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## Vehicle-Derived Metal Pollution in Roundabouts and Roadside Gutters Identified by Magnetic and Elemental Analysis

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### Research Article

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#### ABSTRACT

In order to study the contribution of vehicular emissions to urban environmental pollution, measurements of magnetic susceptibility and elemental analysis was conducted on soil samples collected from roundabouts and roadside gutters in Jalingo Metropolis, Taraba State. Magnetic susceptibility was performed on a total of 61 samples using Bartington MS2B Susceptibility meter while elemental analysis was done on selected samples using Atomic Absorption Spectrophotometer (BUCK 210 Model). Results obtained show magnetic susceptibility enhancement which ranged from 106.3 to 475.1  $\times 10^{-8} \text{ m}^3\text{kg}^{-1}$  and 42.8 to 289  $\times 10^{-8} \text{ m}^3\text{kg}^{-1}$  in the roundabouts and gutters samples respectively which implies increase in ferrimagnetic minerals in the samples. The frequency dependence of magnetic susceptibility indicates the dominance of non-super paramagnetic fraction resulting from anthropogenic sources. The concentrations of Fe, Pb, Cu, Zn and Mn on selected samples show comparable values in both gutter and roundabout samples. Their mean values in mg/kg for gutter and roundabout samples respectively are 21.80 and 21.94 for Fe; 0.01 and 0.02 for Pb; 1.74 and 0.98 for Cu; 1.75 and 1.86 for Zn and 4.22 and 4.71 for Mn. Correlation analysis between magnetic susceptibility and heavy metals shows that magnetic susceptibility can be used as a proxy for assessing Pb, Cu and Zn pollution in the gutter samples but no correlation was obtained between both parameter in the roundabout samples. Organic matter content did not show any effect on magnetic susceptibility in all samples but might affect the concentration of some heavy metals.

### INTRODUCTION

Industrialization and urbanization have their advantages and disadvantages to the urban environment. One of the major demerits is the pollution of land, air and water. The level of pollution is most often assessed and monitored using chemical and geochemical methods<sup>[1,2]</sup>. This approach requires expertise, wastes a lot of time and finance and therefore cannot meet the ever increasing demand on pollution data. The use of magnetic methods which is non destructive, cost and time effective can be used as a faster means of assessing pollution hotspots in soil/sediments<sup>[3,4]</sup>.

Measurement of magnetic properties and in particular magnetic susceptibility is used to indicate the concentration of metal pollution. Increase in the magnetic susceptibility of top soils and sediments resulting from the input of industrial and vehicular magnetic particles and their relationship with some heavy metals have been described by many authors<sup>[5-7]</sup>. The use of magnetic susceptibility for heavy metal pollution assessment is based on the co-existence and similar sources of heavy metals and anthropogenic magnetic particles. Usually, the heavy metals are incorporated into the lattice structure or are absorbed on the surface of iron oxides<sup>[8,2]</sup>. A major contribution of anthropogenic magnetic particles is from vehicular sources which include emissions from vehicle exhausts, wear and tear of automobile parts, corrosion of vehicle parts, brake lining etc. Studies on the

anthropogenic magnetic particles from vehicular emissions and their correlations with heavy metals revealed that magnetic parameters can serve as potential heavy metal pollution proxies [9-12].

This study reports the results of statistical correlations between magnetic susceptibility and some heavy metals in soil samples collected from roundabouts and roadside gutters in Jalingo major streets roads. The objectives of this study are

- (1) To find the relationship between the presence of magnetic minerals detected by magnetic susceptibility measurements and the concentrations of some heavy metals in soils from roundabouts and roadside gutters
- (2) Compare the results obtained from both study sites (roundabouts and roadside gutters) and hence establish which is a better carrier of magnetic signal from vehicular sources.

## MATERIALS AND METHODS

### Study Area

Jalingo, the study area is the capital city of Taraba State which is located between latitude 6°30' and 8°30' North and between 9°00' and 12°00' East (Figure 1). According to the 2006 census figures released by the National Population Commission, Nigeria, Jalingo has a total population of 118,000 inhabitants. Jalingo is a city with no major industry. The major pollution sources are from vehicular sources, alternating current generators, and indiscriminate refuse dumps. The detailed geology of the study area can be found in our earlier paper [13] (Figure 1).



Figure 1: Map of study area (insert: map of Nigeria, showing study area).

### Sampling and Analysis

A total of 61 topsoil/dusts samples were collected randomly from three major roundabouts, namely road block roundabout (RBRA), Patanya roundabout (PRA) and Forest roundabout (FRA) and three township roadside gutters, namely, Hammaruwa way gutter (HWG), palace way gutter (PWG) and Umaru sale street gutter (USSG). The samples were packaged in a plastic bag and transported to the laboratory. In the laboratory, the samples were air dried for some days to reduce mass contribution of water and to avoid any chemical reactions. They were then gently disaggregated using agate mortar and a pestle, sieved using a 1 mm sieve mesh [14] and stored in plastic containers. The mass specific magnetic susceptibility measurements were carried out on the sieved samples packaged in a 10 ml plastic container at laboratory temperature. Measurements of magnetic susceptibility were made at both low (0.465 kHz) and high (4.65 kHz) frequencies using MS2B dual frequency susceptibility meter linked to a computer operated using a Multisus2 software. All measurements were conducted at the 1.0 sensitivity setting. Each sample was measured three times with an air reading before and after each series for drift correction.

The Percentage frequency dependent susceptibility ( $\chi_{fd}\%$ ) was then calculated following Dearing (1999) as:

$$\chi_{fd} (\%) = \left( \frac{\chi_{lf} - \chi_{hf}}{\chi_{lf}} \right) \times 100 \quad (1)$$

Where  $\chi_{lf}$  and  $\chi_{hf}$  are the low and high frequencies susceptibility respectively.

Eleven roundabout and eight gutter samples were selected based on their magnetic susceptibility values for heavy metal

analysis. 2 g of samples was mixed with 20 ml of conc. HNO<sub>3</sub> and allowed to stand for one hour. HClO<sub>4</sub> was added and hot plate digestion was carried at about 200-220°C. The digest was dissolved in 0.1M HCl, filtered and made up to 50 ml by adding distilled water. Heavy metal concentrations (Fe, Pb, Cu, Zn and Mn) were determined using atomic absorption spectrophotometer (BUCK 210 model). Organic matter content was determined by loss-on-ignition method following [12].

## RESULTS AND DISCUSSION

### Magnetic Susceptibility Of Topsoil From Jalingo Township Roundabouts And Roadside Gutters

The mass specific low frequency magnetic susceptibility ( $\chi_{lf}$ ) values measured in both roundabout and gutter samples show enhancement in magnetic susceptibility with the roundabout samples showing the highest enhancement. The  $\chi_{lf}$  enhancement indicates the predominance of secondary ferrimagnetic minerals in the samples. The higher  $\chi_{lf}$  values in the roundabouts might be as a result of accumulation of pollutants released during braking and acceleration since vehicles slows down (applies break) when approaching or negotiating a roundabout. According to Mathissen *et al* [15] in Bućko [16], both acceleration and braking enhance particle concentration, but braking causes higher emissions than acceleration. Similar observations were also made by Marie *et al* [10] around a tollbooth area in Argentina. In the roundabout samples, the mean values are  $250.15 \pm 48.73 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$ ,  $230.44 \pm 140.03 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$  and  $321.34 \pm 108.29 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$  for the RBRA, PRA and FRA respectively (Table 1). These mean values suggest that magnetic particles are more abundant in the FRA compared to RBRA and PRA. The mean  $\chi_{lf}$  values of the gutter samples are  $130.69 \pm 61.43 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$ ,  $132.07 \pm 74.04 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$  and  $126.40 \pm 74.04 \times 10^{-8} \text{ m}^3\text{kg}^{-1}$  for PWG, HWG and USSG respectively (Table 2). The gutter samples displayed comparable magnetic susceptibility values.

**Table 1:** Magnetic parameters measured for Roadblock (RBRA), Patanya (PRA) and Forest.

Sample	$\chi_{lf}$	$\chi_{hf}$	$\chi_{fd}\%$	Sample	$\chi_{lf}$	$\chi_{hf}$	$\chi_{fd}\%$	Sample	$\chi_{lf}$	$\chi_{hf}$	$\chi_{fd}\%$
RBRA 1	112.4	110.4	1.78	PRA 1	166.7	164.9	1.08	FRA 1	475.1	473.1	0.42
RBRA 2	273.7	269.9	1.39	PRA 2	376.8	373.8	0.80	FRA 2	454.9	453.1	0.40
RBRA 3	274.0	270.2	1.39	PRA 3	544.4	543.3	0.20	FRA 3	254.7	253.7	0.39
RBRA 4	242.5	240.1	0.99	PRA 4	197.2	196.9	0.15	FRA 4	298.6	296.3	0.77
RBRA 5	298.3	293.6	1.58	PRA 5	106.3	104.0	2.16	FRA 5	336.0	334.4	0.48
RBRA 6	282.3	278.2	1.35	PRA 6	117.8	116.1	1.44	FRA 6	281.4	280.1	0.46
RBRA 7	231.5	229.7	0.78	PRA 7	145.5	145.1	0.27	FRA 7	137.7	137.5	0.15
RBRA 8	248.3	247.0	0.52	PRA 8	293.5	297.2	0.27	FRA 8	332.3	327.8	1.35
RBRA 9	217.0	214.9	0.97	PRA 9	120.9	120.2	0.58	<b>MEAN</b>	<b>321.34</b>	<b>319.5</b>	<b>0.55</b>
RBRA 10	305.2	302.9	0.75	PRA 10	235.3	233.5	0.76	<b>MEDIAN</b>	<b>315.45</b>	<b>312.05</b>	<b>0.44</b>
RBRA 11	268.2	264.0	1.57	<b>MEAN</b>	<b>230.44</b>	<b>229.5</b>	<b>0.77</b>	<b>S.D</b>	<b>108.29</b>	<b>107.57</b>	<b>0.36</b>
RBRA 12	239.7	237.6	0.88	<b>MEDIAN</b>	<b>181.95</b>	<b>180.9</b>	<b>0.67</b>				
RBRA 13	258.8	258.0	0.31	<b>S.D</b>	<b>140.03</b>	<b>140.16</b>	<b>0.64</b>				
<b>MEAN</b>	<b>250.15</b>	<b>247.42</b>	<b>1.09</b>								
<b>MEDIAN</b>	<b>258.8</b>	<b>258.0</b>	<b>0.99</b>								
<b>S.D</b>	<b>48.73</b>	<b>48.19</b>	<b>0.45</b>								

(FRA) roundabouts

**Table 2:** Magnetic parameters measurements for Palace Way Gutters (PWG), Hammaruwa Way Gutter (HWG) and Umaru Sale Street Gutter (USSG)

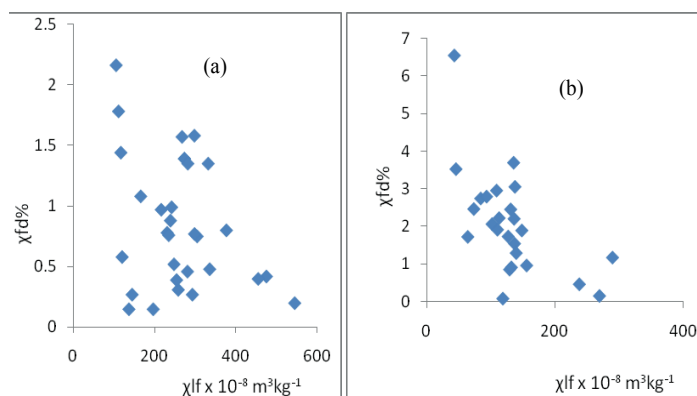
Sample	$\chi_{lf}$	$\chi_{hf}$	$\chi_{fd}\%$	Sample	$\chi_{lf}$	$\chi_{hf}$	$\chi_{fd}\%$	Sample	$\chi_{lf}$	$\chi_{hf}$	$\chi_{fd}\%$
PWG 1	129.1	128.0	0.85	HWG 1	238.0	236.9	0.46	USSG 1	110.2	108.1	1.91
PWG 2	108.8	105.6	2.95	HWG 2	118.6	118.5	0.08	USSG 2	135.4	130.4	3.69
PWG 3	84.0	81.7	2.74	HWG 3	269.5	269.1	0.15	USSG 3	93.2	90.6	2.79
PWG 4	63.8	62.7	1.72	HWG 4	126.9	124.7	1.73	USSG 4	155.7	154.2	0.96
PWG 5	131.9	130.7	0.91	HWG 5	45.4	43.8	3.52	USSG 5	137.5	133.3	3.05
PWG 6	101.7	99.6	2.06	HWG 6	42.8	40.0	6.54	<b>MEAN</b>	<b>126.4</b>	<b>123.32</b>	<b>2.48</b>
PWG 7	112.8	110.3	2.22	HWG 7	130.7	127.5	2.45	<b>MEDIAN</b>	<b>128.8</b>	<b>130.40</b>	<b>2.79</b>
PWG 8	148.2	145.4	1.89	HWG 8	73.2	71.4	2.46	<b>S.D</b>	<b>74.04</b>	<b>24.52</b>	<b>1.06</b>
PWG 9	289.8	286.4	1.17	HWG 9	136.2	133.2	2.20				
PWG 10	136.8	134.7	1.54	HWG 10	139.4	137.6	1.29				
<b>MEAN</b>	<b>130.69</b>	<b>128.51</b>	<b>1.81</b>	<b>MEAN</b>	<b>132.07</b>	<b>130.27</b>	<b>2.09</b>				
<b>MEDIAN</b>	<b>120.95</b>	<b>119.95</b>	<b>1.81</b>	<b>MEDIAN</b>	<b>128.8</b>	<b>126.1</b>	<b>1.97</b>				
<b>S.D</b>	<b>61.43</b>	<b>60.98</b>	<b>0.72</b>	<b>S.D</b>	<b>74.04</b>	<b>74.52</b>	<b>1.93</b>				

### Frequency Dependence of Magnetic Susceptibility

The measurement of frequency dependent magnetic susceptibility ( $\chi_{fd}\%$ ) is used to detect the presence of ultrafine

ferrimagnetic [also called super paramagnetic (SP) fraction less than  $0.03\mu\text{m}$ ] magnetic grains [17-19]. When SP minerals are present in soil samples, the magnetic susceptibility values at high frequency are slightly lower than the magnetic susceptibility at low frequency. If there are no SP minerals, the two measurements are identical [20] and coarse multi-domain (MD) magnetic grains are present. The results of  $\chi_{fd}\%$  are shown in Tables 1 and 2 respectively for the roundabouts and gutter samples. The mean values of  $\chi_{fd}\%$  are  $1.09 \pm 0.99\%$  for RBRA,  $0.77 \pm 0.67\%$  for PRA and  $0.55 \pm 0.36\%$  for FRA (Table 1). The results indicates that samples for these roundabouts are dominated by coarse non SP multidomain and stable single domain (SSD) magnetic grain sizes from pollution sources. Compared to fine SP particles usually of pedogenic origin, the coarser particles such as MD and SSD are frequency independent [7,17]. According to Dearing [20],  $\chi_{fd}\% \leq 2\%$  indicates a negligible proportion of ultrafine pedogenic ferrimagnetic minerals while  $\chi_{fd}\%$  between 2 and 10% indicates a mixture of SP and MD/SSD grains. The mean values of  $\chi_{fd}\%$  of the gutter samples also show the dominance of MD and SSD grains with values of  $1.81 \pm 0.72\%$  for PWG,  $2.09 \pm 1.97\%$  for the HWG and  $2.48 \pm 1.06\%$  for the USSG (Table 2). Generally, MD and SSD particles originate from anthropogenic sources [21]. In this case, it could be originating mostly from vehicular sources.

A negative trend was obtained in the plot of  $\chi_{fd}\%$  against  $\chi_{lf}$  shown in Figures 2 for the roundabouts and gutter data. Such negative trend indicates that the magnetic susceptibility signal originate from industrial/anthropogenic sources [21].



**Figure 2:**  $\chi_{fd}\%$  -  $\chi_{lf}$  scattergram for (a) roundabout and (b) gutter samples.

## Heavy Metal Concentration

The concentrations of Fe, Pb, Cu, Zn and Mn in selected samples from the roundabouts and gutter samples are shown in Tables 3 and 4 respectively. In both cases, Fe had the highest concentrations with mean values of  $21.94 \pm 1.50\text{ mg/kg}$  and  $21.82 \pm 0.84\text{ mg/kg}$  respectively for the roundabouts and gutter samples. Lead had the least concentration in all samples. Generally, the concentration of these heavy metals did not exceed the limits set by United States Environmental Protection Agency (USEPA, 1999) and World Health Organization (WHO, 2004)

**Table 3:** Heavy metal concentrations and Organic Matter content (OM) for Roundabout samples.

SAMPLE	OM (%)	Fe (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Mn (mg/kg)
RBRA 1	82	22.65	0.05	0.78	2.25	4.59
RBRA 5	78	21.80	0.02	0.40	3.27	6.17
RBRA 6	86	22.40	0.02	2.47	1.57	5.79
RBRA 10	84	23.35	0.03	0.12	2.99	5.49
PRA 2	80	19.28	0.01	3.52	2.70	2.13
PRA 3	78	24.20	0.01	0.62	2.42	5.88
PRA 8	80	20.13	0.03	2.00	2.96	7.07
PRA 9	78	22.55	0.01	0.21	0.36	3.40
FRA 1	80	22.65	0.02	0.26	0.17	3.05
FRA 7	78	20.10	0.02	0.15	0.99	2.88
FRA 8	80	22.23	0.01	0.20	2.13	6.11
MEAN	80.36	21.94	0.02	0.98	1.98	4.78
MEDIAN	80.00	22.40	0.02	0.40	2.25	5.49
S.D	2.66	1.50	0.01	1.16	1.07	1.65

## Correlation between Magnetic Susceptibility and Heavy Metals

To investigate the relationship between magnetic susceptibility and heavy metal contents, a correlation table was established using Microsoft Excel 2007 (Tables 5 and 6). In the roundabout samples, poor and negative correlations were obtained between  $\chi_{lf}$  and Fe, Pb and Mn concentrations. Cu and Zn show weak and positive correlation with  $\chi_{lf}$  (Table 5). This result indicates that magnetic susceptibility may not be a good measure of heavy metal contamination in the roundabout samples. Similar result was obtained by Carraz *et al* [6] in road deposited sediment from Greater Manchester, UK. According to Carraz *et al* [6], the non-

correlation between  $\chi_{lf}$  and heavy metals is because the metals and mineral magnetic components are derived from different sources or there are more than one contamination sources. Another possible cause of non correlation could be attributed to the coarse grained nature of the magnetic particles of the samples. Adsorption of heavy metals is greater on finer particles [1].

The lack of correlation between the heavy metals indicates variable sources of contamination. Only Mn and Zn show good positive correlation indicating similar contamination source

**Table 4:** Heavy metal concentrations and Organic Matter content (OM) for gutter samples.

SAMPLE	OM (%)	Fe (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Mn (mg/kg)
HWG 3	82	20.65	0.01	0.13	1.15	2.03
HWG4	82	21.1	0.01	0.22	1.19	3.86
HWG 6	80	23.4	0.01	0.22	1.03	8.34
PWG 4	82	21.85	0.01	0.15	1.21	3.55
PWG8	77	22.00	0.01	0.80	1.41	4.58
PWG 9	78	22.15	0.02	10.21	3.57	4.07
USSG 2	90	21.25	0.02	2.01	1.98	3.86
USSG 4	82	22.15	0.02	0.20	2.45	3.47
<b>MEAN</b>	<b>81.63</b>	<b>21.82</b>	<b>0.014</b>	<b>1.74</b>	<b>1.75</b>	<b>4.22</b>
<b>MEDIAN</b>	<b>82.00</b>	<b>21.93</b>	<b>0.010</b>	<b>0.22</b>	<b>1.31</b>	<b>3.86</b>
<b>S.D</b>	<b>3.93</b>	<b>0.84</b>	<b>0.005</b>	<b>3.48</b>	<b>0.88</b>	<b>1.82</b>

**Table 5:** Correlation matrix between  $\chi_{lf}$  and heavy metals for roundabout samples.

	$\chi_{lf}$	OM	Fe	Pb	Cu	Zn	Mn
$\chi_{lf}$	1						
OM	-0.05209	1					
Fe	-0.00347	0.448504	1				
Pb	-0.48935	0.420473	0.067114	1			
Cu	0.334479	0.143231	-0.55807	-0.07548	1		
Zn	0.100548	0.116175	-0.11532	0.237298	0.29389	1	
Mn	-0.25042	0.401618	0.336546	0.200046	-0.09524	0.582582	1

**Table 6:** Correlation matrix between  $\chi_{lf}$  and heavy metals for gutter samples.

	$\chi_{lf}$	OM	Fe	Pb	Cu	Zn	Mn
$\chi_{lf}$	1						
OM	-0.18356	1					
Fe	-0.46459	-0.4299	1				
Pb	0.375641	0.360357	0.030743	1			
Cu	0.618254	-0.25063	0.121536	0.570369	1		
Zn	0.594202	-0.09497	0.113567	0.861087	0.859648	1	
Mn	-0.5912	-0.2463	0.865621	-0.19107	-0.03777	-0.18601	1

In the gutter samples,  $\chi_{lf}$  is strongly positively correlated with the concentration of Cu and Zn, implying that magnetic susceptibility could be used as proxy for these metals concentration. Pb is moderately correlated with  $\chi_{lf}$  while Fe and Mn are negatively correlated with  $\chi_{lf}$  (Table 6). Correlation analysis between heavy metals in the gutter samples revealed strong positive correlation between Fe and Mn, Pb and Cu, Pb and Zn, and Cu and Zn (Table 6). This implied similar sources of contamination. Zn has been suggested to be derived from tyre wear, Cu has been traced to vehicle activity from corroded car body work [6]. Fe and Mn have been suggested to be derived from a number of sources including geogenic background sources [22].

### Effect of Organic Matter Content on Magnetic Susceptibility and Heavy Metals Content

High organic matter (OM) content was obtained in both roundabout and gutters samples. The mean values are  $80.36 \pm 2.66\%$  and  $81.63 \pm 3.93\%$  in the roundabout and gutter samples respectively (Tables 3 and 4). Organic matter has a diamagnetic character and is expected to decrease magnetic susceptibility [23]. In this study, negative and poor correlation was found between OM and  $\chi_{lf}$  in both roundabout and gutter samples (Tables 5 and 6). Correlation analysis between heavy metals and OM indicates that in the roundabout samples all the metals are positively correlated with OM with Fe, Pb and Mn displaying the highest correlation (Table 5). Whereas, all the metals except Pb are negatively correlated with OM in the gutter samples (Table 6).

## CONCLUSIONS

Some of the major conclusions reached in this study are:

1. The roundabout samples and gutter samples show magnetic susceptibility enhancement which indicates the presence of secondary ferrimagnetic minerals.



2. Frequency dependent susceptibility results indicates the dominance of coarse grained multidomain and stable single domain grain sizes which implied that samples contained pollution particles from anthropogenic loadings.

3. The heavy metal concentrations in all samples were within permissible limits set by USEPA and WHO.

4. Strong positive correlation between magnetic susceptibility and concentration of Cu, Zn and Pb in the gutter samples indicates that magnetic susceptibility could be used as a faster means of assessing these metals. Lack of correlation between magnetic susceptibility and heavy metal could results from variable sources of contamination and grain sizes.

5. Organic matter content is negatively correlated with magnetic susceptibility but displayed variable correlation with heavy metals.

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