matter contents .

site soil sample	**T.O.C content (%)**	**T.O.M content (%)**
K1	0.918	1.582
K2	2.494	4.299
K3	1.039	1.788
K4	1.317	2.270
O1	1.696	2.923
O2	0.918	1.582
O3	1.796	3.095
O4	1.556	2.682
N1	1.153	1.988
N2	1.895	3.267
N3	1.077	1.857
N4	0.798	1.376

There were significant variation on TOM contents on the samples 1.376-4.299 %, the determinations were within 0.0-9.4% measurement accuracy RSD%, and they had an evident relation with the studied heavy metal concentrations in the roadside soil samples. The results showed that the samples which have the highest contents of organic matter also had the highest heavy metals contents specifically copper and nickel, and those which had the least OMC at the same time had the least metal contents specifically copper and cadmium which were conform with the literature values (Anxiang et al, (2005). This indicates that OMC had significant role to retain heavy metals in roadside soil via adsorption and complexation interactions. it seems that some samples had less OMC than others but higher certain metals may be due to the types of OMC and its humic and fulvic acids contents which are responsible for complexation reactions with metals in roadside soil samples because humic acid decreases the soluble metal complex ratio and fulvic acid increases it. Also the interference with the other contributing factors of soil properties such (TDS) and particle size distribution (texture properties).

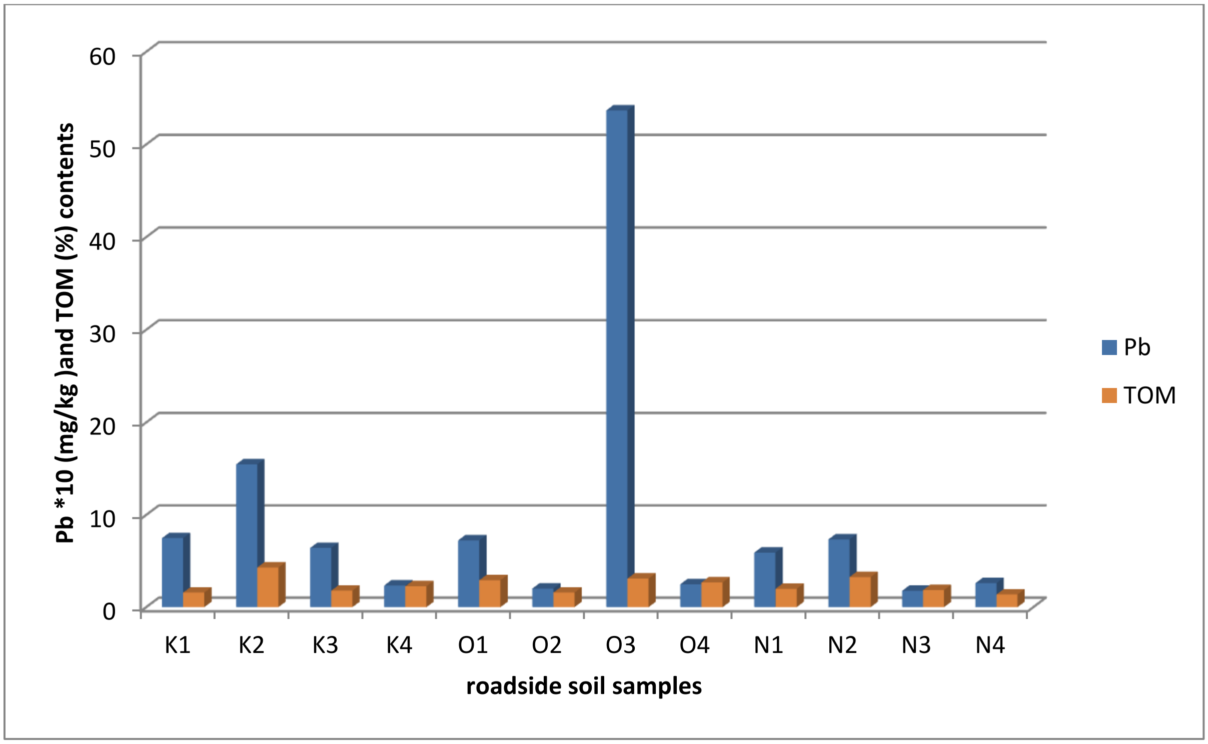


Figure (9): The relation between Pb concentrations and total organic matter contents in each roadside soil site sample.

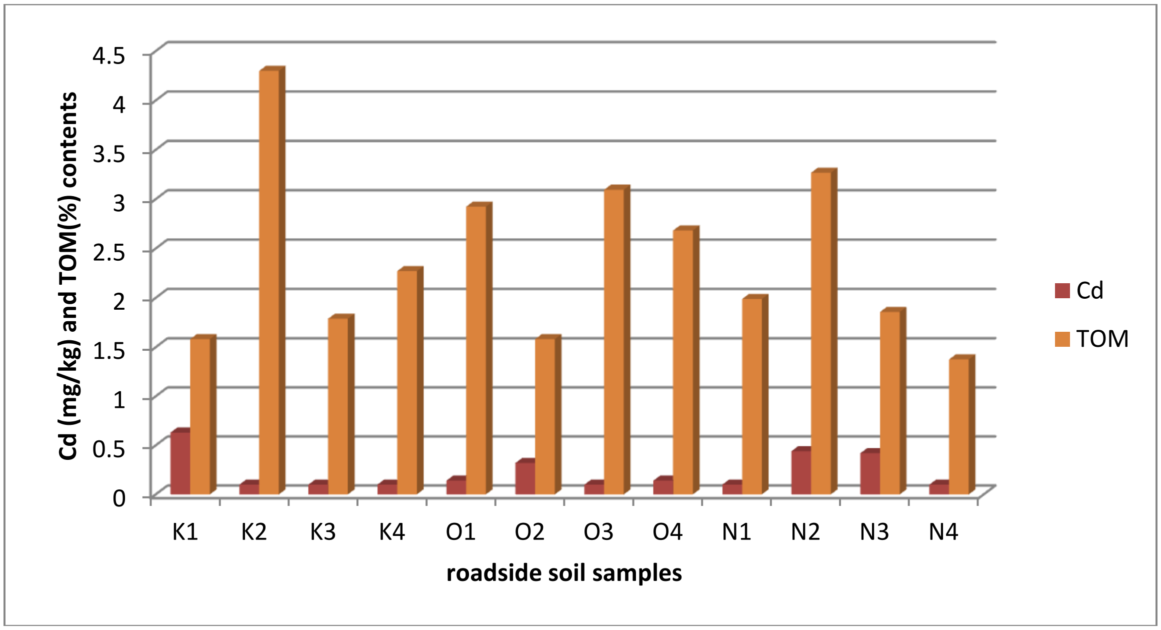


Figure (10): The relation between Cd concentrations and total organic matter contents in each roadside soil site sample.

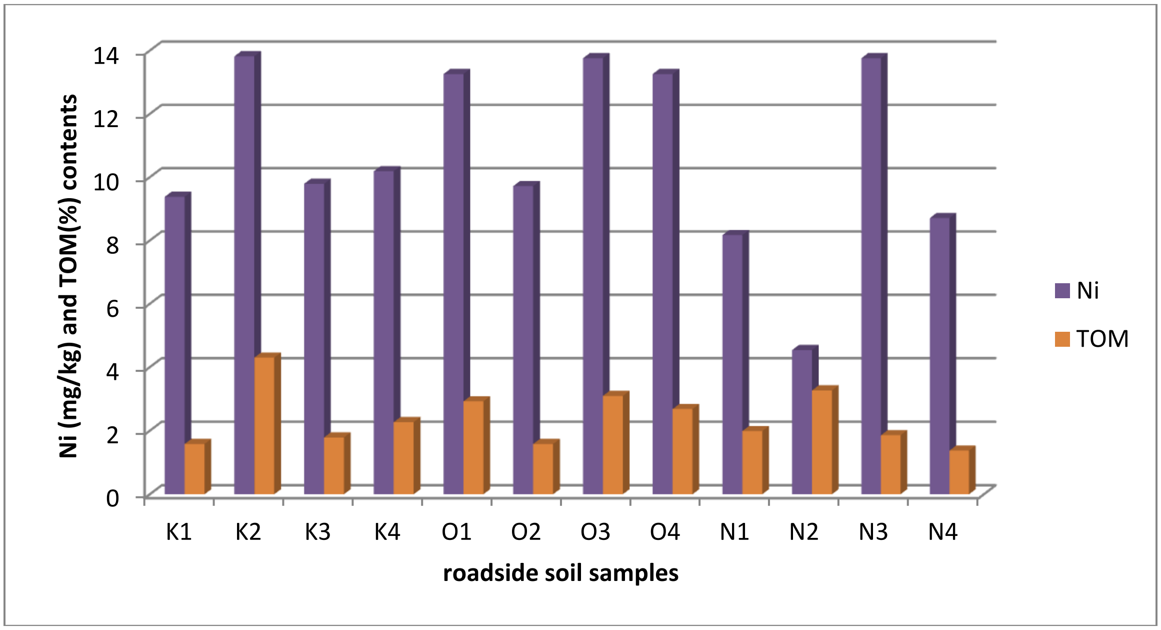


Figure (11): The relation between Ni concentrations and total organic matter contents in each roadside soil site sample.

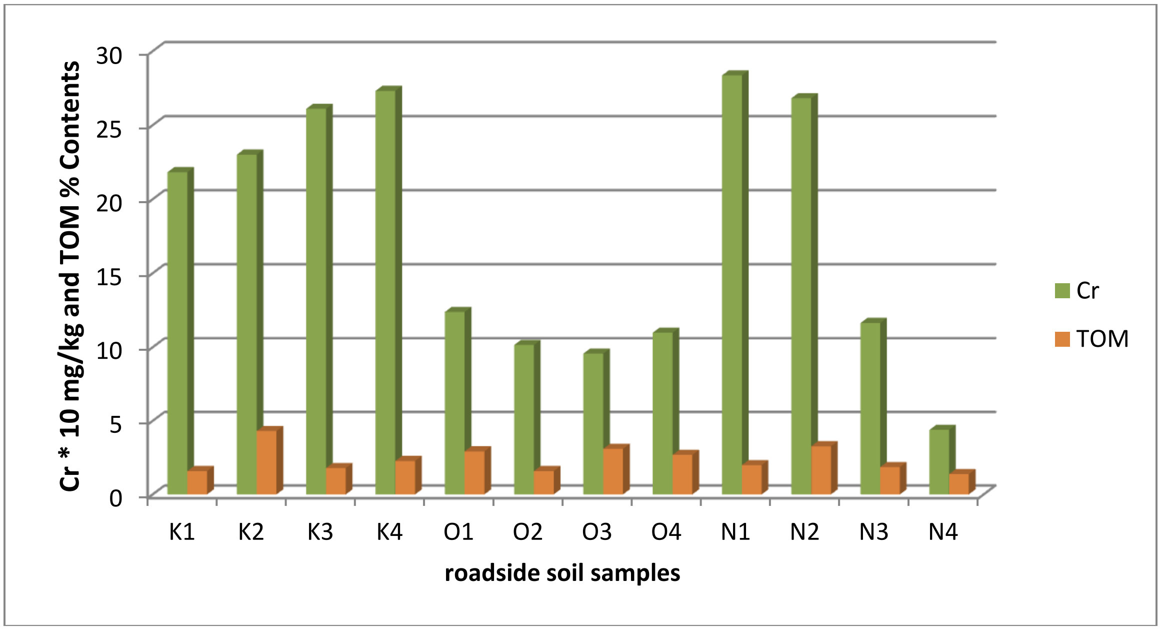


Figure (12): The relation between Cr concentrations and total organic matter contents in each roadside soil site sample.

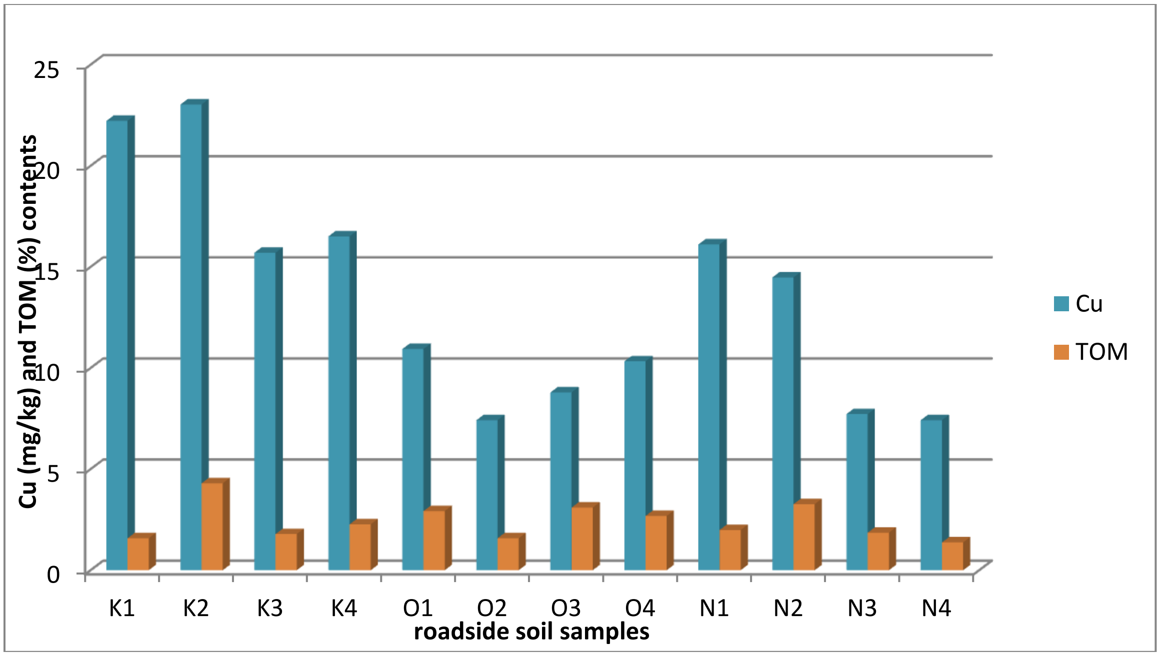


Figure (13): The relation between Cu concentrations and total Organic matter contents in each roadside soil site sample.

3.3. Roadside top soils electrical conductivity (EC) and total dissolved solids content (T.D.S) determination results and discussion.

Table (16): EC and TDS contents of the soils samples results

SOIL SITE SAMPLE	EC R mean (ms cm^{-1})	TDS mean (mg/L)
K1	9.625	6160.00
K2	4.020	2572.00
K3	0.943	603.52
K4	1.419	908.16
O1	3.510	2246.40
O2	3.625	2320.00
O3	4.435	2838.40
O4	3.190	2041.60
N1	5.275	3376.00
N2	1.653	1057.92
N3	1.879	1202.56
N4	1.540	985.60

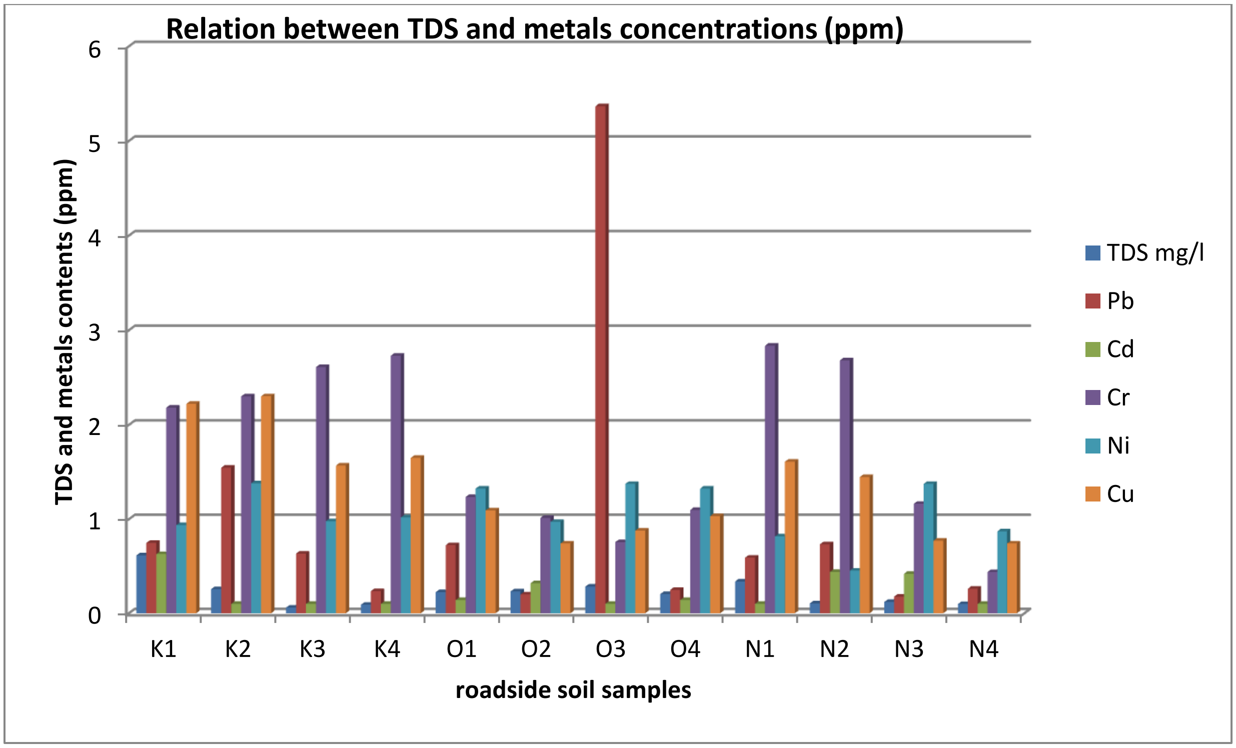


Figure (14): The relation between heavy metal concentrations and the total dissolved solids contents (TDS) in each roadside soil site sample.
Cu*10^{-1}, Cr*10^{-1}, Ni* 10^{-1}, Pb * 10^{-2}, TDS * 10^{-4} (ppm).

The determinations were within 0.0-2.7% of RSD of the measurements. In samples from K1 to K3 as the TDS decreases the Cr concentration increased which similar to the literature results (T. Sherene, 2010). Sample K4 had the same manner of EC related to metals concentrations but there was a little increment than K3 which may be due to the contribution of the other factors like OMC and its types, pH, clay and sand contents. From sample O1 to O4, there was small differencies in EC which led to less differencies in the metals concentrations. The small differiencies were due to the influence of the other facotors of soil properties specially OMC and its HAs and FAs contents because it provide larger variations between the studied soil samples and the very high content of Pb in the O3 site is due to the high traffic activity and it is a main station of transport vehicles. From sample N1 to N4, there was increase in Pb and Cd concentration from N1 to N2 which is compatible with the decrease in the TDS values. From sample N3 to N4 there was a little deviation on TDS values but they provide less metals concentration. This reflects the decreasing in the level of pollution sources due to less traffic activity (away from the metropolis center) in those sites and also their smaller OMC percentages were less than the first N1 and N2 representating samples sites.

3.4. Moisture content of roadside soils pretreated samples results and discussion.

Table (17): Results of the moisture contents determination for soil samples

Site Soil Sample	K1	K2	K3	K4	O1	O2	O3	O4	N1	N2	N3	N4
Moisture content%(m/m)	0.167	0.353	0.120	0.214	0.278	0.153	0.221	0.242	0.411	0.179	0.177	0.198

It was observed that the dryness of the soils increased the mobility of TOM and thus for the studied metals. This conforms to the reported data (Lena and Yan, 2004). There were some relation between the two variables displayed from the results, sample K2 had the highest moisture (0.353%) and the highest TOM (4.299%), and according to Naok et al, dryness would increase colloidal particles interaction forming large particle size thus increasing the filtration effect (Naok et al, 2000).

3.5. Roadside soils texture determination results and discussion

Table (18): Ratios of clay, silt and sand in roadside soils samples results

Sample ID	**Clay %**	**Silt %**	**Sand %**
K1	3.2817	11.0661	85.6522
K2	5.6771	8.6972	85.6257
K3	8.9060	13.4446	77.6494
K4	5.6693	3.9131	90.4176
O_1	5.6729	3.9156	90.4115
O_2	5.6658	1.5261	92.8081
O_3	5.6696	1.5272	92.8032
O_4	8.0575	1.5275	90.4150
N_1	8.0711	3.9208	88.0081
N_2	8.0525	1.5265	90.4210
N_3	10.4375	3.9117	85.6508
N_4	10.4397	8.6838	80.8765

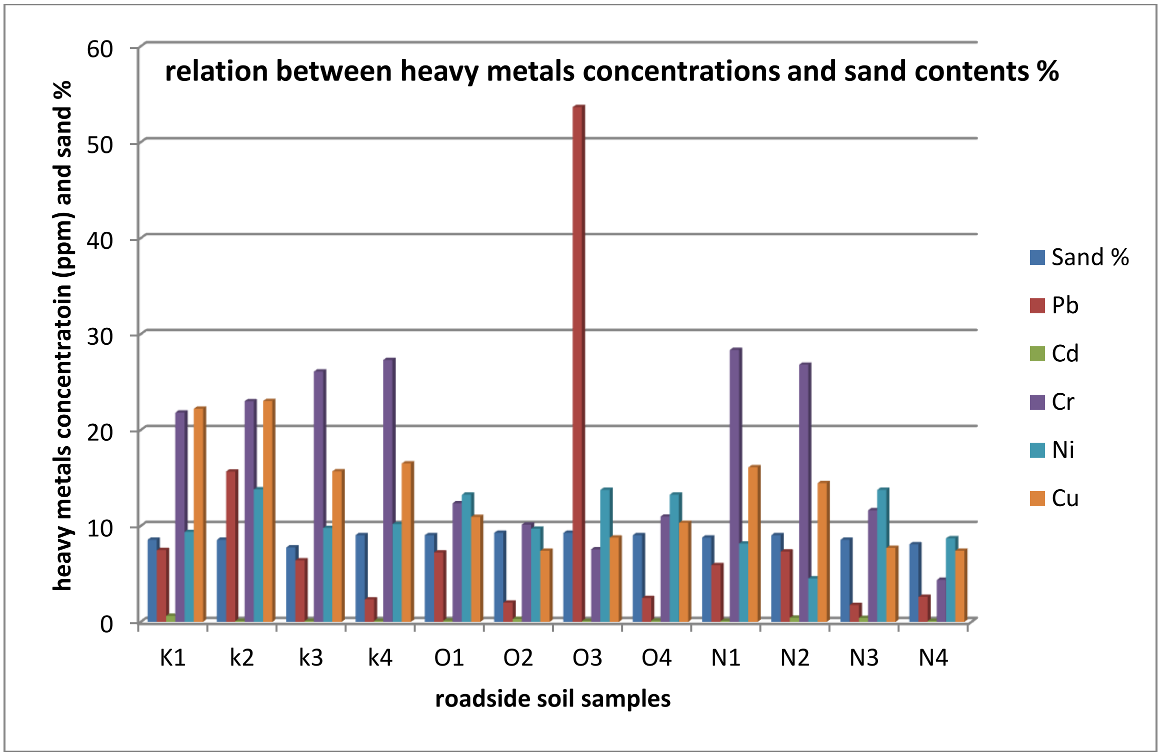


Figure (15): The relation between heavy metal concentrations and the sand % in each roadside soil site sample.

Cu*10^{-1} , Cr*10^{-1} , Ni* 10^{-1} , pb * 10^{-1}(ppm) , sand * 10^{-1} (%) .

The percentage content of sand in sample K1 and K2 are closed to each other and this lead to a similar adsorbed amounts of Cr and Cu on the both sides because as the amount of sand decreases in the roadside soil the amount of adsorbed contaminant metals increase on the other smaller clay portion species which have much more surface area and adsorption forces. The other metals Pb and Ni were higher in sample k2 because it had larger clay concentration, the higher concentration of Cd in K1was due to the higher pH value because alkalinity restrict Cd movement more much than other metals (T. Sherene, 2010), also the variation on the EC values between the two soil sites and the vehicle emissions level could lead to accumulate more amount of Cd in K1 than k2. In the k3 and k4 Pb obey the rule exactly by its high value on k3 compared to K4 because the latter had less clay and more sand percentage contents, from O1 to O4 all sites had high and quite closed values of clay and sand percentage, so its effect on metals adsorption was similar, however the displayed variations in the metals concentrations was due to the traffic density and OMC and EC of each site soil. From N1 to N4 it was concluded that N2 had slightly less value of the clay content than N1 so it had less values of Cr, Cu and Ni. We conclude previously that N4 had less OMC, EC and TDS values, and here also it had least value of sand and largest value of clay percentages, although it had the lowest level of the five heavy metals, this indicate that the level of the contamination source at this site is the least one because it is located far away from the commercial area and metropolis center. Sand form the predominant fraction of particle size distribution in soils, it ranged from 30-100% whereas silt and clay fractions ranged from 0.00-45.8 and 0.00-30% respectively. The results of this study were conforms with the normal range (C.M.A. Iwegbue et, al 2006). Despite the light alkalinity which might restrict the metals movement especially Cd, the presence of DOM, high content of sand with its suitable permeability specially for Cd, and quite low OMC, all of them could lead to increase of mobility of heavy metals species in studied soil sites (T. Sherene, 2010), (M.B.Ogundiran et al, 2015). Also it could accumulate some of it in the inner layers of Khartoum state soils or even reach the ground water by rain session water leaching.

The differences between the sites of the three studied roadsides were due to its soil properties variations, kind and number of vehicles in these roads, geological nature, historical of the past period, surface structure roughness and traffic volume of each one of them.

3.6. Determination of heavy metals (Pb, Cd, Ni, Cu and Cr) in the roadside top soils samples results and discussion.

Table (19): Validation of the proposed method for determination of roadside topsoils samples against certified reference values (mg/kg) content.

Determined metal	Observed value (mg/kg)	Certified value (mg/kg)	95% confidence interval (mg/kg)	Recovery %
Pb	63.72	60.0	55 - 71	106.20
Cd	1.54	1.3	1.1 - 2.7	118.64
Cr	61.39	60.0	49 - 74	102.31
Ni	23.87	26.0	21 - 37	91.80
Cu	10.29	11.0	9 - 13	93.54

3.6.1. Experimental quality control of the metals determinations

Series of standard solutions were used to calibrate the analytical procedure, the standard stock solutions were diluted to multilevel standards solutions with the same blank acids mixture ratios for all the measured metals to minimize the physical interference error effects, calibration curves were prepared for each of the metals investigated by least square fitting, correlation coefficients (r) were better than 0.999 (0.9996 , 0.9997, 0.9996 , 0.9998, 0.9991) for Pb, Cr, Cd, Cu and Ni respectively. In addition plank samples were run simultaneously as a signal obtained using the reagents for all the determinations with background correction lamp mode to remove the deviations of the measurements. Beside blanks, certified standard reference material soil-7 was used to assess the accuracy of the method, the results were checked by using Shimadzu AA-6800 wizard software. The accuracy is within 95% confidence interval values for the measured heavy metals, and the analytical precision measured as the relative standard deviation which gave RSD% < 5% .

Table (20): Results of the heavy metals contents in top soils sites.

	Total heavy metal contents (mg / Kg)				
Sample ID	**Pb**	**Cd**	**Cr**	**Ni**	**Cu**
K1	74.85	0.63	218.21	9.38	22.22
K2	154.68	ND*	230.10	13.82	23.03
K3	63.42	ND	261.01	9.79	15.70
K4	23.50	ND	273.11	10.19	16.51
O1	72.44	0.14	123.75	13.26	10.94
O2	20.11	0.32	101.49	9.72	7.42
O3	536.65	ND	75.72	13.76	8.79
O4	24.87	0.14	109.80	13.26	10.33
N1	59.15	ND	283.60	8.17	16.11
N2	73.40	0.44	268.15	4.54	14.48
N3	17.74	0.42	116.37	13.76	7.72
N4	26.06	ND	43.82	8.71	7.42
B*	20.51	ND	54.42	33.72	17.12

B* represents background sample from assumed uncontaminated soil zone.

ND* represents Not Detectable by the used instrument condition (C< 0.1 mg/ kg).

The Pb levels in the study ranged within 20.11-536.65 μg/g, which is conclude that there are low to high levels of Pb pollution in these sites because the reported level values are 25-1198 μg/g in England , 0.0-50.1μg/g in India, 47-151 μg/g in Lagos, Nigeria (O.J.Achadu, 2015). This indicates that most of the roadside soil sites are polluted with lead. N3 is the only one site that was not polluted with Pb, whilst O_2 and K_4 were the less polluted soil sites with lead and this is consistent with its lowest TOM contents.

According to the background value the four soil sites of the Sahafa Asphalt street are polluted with Pb especially K2 which is across zone and this is conforms to the literature values (E.S.Abechi, 2010). On Arbaeen street except O_2 all other sites are polluted with Pb specifically O_3 which is a very old station site and positioned near automobiles repairing garage so there was more wearing specially from brake pads. On Mauna Street except N3 the other three sites are polluted with Pb specifically N1and N2 which is consists with their large traffic density and more near to the metropolis.

The Cd level ranged within less than ND to 0.63μg/g inferring that there are moderately to considerably levels of Cd contamination in the studied sites comparison with the reported level values which are 4.2 μg/g on a roadside soil in London, 0.15-5.3 μg/g in Wukari , Nigeria (O.J.Achadu , 2015). This refers that most of the roadside soils sites are less polluted with Cd compared to Pb and Cr, the presence of contamination sites specifically K1 this as a result of lubricating oils and/or old tires that are frequently used because the rough surface in this site would increase the wearing of tire rubbers and vehicle components as the result of stop- start traffic patterns and this is conforms with literature data (E.S. Abechi et al, 2010) (Joseph clement et al, 2013).

According to the background value, from the four sites of Sahafa Zalat street only the K_1 is polluted with Cd. This may be due to the old and bad road surface structure and engine oil consumption; this conforms to the literature value (O. J. Achadu, 2015). On Arbaeen Street except O_3 all the sites are polluted with values conformable with the literate value (O. J. Achadu, 2015). On Mauna street N2 and N3 are polluted with similar values, while N_1 and N_4 are not contaminated with Cd because N1 had higher TDS value and N4 is far away from the busy traffic activity.

The Cr level ranged within 43.82-218.21 μg/g which indicates the high level of pollution in most the sites which was higher than the toxic level in soil (50μg/g) (Ahmed Osman and Omer Ibrahim, 2013), which is very close to the background value in this study (54.42 μg/g). All the soil sites were polluted with Cr in the three studied roads except N4. Sahafa Zalat is found to be the more polluted road. This indicates a high level of Cr in brake pads and tire rubbers or the asphalt of the road itself because those are the main pollution sources in roadside top soils for Cr according to (David and David, 2012), (Fan Zhang et al, 2012).

The Ni level ranged (4.54-13.82μg/g) which indicates clearly that all the three roadside soils are not contaminated with Ni compared to the background value 33.62 μg /g. This high value might be due to the chemical nature and geological structure or past usage of the background side or attributed to the rain season. Ni is usually found in soil in concentration range (5-500 μg /g) (EPA, 1983) and so, these values on this study are similar to some literate reported values and less than some other one, the background level value (Joseph et al, 2013) (David and David, 2012). Although the obtained values were less than background level value, they were higher than the lowest concentrations reported in Lagos 0.94 mg/kg, United States 2.44 mg/kg, Poland 2mg/kg (David and David, 2013) so It may indicate some accumulation risk of these heavy metals.

The Cu level ranged (7.42-23.02 μg/g). There were only two samples their Cu concentration was higher than the background value (17.12μg /g), the two clearly contaminated sites were located in Sahafa Zalat street (K1and K2) because K1 had higher pH value and K2 had higher OMC, this indicates that the road was partially polluted with Cu and consistent with the values of North Wales and lower than the values of Amman, Auckland and Hong Kong (Qasem. M. Jaradate et al, 1999). The other two roads were not polluted surface soil, the background value was near that found in Amman. according to Jaradate et al, Cu is derived from engine wear, thrust bearings, bushing and bearing metals (Qasem.M. Jaradate et al, 1999) and this conforms to the stop and go traffic pattern due to the cross position of these polluted sites with Cu in this study. The average concentration in natural soil is 30 μg/g of Cu, the normal range (2-100) μg/g of Cu (EPA, 1983). (1.2-150.7 μg/g) for soils of England and Wales (Ahmed Usman and Umar Ibrahim, 2013).

3.7. Assessment of the roadside soils heavy metal contamination

The commonly used pollution indices were classified into two types:-

(i) Single indices.

(ii) Integrated indices in an algorithm point of view.

Single indices are indicators used to calculate only one metal contamination which include contamination factor (CF), ecological risk factor (ER) and index of geo-accumulation (I geo) as single indices. The pollution load index (PLI) and the degree of contamination (DC) and the potential ecological risk Index (RI) as integrated indices are indicators used to calculate more than on metal contamination.

Contamination factor (CF) and pollution load index (PLI)

The level of contamination can be expressed by contamination factor (CF). The CF is a ratio obtained by dividing the concentration of each metal in the contaminated soil by the baseline or background value. The background value corresponds to the baseline concentrations and is based in element abundances in sedimentary rocks (shale) (Abdolhossein .H et al, 2012).

CF = Cm sample / Cm baseline or background value

Where the contamination factor $CF < 1$referes to low contamination;

$1 < CF < 3$ means moderate contamination; 3 <- CF <- 6 indicates considerable contamination, and $CF > 6$ indicates very high contamination.

The PLI proposed by Tomlinson et al (1980) provide some understanding to the public of the area about the quantity of a component in the environment, it is aimed at providing a measure of the degree of overall contamination at a sampling site. The PLI of a single site is the nth root of n number of multiplied together contamination factor CF values (O.J.Achadu et al, 2015).

$PLI = (CF1* CF2*CF3*.....*CFn)^{1/n}$

Where n is the number of metal studies (five metals at this study) and CF is the calculated contamination factor.

PLI provide comparative means of assessing a site quality. Where a value of $PLI <1$ denotes perfection , a value of one indicates the presence of only baseline levels of pollutants and values above one will indicates progressive deterioration of the site and estuarine quality, The PLI value > 1 is polluted whereas PLI value < 1 indicates no pollution(O.J.Achadu et al, 2015).

Degree of contamination (DC)

Another index that can be derived from the CF values is the degree of contamination (DC) defined as the sum of all contamination factors for a given site:

$$DC = \sum_{1}^{n} CF$$

Where CF is the single contamination factor, and n is the count of the elements present. DC values less than n would indicate low degree of contamination; $n \leq Dc < 2n$, moderate degree of contamination; $2n \leq DC < 4n$, considerable degree of contamination; and $Dc > 4n$, very high degree of contamination.

* For the description of the degree of contamination in the study area the following terminologies have been used: $Dc < 5$ low degree of contamination; $5 < Dc < 10$ moderate degree of contamination; $10 \leq DC < 20$ considerable degree of contamination; $DC > 20$ very high degree of contamination. Where n=5 which the count of the studied heavy metals.

Table (21): Contamination factor (CF), degree of contamination (DC) and pollution load index (PLI) for the determined heavy metals in roadside top soils samples.

	CF					DC	PLI
Sample ID	Pb	Cd	Cr	Ni	Cu		
K1	3.65	6.30	4.01	0.28	1.30	15.54	2.02
K2	7.54	1.00	4.23	0.41	1.35	14.53	1.78

K3	3.09	1.00	4.78	0.23	0.92	10.02	1.26
K4	1.15	1.00	5.02	0.30	0.96	8.43	1.11
O1	3.53	1.4	2.27	0.39	0.64	8.23	1.23
O2	0.98	3.2	1.86	0.29	0.43	6.76	0.94
O3	26.17	1.00	1.76	0.41	0.51	29.85	1.57
O4	1.21	1.4	2.02	0.39	0.60	5.62	0.95
N1	2.88	1.00	5.21	0.24	0.94	10.27	1.28
N2	3.58	4.4	4.93	0.13	0.85	13.89	1.54
N3	0.86	4.2	2.14	0.41	0.45	8.06	1.07
N4	1.27	1.00	0.81	0.26	0.43	3.77	0.65

Index of geo-accumulation

Index of Geo-accumulation (Igeo) has been used widely to define and determine the presence of metal contamination or pollution in terrestrial, aquatic and marine environment. The Igeo of a metal in soil can be calculated with the following formula:

$$Igeo = \log 2 C_{metal}/1.5\ C_{metal\ (background)}$$

Where C_{metal} is the concentration of the heavy metal in the enriched sample and $C_{metal(background)}$ is the concentration of the metal in the unpolluted or control sample. The factor 1.5 is introduced to minimize the effect of the possible variations in the background or control values which may be attributed to lithogenic variations in the sediment. The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as follows

$Igeo < 0$ = means unpolluted.

$0 \leq Igeo < 1$ means unpolluted to moderately polluted.

$1 \leq Igeo < 2$ means moderately polluted.

$2 \leq Igeo < 3$ means moderately to strongly polluted.

$3 \leq Igeo < 4$ means strongly polluted.

$4 \leq$ Igeo < 5 means strongly to very strongly polluted.

Igeo ≥ 5 means very strongly polluted.

Ecological risk factor

An ecological risk factor (Er) is used to quantitatively express the potential ecological risk of a given contaminant which suggested by Håkanson .L ,1980).

$$Er = Tr \times CF$$

Where Tr is the toxic-response factor for a given substance, and CF is the contamination factor. The Tr values of heavy metals suggested by Håkanson (Hakanson. L, 1980). The Tr values of Pb, Cd, Cr, Ni and Cu are 5, 30, 2, 3, and 5, respectively. The following terminologies are used to describe the risk factor: $Er < 40$, low potential ecological risk; $40 \leq Er < 80$, moderate potential ecological risk; $80 \leq Er < 160$, considerable potential ecological risk; $160 \leq Er < 320$, high potential ecological risk; and $Er \geq 320$, very high ecological risk.

The potential ecological risk (RI) of the heavy metals is quantitatively evaluated by the potential ecological risk index (Er) (Håkanson . L, 1980;) which takes into account both contamination factor (CF), and the "toxic-response" factor.

The potential ecological risk values obtained were compared with categories grade of Er and RI of metal pollution risk on the environment . The potential ecological risk index (RI) was in the same manner as degree of contamination defined as the sum of the risk factors.

$$RI = \sum_{1}^{n} Er$$

Where Er is the single index of ecological risk factor, and n is the count of the heavy metal species. The following terminology was used for the potential ecological risk index: RI < 150, low ecological risk; 150 ≤ RI < 300, moderate ecological risk; 300 ≤ RI < 600, considerable ecological risk; and RI > 600, very high ecological risk (Håkanson.L, 1980). Where, Er and RI denote the potential ecological risk factor of individual and multiple metals, respectively.

Table (22): Index of geoaccumalation (Igeo) for the determined heavy metals in roadside topsoils samples.

	Igeo				
Sample ID	Pb	Cd	Cr	Ni	Cu
K1	0.89	0.92	0.73	-0.43	0.24
K2	1.00	0.12	0.75	-0.26	0.25
K3	0.62	0.12	0.81	-0.4	0.09
K4	0.18	0.12	0.83	-0.39	0.11
O1	0.67	0.27	0.48	-0.28	-0.07
O2	0.12	0.63	0.4	-0.42	-0.24
O3	1.54	0.12	0.37	-0.26	-0.16
O4	0.21	0.27	0.43	-0.28	-0.09
N1	0.58	0.12	0.84	-0.49	0.10
N2	0.68	0.77	0.82	-0.75	0.05
N3	0.06	0.75	0.46	-0.26	-0.22
N4	0.23	0.12	0.03	-0.49	-0.24

Table (23): Ecological Risk factor (Er), and potential ecological risk index (RI) for the determined heavy metals in roadside top soils samples.

	Er					RI
Sample ID	Pb	Cd	Cr	Ni	Cu	
K1	18.85	18.9	8.02	0.84	6.50	53.11
K2	37.77	30.0	8.46	1.23	6.75	84.39
K3	15.45	30.0	9.56	0.69	4.60	60.30
K4	5.75	30.0	10.04	0.90	0.96	47.65
O1	17.65	42.0	4.54	1.17	4.80	70.16
O2	4.90	96.0	3.72	0.29	2.15	107.06

O3	130.15	30.0	3.52	0.87	2.55	167.09
O4	6.05	42.0	4.04	1.17	3.00	56.26
N1	14.40	30.0	10.42	0.72	4.70	60.24
N2	17.90	132.0	9.86	0.39	4.25	164.40
N3	4.30	126.0	4.28	1.23	2.25	138.06
N4	6.35	30.0	1.62	0.78	2.15	40.90

3.8. Conclusion and Recommendations

12 roadside soil samples from three major roads in Khartoum state were analyzed by improved wet digestion method followed by atomic absorption spectrometry measurements. This used method gave good analytes recoveries and calibration curves linearity, contamination judgment sample which was taken from a suburban area was used as a background control sample to assess the pollution level by heavy metals Pb, Cr, Cd, Cu, and Ni. The results showed that there are moderate to considerable level of contamination by Pb and Cr in all the sites except N3 and N4. O3 is very highly contaminated site with Pb (536.65 µg /g) which is too much higher than the background value (20.51µg/g). O1 and O4 are moderately contaminated by Cd but O2, N2 and N3 are considerably contaminated and K1 is very high contaminated site by Cd (CF is 6.3). Nonetheless the runoff, rain and anthropogenic activities could lead to the leaching of these metals to adjacent runlets and streams and potable water sources which would eventually find their way into the food chain by the bioaccumulations. K1 and K2 are the only moderately contaminated sites with Cu, No contamination detected for Ni in all the roads sampling sites. Ditto N4 is the least contaminated roadside site with these heavy metals, because it was

somewhat away from the city centre. The trend in the accumulation and contamination with these heavy metals were Ni < Cu < Cd < Pb and Cr.

pH, TOM, TDS and soil texture were determined with the more accurate and precise methods, and their values were related to the heavy metal contents in each site sample. The pH values ranged from 7.58-8.2 which were moderately alkaline for all the sites soils, so it will increase the adsorption rate of metals and decrease its solubility, toxicity and migration down the soil profile. OMC were ranged 1.376-4.299%, its values were different among the sampling sites, which had a positive direct relation with the metals contents due to the complexation with metals that gave undissolved species. The TDS values were significantly different across all the sampling points 603.52-6160 ppm, it had some negative relation with the studied metals concentrations. The soil texture had quite relation with metals hence the samples which had similar contents of sand, clay and silt with the predominant sand portion in all the sites soils (77.6494-92.8032 %), which was led to give near amounts of some metals contents, the considerable variations in metal concentrations were due to the clay variation contents with interfering contributing factors that affect metals mobility and adsorption in soils such as TOM and TDS contents.

-Recommendations

1/ More studies should be conducted on Zn, Fe, Mn and As with a chemical speciation to determine the chemical species of those heavy metals with different depth layers down the roadside topsoils in the state to estimate their bioavailability in the environment.

2 / Fuels with low heavy metals contents, biodiesel or electric energy, with particulates and gases filters in the vehicles design technology for manufacturers and exporters should be encouraged.

3/ All these metals are used in parts of motor vehicles that are subjected to wear, and to reduce the source of these heavy metals in streets environments, very old cars shouldn’t be used as well to establish broad roads, also streets should be initiated with low metal contents asphalt and acceptable infrastructure, old surfaces should be coated with low metal content bitumen and asphalt to be soft so it lessen the wear of vehicles parts.

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Appendixes

Appendix (1) Results of titrant volumes and T.O.C and T.O.M contents and RSD %.

Sample ID	Volume1(ml)	Volume2(ml)	Average volume (ml)	T.O.C content (%)	T.O.M content (%)	RSD%
BLANK SOLUTION	2.50	2.50	2.50	-	-	
K1	1.30	1.40	1.35	0.918	1.582	5.2
K2	1.20	1.30	1.25	2.494	4.299	5.6
K3	1.20	1.20	1.20	1.037	1.788	0.0
K4	0.80	0.90	0.85	1.317	2.270	8.2
O1	0.40	0.35	0.375	1.696	2.923	9.4
O2	1.40	1.30	1.35	0.918	1.582	5.2
O3	0.25	0.25	0.25	1.796	3.095	0.0
O4	0.55	0.55	0.55	1.556	2.682	0.0
N1	1.05	1.10	1.06	1.153	1.988	3.3
N2	1.50	1.60	1.55	1.895	3.267	4.5
N3	1.10	1.20	1.15	1.077	1.857	6.2
N4	1.50	1.50	1.50	0.798	1.376	0.0

Appendix (2) Results of EC values and calculated TDS content and RSD%.

Sample ID	EC R1 (ms cm^{-1})	EC R2 (ms cm^{-1})	EC R average (ms cm^{-1})	TDS (mg/L)	RSD%
K1	9.620	9.630	9.625	6160.00	0.07
K2	4.030	4.010	4.020	2572.00	0.19
K3	0.943	0.943	0.943	603.52	0.00
K4	1.438	1.399	1.419	908.16	1.9
O1	3.580	3.440	3.510	2246.40	2.8
O2	3.620	3.630	3.625	2320.00	0.19
O3	4.520	4.350	4.435	2838.40	2.7
O4	3.180	3.200	3.190	2041.60	0.44
N1	5.290	5.260	5.275	3376.00	0.4
N2	1.645	1.661	1.653	1057.92	0.68
N3	1.880	1.877	1.879	1202.56	0.11
N4	1.538	1.542	1.540	985.60	0.18

Appendix (3) Results of the soil moisture contents determination

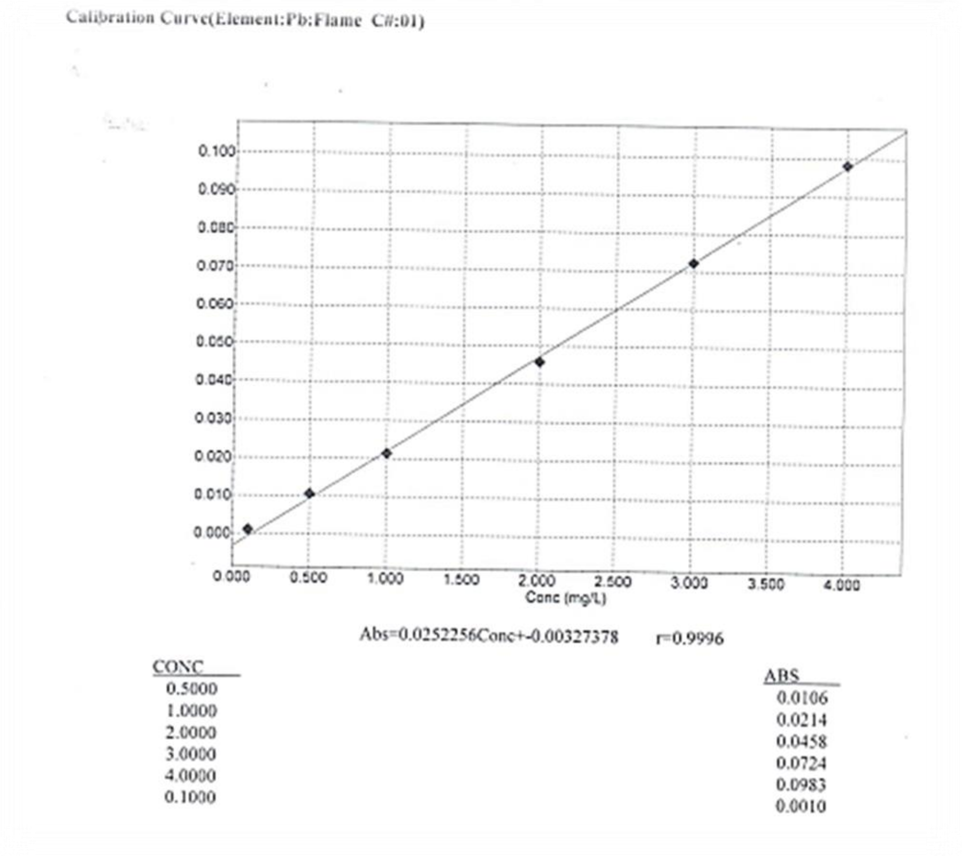
Sample ID	**Mass of empty container m_0(g)**	**Mass of sample (g)**	**Mass of empty container and sample m_1(g)**	**Mass of container and sample after drying m_2(g)**	**Moisture content %(m/m)**
S1	34.8481	10.0015	44.8496	44.8329	0.167
S2	35.6765	10.0009	45.6774	45.6421	0.353
S3	34.9436	10.0011	44.9447	44.9327	0.120
S4	35.7660	10.0008	45.7668	45.7454	0.214
O1	34.9664	10.0007	44.9671	44.9393	0.278
O2	34.8754	10.0011	44.8765	44.8612	0.153
O3	36.0836	10.0005	46.0841	46.0620	0.221
O4	35.3470	10.0003	45.3473	45.3231	0.242
N1	34.8610	10.0004	44.8614	44.8203	0.411
N2	36.0436	10.0007	46.0443	46.0264	0.179
N3	34.1974	10.0008	44.1982	44.1805	0.177
N4	36.2955	10.0008	46.2963	46.2759	0.198

Appendix (4) Results of Soil texture Determination

Sample ID	**H $R_{1(g/l)}$**	**T C^0**	**H $R_{2(g/l)}$**	**T C^0**
Blank	0	25	0	26
S1	4	25	-1	26
S2	4	25	0	26
S3	7	26	1	27
S4	2	25	0	26
O1	2	25	0	26
O2	1	25	0	26

O3	1	25	0	26
O4	2	25	1	26
N1	3	25	1	26
N2	2	25	1	26
N3	4	25	2	26
N4	6	25	2	26

Appendix (5) multilevel calibration Curve of the Lead measurement results

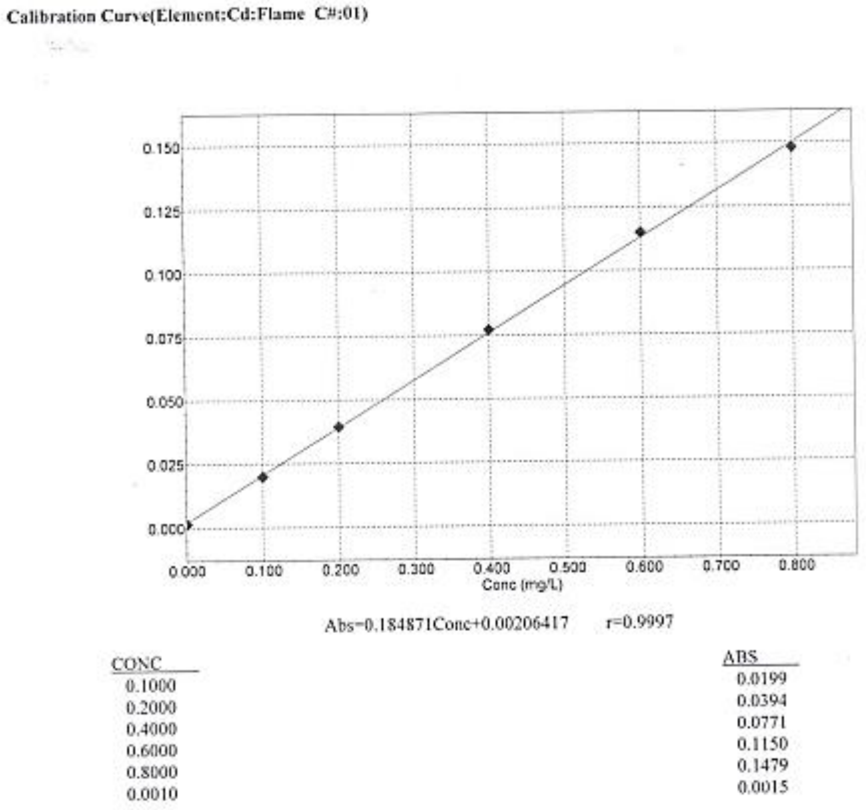


Calibration Curve(Element:Pb:Flame C#:01)

Abs=0.0252256Conc+-0.00327378 r=0.9996

CONC	ABS
0.5000	0.0106
1.0000	0.0214
2.0000	0.0458
3.0000	0.0724
4.0000	0.0983
0.1000	0.0010

Appendix (6) multilevel calibration Curve of the Cadmium measurement results

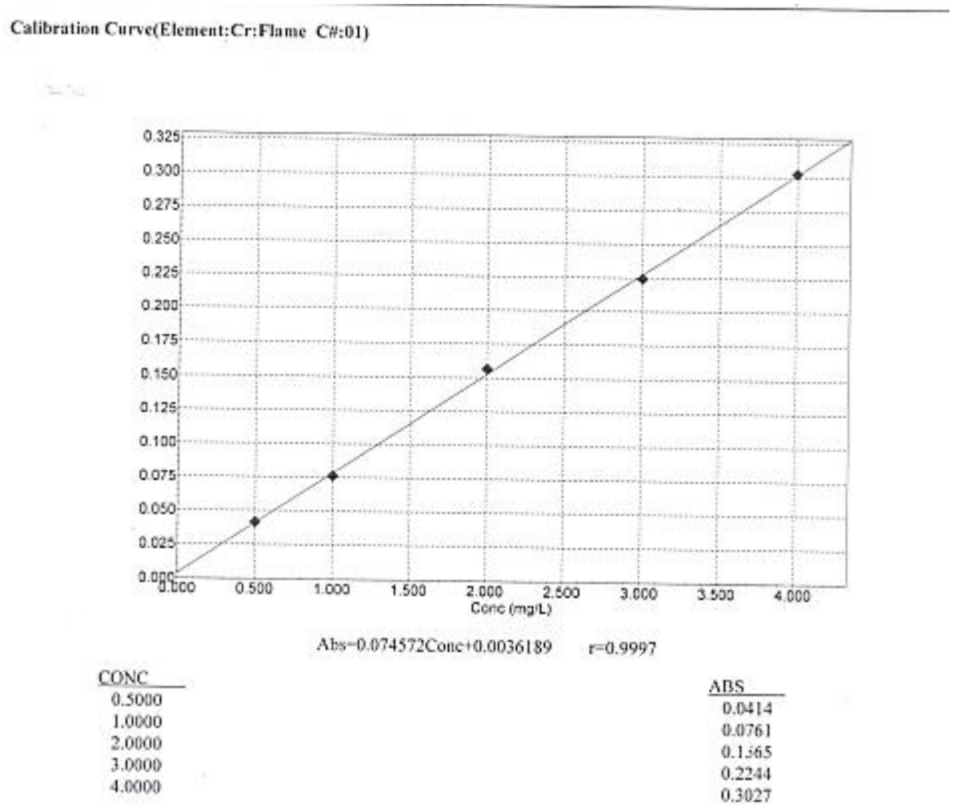


Calibration Curve(Element:Cd:Flame C#:01)

Abs=0.184871Conc+0.00206417 r=0.9997

CONC	ABS
0.1000	0.0199
0.2000	0.0394
0.4000	0.0771
0.6000	0.1150
0.8000	0.1479
0.0010	0.0015

Appendix (7) multilevel calibration Curve of the Chromium measurement results



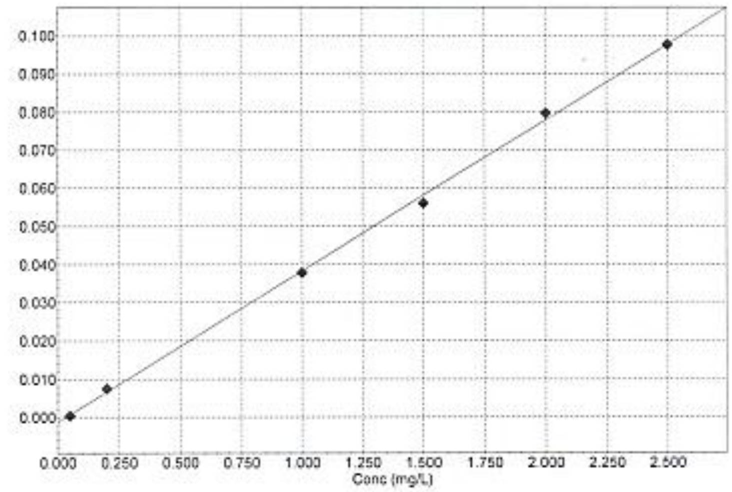
Calibration Curve(Element:Cr:Flame C#:01)

Abs=0.074572Conc+0.0036189 r=0.9997

CONC	ABS
0.5000	0.0414
1.0000	0.0761
2.0000	0.1565
3.0000	0.2244
4.0000	0.3027

Appendix (8) multilevel calibration Curve of the Nickel measurement results

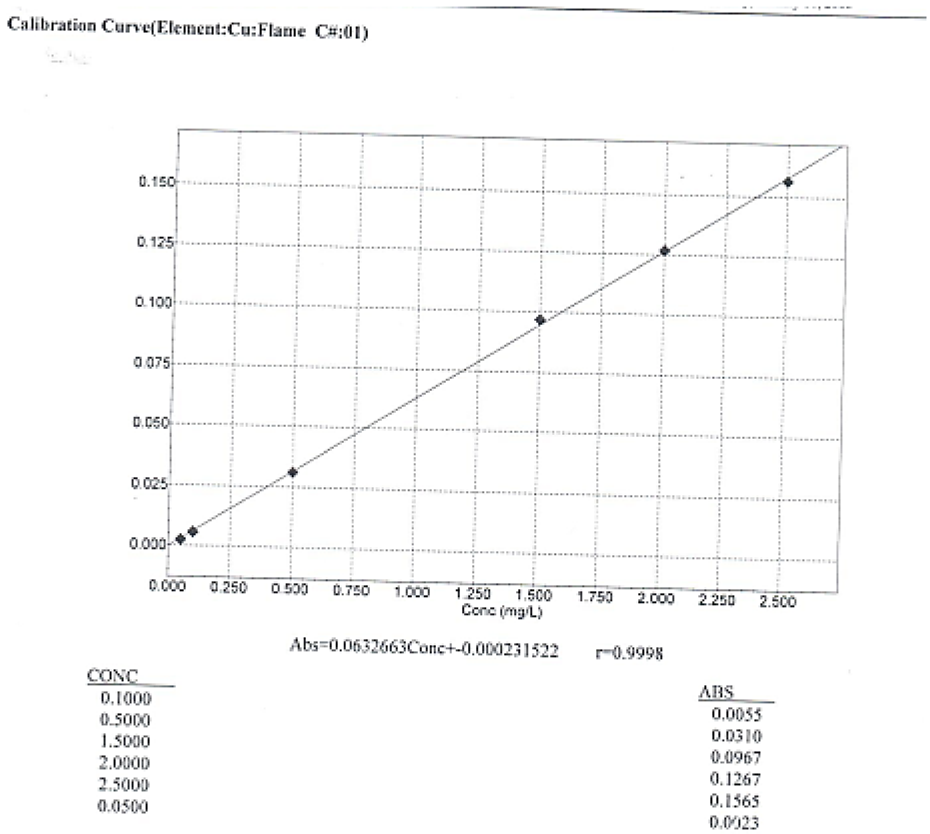
Calibration Curve(Element:Ni:Flame C#:01)



Abs=0.0395895Conc+-0.00124893 r=0.9991

CONC	ABS
0.2000	0.0075
1.0000	0.0379
1.5000	0.0560
2.0000	0.0797
2.5000	0.0977
0.0500	0.0004

Appendix (9) multilevel calibration Curve of the Copper measurement results

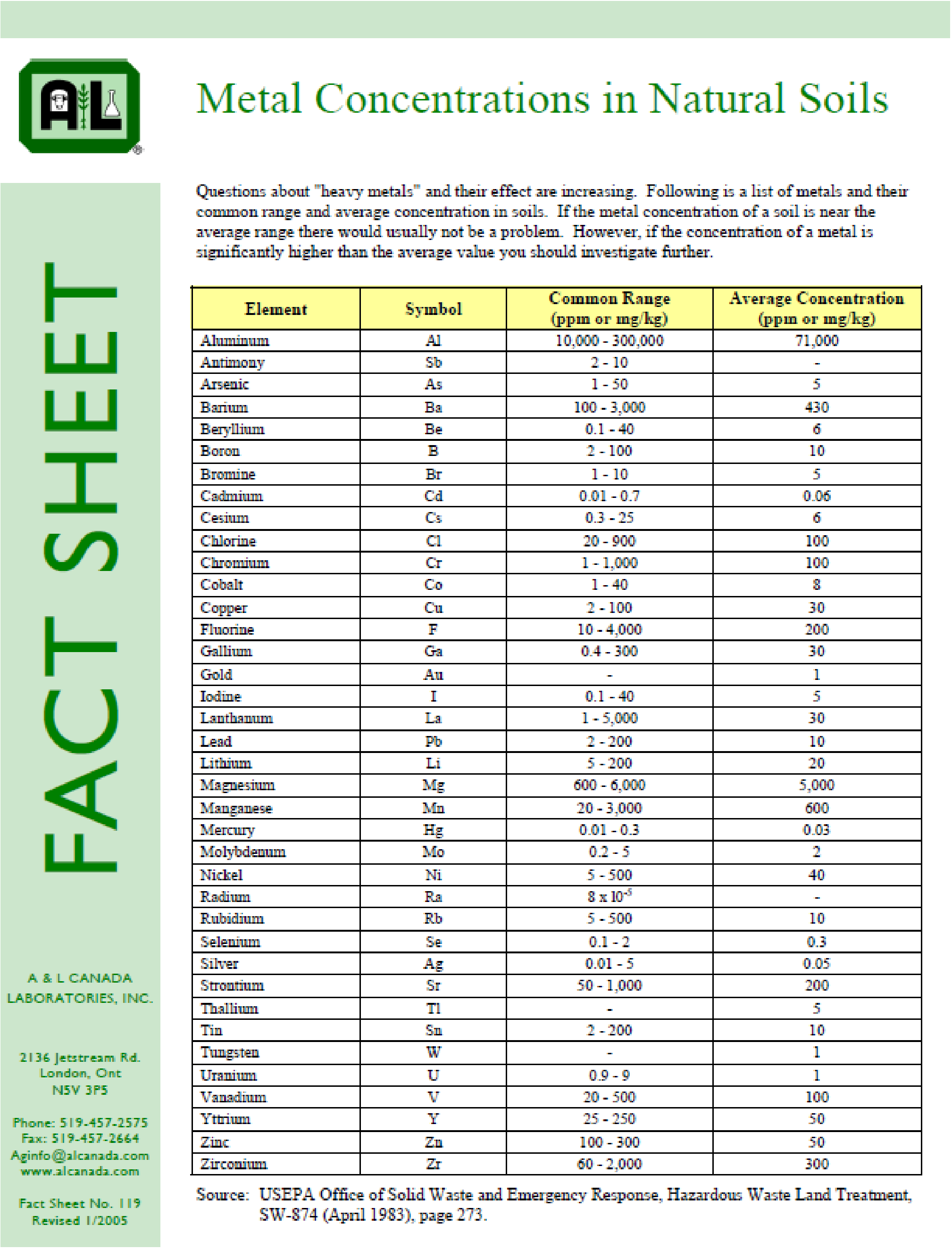


Calibration Curve(Element:Cu:Flame C#:01)

Abs=0.0632663Conc+-0.000231522 r=0.9998

CONC	ABS
0.1000	0.0055
0.5000	0.0310
1.5000	0.0967
2.0000	0.1267
2.5000	0.1565
0.0500	0.0023

Appendix (10) normal Range and Average Concentrations of metals in Soils



FACT SHEET

Metal Concentrations in Natural Soils

Questions about "heavy metals" and their effect are increasing. Following is a list of metals and their common range and average concentration in soils. If the metal concentration of a soil is near the average range there would usually not be a problem. However, if the concentration of a metal is significantly higher than the average value you should investigate further.

Element	Symbol	Common Range (ppm or mg/kg)	Average Concentration (ppm or mg/kg)
Aluminum	Al	10,000 - 300,000	71,000
Antimony	Sb	2 - 10	-
Arsenic	As	1 - 50	5
Barium	Ba	100 - 3,000	430
Beryllium	Be	0.1 - 40	6
Boron	B	2 - 100	10
Bromine	Br	1 - 10	5
Cadmium	Cd	0.01 - 0.7	0.06
Cesium	Cs	0.3 - 25	6
Chlorine	Cl	20 - 900	100
Chromium	Cr	1 - 1,000	100
Cobalt	Co	1 - 40	8
Copper	Cu	2 - 100	30
Fluorine	F	10 - 4,000	200
Gallium	Ga	0.4 - 300	30
Gold	Au	-	1
Iodine	I	0.1 - 40	5
Lanthanum	La	1 - 5,000	30
Lead	Pb	2 - 200	10
Lithium	Li	5 - 200	20
Magnesium	Mg	600 - 6,000	5,000
Manganese	Mn	20 - 3,000	600
Mercury	Hg	0.01 - 0.3	0.03
Molybdenum	Mo	0.2 - 5	2
Nickel	Ni	5 - 500	40
Radium	Ra	8×10^{-5}	-
Rubidium	Rb	5 - 500	10
Selenium	Se	0.1 - 2	0.3
Silver	Ag	0.01 - 5	0.05
Strontium	Sr	50 - 1,000	200
Thallium	Tl	-	5
Tin	Sn	2 - 200	10
Tungsten	W	-	1
Uranium	U	0.9 - 9	1
Vanadium	V	20 - 500	100
Yttrium	Y	25 - 250	50
Zinc	Zn	100 - 300	50
Zirconium	Zr	60 - 2,000	300

Source: USEPA Office of Solid Waste and Emergency Response, Hazardous Waste Land Treatment, SW-874 (April 1983), page 273.

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