Original Research Article

Pollution status of heavy metals in spent oil-contaminated soil in Gwagwalada

ABSTRACT

The pollution status of the some selected heavy metals: Pb, Fe, Zn, Cu, Cr, Ni and Cd, in spent oil-contaminated soil was investigated through wet digestion of the soil samples obtained from different spots of the automobile mechanic workshop and the concentrations determined using Atomic Absorption Spectrophotometer (AAS). The concentration of Pb was significantly higher than the concentrations of each of the other six heavy metals while cadmium had the least concentration. Cd concentrations in most of the spots analyzed were below the detection limit of the instrument used. The order of the concentrations of the heavy metals were Pb> Fe> Zn> Cu> Cr> Ni> Cd and Fe > Cr > Zn> Pb> Cu> Ni> Cd for the spent oil-contaminated and control soils respectively. The concentration of iron, cadmium, copper, nickel and zinc in the control soil were significantly lower than the concentration of iron, zinc and lead in the oil-contaminated soil. The concentration of Pb exceeded the limits of both the background and intervention lead value set by DPR (Department of Petroleum Resources) of Nigeria. The contamination and potential ecological factors of Zn, Cu, Fe, Cr and Cd were categorized low except Pb which was categorized as having very high contamination factor and moderate potential ecological risk factor. The entire spots studied showed moderate degree of contamination. The potential risk index of the heavy metals ranged from 44.23 to 51.91, which had a low grade category; thus have not caused any harm to the soil of the workshop

Keywords: heavy metals; spent oil; contamination factors; potential ecological factors; pollution status; Gwagwalada

1. Introduction

Metals with a specific density of at least 5 times greater than that of water, 1 g cm^{-3} are known as Heavy metals. Therefore, a heavy metal has a specific density greater than 5 g cm^{-3} [1]. Heavy metal pollution can be of natural or anthropogenic origins, which include: soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and spent oil [1, 2]. They find their way into the human system via food, water and air, affecting mostly the central and peripheral nervous, gastrointestinal (GI), cardiovascular, hematopoietic and renal systems [3,4]. All heavy metals, both essential and non-essential can cause toxic effects on plants and humans, if found in high concentrations [5] and have an adverse affect on the environment [6, 7]. So heavy metals contamination has been a worldwide environmental concern with its potential ecological effect [8-10].

Spent oil, also know as used engine oil, is any oil, refined from crude oil or any synthetic oil made from coal, shale or polymer-based starting material, which must have been used in the engine [11]. Abdulhadi and Kawo [12] defined used or spent motor oil as any lubricating oil that has: served its service properties in a vehicle, been withdrawn from the meant area of application and considered not fit for its initial purpose because it is contaminated by physical or chemical impurities. This oil which is disposal off indiscriminately at the mechanic workshops soil in addition to the various other repair services ranging from complex engine rebuilding to auto body repair, electrical, welding and spraying services, have been found to cause heavy metal contamination of the mechanic workshop soils [13-17]**.** Hence, this study is centered on the determination of the concentration and interpretation of the pollution status of the heavy metals of a spent oil contaminated soil from a mechanic workshop.

2. MATERIALS AND METHODS

Sample Preparation and Analysis

A mechanic workshop located at Dagiri, Gwagwalada Abuja was marked and soil samples were collected from selected seven spots p at the 0 -15 cm using a previously washed shovel. The soil samples were stored in a black polyethylene bag and labelled accordingly. At the laboratory, the samples were air dried for 1 week and passed through a 2 mm sieve. The physicochemical properties of the soil were determined as follows: total Calcium trioxocarbonate (IV) [18]; wet Digestion of Soil samples for metal analysis of: Fe, Cd, Cr, Cu, Ni, Zn and Pb; carried out in duplicates using 2 M HNO_3 [19-21]; pH in water and KCl was done using the pH meter [22]; organic matter of the soil samples were determined based on Walkey- Black method according to the procedure of Estefan et al [18].

One-way ANOVA analysis was use to test the significant difference of the mean of the heavy metals while descriptive was to reveal the minimum, maximum, mean and standard deviation of the concentrations of the heavy metals obtained after AAS analysis. Correlation analysis was used to ascertain the probable common source of the heavy metal pollutants in the contaminated soil [23, 24].

The assessment and interpretation of the contamination status of heavy metals in the soil has been possible by the application of various quantitative indices such as: contamination factor and degree of contamination; potential ecological risk factor and index; index of geo-accumulation, etc.

Contamination factor is used to express the contamination of a given toxic substance [25].

Mathematically, it is expressed as

$$C_f^i = \frac{C_r^i}{C_R^i} \qquad (1)$$

Where:

C_f^i = contamination factor of a single metal;

C_r^i = Measured concentration of the metal in the sample;

C_R^i = Background concentration of the soil according to DPR [26]

Contamination factor is defined according to four categories. The sum of the contamination factors of all the elements in the sample is referred to as the degree of contamination, which is mathematically expressed as:

$$C_d = \sum_{i=1}^{n} C_f^i \qquad (2)$$

Where:

C_d = Degree of contamination

C_f^i =Contamination factor of a single element i

n =Count of the heavy metal

According to Hakanson, the degree of contamination in soil and sediments may be termed the sum of pollution [25]. The terminologies used to describe the contamination factor and degree of contamination, as explained by authors [15, 27], is that if C_f and C_d are expressed as:

(i) $C_f < 1$ and $C_d < 8$, then it is of low degree of contamination,

(ii) $1 < C_f < 3$ and $8 \leq C_d < 16$, then it is of moderate degree of contamination

(iii) $3 < C_f < 6$ and $16 \leq C_d < 32$, then it is of considerable degree of contamination

(iv) $C_f > 6$ and $C_d \geq 32$, then it is of Very high degree of contamination

Hakanson [25] stated that potential ecological risk factor was initially only applicable to water pollution control but have in recent times been effectively applied to determine the extent of pollution in soils and sediments. Therefore, this factor evaluates the potential harm of a given heavy metals in the studied soil. The categories of potential ecological risk factor and Index are as shown on Table (1).The proposal by [25] as shown in equation (3) was followed in determining the potential ecological risk index of the heavy metals studied in the contaminated soil.

$$E_f^i = T_f^i \; x \; C_f^i \qquad (3)$$

Where:

E_f^i = Potential ecological risk factor of single metal;

T_f^i = Toxicity response factor of a given metal; and

C_f^i =Contamination factor of a single element, i

The toxicity response factors of metals [24] are:

Cd = 30; Cr = 2; Cu = Pb = Ni = 5; Zn = 1

The Potential Ecological risk index was calculated based on equation (4), which is a sum of the potential ecological risk of the single heavy metal in the sample from each spot. The format of calculating degree of contamination applies to potential risk index.

$$RI = \sum_{(i=1)}^{n} E_f^i \qquad (4)$$

Where:

E_f^i = the potential ecological risk factor of single metal;

RI = the potential ecological risk index of many metals

n = Count of the heavy metal

3. RESULTS AND DISCUSSIONS

The physicochemical properties of the soil are as shown in Table (2). The mean pH in water of the soil is 7.92 ± 0.02 while that measured in KCl was 7.75 ± 0.06. Therefore, the pH of the soil is very slightly alkaline in nature. There was no significant difference between the measured values of pH in both electrolytes. The pH of the soil studied by Olatunji and Osibanjo [28] was 6.55 ± 0.70, lower than that from the present study. The dump site studied by Olayinka et al. [29] was acidic with an average pH value of 5.0 while the pH of their control soil was slightly alkaline in nature with an average value of 7. 24. Agbaji et al. [30]; Odor et al [31] also reported slightly alkaline soil while Ogundiran and Osibanjo [32] reported a pH of near neutral. More so, the pH of Oluyemi et al. [33] recorded pH of neutral to 7.4 while the pH accounted by Orji et al [7] in both water and KCl was 7.4. The mechanic workshop of Pam et al. [17] was acidic.

From the result, the electrical conductivity, which gives an estimate of the total salt content of the soil under study, had a mean value of 24.72 ± 1.10 dS m $^{-1}$ and ranges from 22.79 to 25.83 dS m^{-1}. Soil samples of this nature, with electrical conductivity exceeding 8 dS m $^{-1}$ affect the growth of many cash and food crop [18]. The electrical conductivity of this soil was higher than that recorded by [34-36] but lower than the value reported by Idugboe et al. [37]. The soil mean carbonate content which is related to alkaline pH was 1.04 ± 0.021 %. The total organic matter which represents the remains of plants and soil organisms was 4.64 ± 0.003 %.

Fig 1 represents the concentration of iron obtained at the different spots sampled at the mechanic workshop. The lowest and highest concentrations of iron in the contaminated soil were 318.42 ± 1.78 and 514.845 ± 0.375 mg kg $^{-1}$, respectively, with an average value of 452.05 ± 70.90 mg kg $^{-1}$. From the results, the concentration of iron in the contaminated soil was significantly higher than that of the control, implying that the workshop is contaminated. Olayinka et al. [29] reported a mean iron concentration value of 186 mg kg $^{-1}$, lower than that from this study. Tanee and Eshalomi-Maio [38], also, recorded iron concentration < 210 mg/kg which was also lower than that from this study. The concentration of iron was lower than the limit of the background values set by Nigerian DPR [26].

The results of the copper concentration in the contaminated mechanic workshop are displayed in Fig 1. The concentration of copper in the control soil was significantly lower than that from the mechanic workshop. The Cu concentration ranged from 11.63–17.83 mg/kg with a mean value of 13.54 ± 2.04 mg kg $^{-1}$. The Cu concentration in this study was lower than that reported by Pam et al. [17] with a range of 254-1348 mg kg $^{-1}$; Oluyemi et al. [33], with a Cu, mean concentration of 844.00 ± 0.01mg kg $^{-1}$; Jafaru et al. [39], with mean concentration of 2.14 mg kg $^{-1}$ and 31.73 mg kg $^{-1}$ from their contaminated and waste dump site respectively, Olatunji and Osibanjo [28] with mean concentration of 51.50 ± 7.35 mg kg $^{-1}$; Dasaram et al. [40] (34.3 mg kg $^{-1}$). The concentration of copper in this study was, however, higher than that reported by Olayinka et al. [29] with a mean value of 3.30 ± 0.25 mg kg $^{-1}$, 2.58 ± 0.19 and 1.71 ± 0.08 mg kg $^{-1}$ at depth 0-15, 15-30 and 30-45 cm. Odoh et al. [31] reported a mean value of 204.29 ± 23.04 μg g $^{-1}$. the copper concentration obtained in this study did not exceed the background and intervention copper values set by Nigerian DPR [26]. Copper concentrations in the mechanic workshop soil could be from the components of copper wires, electrodes and copper pipes and alloys from corroding car scrapes added Idugboe et al. [37] and Pam et al. [17]. Adekunle and Abegunde [41] reported that plants hardly survive in soils that are rich in copper.

The concentration of chromium in the contaminated soil is presented in Fig 1. The mean concentration of chromium was 8.66 ± 0.84 mg kg $^{-1}$ with the concentration ranging from 7.64-9.91 mg kg $^{-1}$. The range Cr concentration of 8.18–14.89 mg kg $^{-1}$ reported by Olatunji and Osibanjo [28] was higher than that from this study. Also, some other authors reported the higher concentration of chromium [33, 40, 43, 44]. There was no significant difference between the chromium concentration in the soil from the control site and that of the mechanic workshop. The chromium concentration was below the limits set by Nigerian DPR [26].

The concentration of nickel obtained from the different spots of the mechanic workshop is as shown in Fig 1. The mean concentration of Ni was 2.22 ± 0.86 mg kg $^{-1}$. The highest and lowest concentrations are 0.82 and 3.21 mg kg $^{-1}$ respectively. Some authors: [17, 31, 33, 36, 41- 44] reported higher nickel concentrations. The soil from Evbareke of Idugboe et al. [37] had nickel concentration similar to that obtained from this study. The nickel concentration was much lower than the set background and intervention nickel values by DPR [26]. Idugboe et al. [35] reported that inhalation and ingestion or skin contact of nickel can occur in nickel and nickel alloy production plants as well as in welding, electroplating, grinding and cutting operations which are done in auto-mechanic workshops.

Zinc was found in all the soil sampled from the different spots of the mechanic workshop and the results are as shown in Fig 1. The zinc concentration in the contaminated soil was significantly higher than the concentration of, 5.83 ± 2.98 mg kg $^{-1}$, from the control soil. The mean zinc concentration was 85.72 ± 5.66 mg kg $^{-1}$ and ranges from 77.99 to 91.44 mg/kg. Some literature reported lower zinc concentrations in their studies [36] and Idugboe et al. [37] for soil from Uwelu. However, some literature reported higher concentrations of zinc [44-45] from the results of their mechanic workshop. The zinc concentration of this mechanic workshop did not exceed the background zinc value set by Nigerian DPR [26]. The control soil of Idugboe et al. [37] had a zinc concentration of 11.71 mg kg $^{-1}$, higher than 5.83 ± 2.98 mg kg $^{-1}$, from this study.

The lead concentration of the contaminated soil is displayed in Fig 1. The mean concentration of lead in the soil was 787.06 ± 39.20 mg kg $^{-1}$ and ranges from 710.65 to 826.13 mg kg $^{-1}$. It was significantly higher than the concentration of Pb of the control soil, 3.99 ± 1.18 mg kg $^{-1}$ and exceeded the limits of both the background and intervention lead value set by DPR of Nigeria. This implies that the soil is actually contaminated with lead.

Some authors published lead concentrations that were lower than that obtained from this study: [17, 28, 29, 31, 33, 36-40, 42- 43, 45- 49]. However, the lead levels observed in this study were lower than the concentrations of, 1162 ± 572 mg kg $^{-1}$ of Pb reported by Nwachukwu et al. [44]. The control soil of Utang et al. [49] had a higher concentration of Pb, 60.25 ± 25.36 mg kg $^{-1}$, than 3.99 ± 1.18 mg kg $^{-1}$ obtained in this study

The cadmium concentration was below the detection limit of the instrument used as shown in Fig (1). Therefore, the only concentration that was detected was 0.001 mg/kg at spot 4. Higher concentrations of cadmium were reported in the literature [28, 29, 33, 37- 38, 42- 44, 49]. The contaminated soil had a higher concentration of Cd, 1.79 ± 1.43 mg kg $^{-1}$, more than 0.01 ± 0.01 mg kg $^{-1}$ obtained in the control of this study

From the ANOVA results carried out at 95 % confidence level, the mean concentration of Fe was significantly higher than the concentrations of the other heavy metals analyzed in the soil from mechanic workshop and control soil though it was significantly lower than the concentration of Pb in the soil. There was the extreme significant difference between the concentrations of cadmium and those of iron, zinc and lead in the spent oil contaminated soil. This also applied to copper, chromium and nickel. At $p< 0.05$, the mean concentration of zinc in the oil-contaminated soil was significantly lower than the mean concentration of iron, and lead but higher than the mean concentration of cadmium, copper, chromium and nickel. It was also significantly higher than the each of the concentration of the heavy metals of the control soil. The mean concentration of Pb in the oil-contaminated soil was extremely higher than the mean concentrations of each of the other heavy metals ($p< 0.05$) in the contaminated and control soil as shown in Fig 1. More so, the concentration of iron, cadmium, copper, nickel and zinc in the control soil were significantly lower than the concentration of iron, zinc and lead in the oil-contaminated soil. There was no significant difference between the mean concentration of chromium in the contaminated and control soil at $p< 0.05$.

The correlation analysis result is displayed in Table (3). The analysis showed that there was a significant negative correlation between the mean concentration Fe and Cd ($r = -.894$, $p= .003$), implying that both metals were not from the same source. The mean concentration of Copper was found to be positively correlated with the mean concentrations Zn ($r = .856$, $p= .007$) and Pb ($r= .844$, $p= .008$), meaning that Cu, Zn and Pb were from the same origin. There was also a significant and strong positive correlation between Pb and Ni at $r = .748$ and $p= .027$, showing that they were from the same source. The pH in KCl had a strong positive correlation with the mean concentration of Cr ($r= .955$, $p= .000$) and Ni ($r= .777$, $p= .020$). The total organic matter had a significant negative correlation with Cr ($r= -.790$, $p= .017$), Ni ($r= -.806$, $p= .014$), Pb ($r= -.831$, $p= .010$) and pH in KCl ($r= -.732$, $p= .031$); indicating that the availability of Cr, Ni and Pb had no dependence on the total organic matter content of the soil. The entire correlation analysis shows that the heavy metals were not correlated with the physicochemical properties of the soil. The implication, therefore, is that the heavy metals originated from anthropogenic sources.

Contamination factor and degree of contamination of heavy metals in spent oil contaminated soil are shown in Table (4). The contamination factor of the heavy metals ranged from 0.07–0.11 for Fe; 0–0.001 for Cd; 0.32-0.5 for Cu; 0.08-0.1 for Cr; 0.02-0.09 for Ni; 0.56-0.65 for Zn and 8.36-9.72 for Pb. Lead had the highest mean contamination factor (9.32), followed by zinc (0.61), copper (0.43), iron (0.10), Cr (0.09) and then cadmium (0.0002). The contamination factor of Zn, Cu, Fe, Cr and Cd showed low contamination factor except for Pb which was categorized as very high contamination. Therefore, it can be inferred that lead was the main heavy metal contaminating the mechanic workshop. This very high contamination factor of Pb must have originated from the blend of gasoline with tetraethyl lead which causes an improvement in the octane rating of the fuel. During combustion in the engine of vehicles, this tetraethyl lead is converted to lead (II) and (IV) oxide [41]. Adelekanle and Abegunde [41] reported that lead is one of the more persistent metals, which was estimated to have a soil retention time of 150 to 5000 yr.

The entire spots studied showed a moderate degree of contamination, having values that are greater than 8. The minimum and maximum degree of contamination of the spots studies were 9.44 and 11.07 respectively. This moderate degree of contamination possibly resulted from the increased concentration of Pb that contributed the very high contamination factor of lead as seen in Table (4).

The potential ecological risk factor of the heavy metals ranged from 0.00 to 48.60. The descending order of the potential ecological risk factor of the heavy metals is Pb > Cu > Zn > Ni > Cr > Cd. The potential ecological risk factor of Cu, Zn, Ni, Cr and Cd were categorized low, having values less than 40 as shown in Table (5). However, Pb had a moderate potential ecological risk factor, having a range from 41.80 to 48.60 and was not likely to cause harm or ecological risk to the environment. The potential risk index of the heavy metals ranged from 44.23 to 51.91, which had a low-grade category; thus have not caused any harm to the soil of the workshop.

4. Conclusion

The present study considered the concentration of heavy metals (Fe, Cd, Cu, Cr, Ni, Zn and Pb) in the soil from the mechanic workshop. There was a significant variation of the heavy metals concentrations, with a lead having the highest concentration and Cd, the least. Lead also had a moderate potential ecological risk factor and a very high contamination factor. Therefore, the usual indiscriminate disposal of waste oil on the soil at the mechanic workshop requires adequate management and monitoring to deter further contamination of the land which could affect the farmland, ground and surface water; thereby, reducing drastically the bio-accumulation of heavy metals across the food chain. Awareness should be created to inform the mechanics on the toxic nature of the spent oil, especially the heavy metals content and the possible environmental hazards that could develop due to improper disposal of the waste oil from cars after servicing on the soil surfaces.

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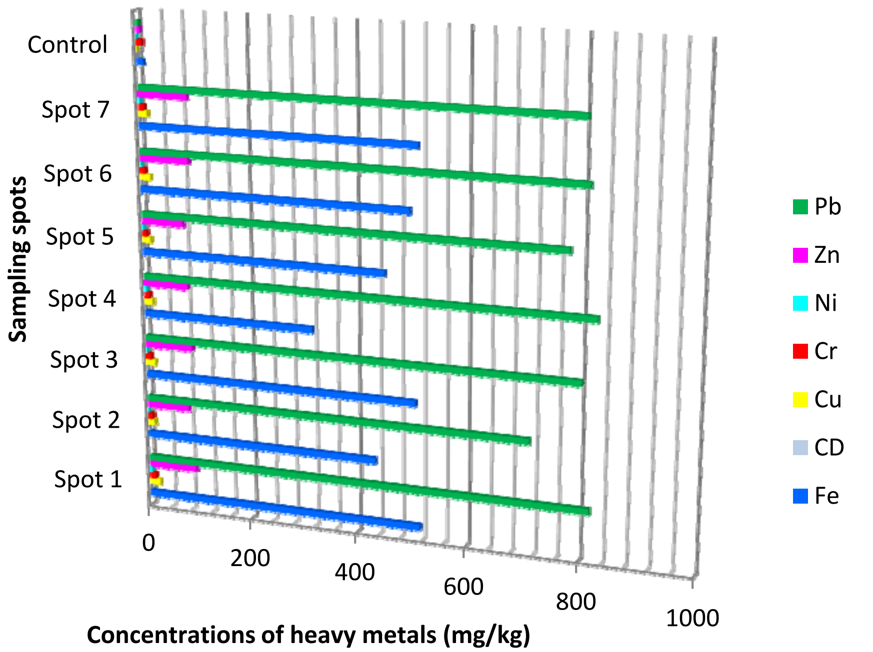

Fig 1: Results of the concentration of the heavy metals in the contaminated soil

Table 1: Categories of E_f^i and RI [24]

Ranges of Potential Ecological risk	Categories of Potential Ecological risk	Ranges of Potential risk index	Categories of potential risk index
< 40	Low	RI < 150	Low grade
$40 \leq E_f^i < 80$	Moderate	150 ≤ RI < 300	Moderate
$80 \leq E_f^i < 160$	Higher	300 ≤ RI <600	Sever
$160 \leq E_f^i < 320$	High	600 ≤ RI	Serious
$320 \leq E_f^i$	Serious		

Table 2: Physicochemical properties of the contaminated soil

Parameters	Values
pH in water	7.92±0.021
pH in KCl	7.75±0.057
Electro-conductivity (dS/m)	24.73±0.021
Carbonate content %	1.04±0.021
Oxidizable organic Carbon (%)	2.02±0.001
Total Organic Carbon (%)	2.69±0.001
Total Organic Matter (%)	4.64±0.003

Table 3: Pearson correlation matrix between variables in spent oil contaminated soil.

	Fe	Cd	Cu	Cr	Ni	Zn	Pb	pH H_2O	pH KCl	EC	CO_3^{2-}	TOM
Fe	1											
Cd	-.894**	1										
Cu	.514	-.122	1									
Cr	.094	.213	.534	1								
Ni	-.193	.423	.569	.663	1							
Zn	.574	-.177	.856**	.445	.157	1						
Pb	.037	.380	.844**	.575	.748*	.658	1					
pH H_2O	.466	-.441	.274	-.587	-.451	.439	-.002	1				
pH KCl	-.019	.277	.469	.955**	.777*	.294	.569	-.647	1			
EC	-.486	.344	-.654	-.180	-.323	-.431	-.332	-.290	-.066	1		
CO_3^{2-}	-.193	.092	-.363	.199	.172	-.540	-.132	-.751*	.271	.387	1	
TOM	.149	-.509	-.661	-.790*	-.806*	-.458	-.831*	.395	-.732*	.418	-.022	1

**. Correlation is significant at the 0.01 level (1-tailed).

*. Correlation is significant at the 0.05 level (1-tailed).

Table 4: contamination factor and degree of contamination of heavy metals in spent oil contaminated soil

Soil points	Contamination factor							C_d
	Fe	Cd	Cu	Cr	Ni	Zn	Pb	
1	0.11	0	0.50	0.10	0.09	0.65	9.62	11.07
2	0.09	0	0.32	0.08	0.02	0.57	8.36	9.44
3	0.11	0	0.43	0.09	0.05	0.63	9.42	10.73
4	0.07	0.001	0.41	0.09	0.09	0.6	9.72	10.98
5	0.1	0	0.4	0.08	0.08	0.56	9.14	10.36
6	0.11	0	0.47	0.08	0.06	0.65	9.53	10.90
7	0.11	0	0.45	0.09	0.06	0.65	9.46	10.82
minimum	0.07	0	0.32	0.08	0.02	0.56	8.36	9.44
maximum	0.11	0.001	0.50	0.10	0.09	0.65	9.72	11.07

Table 5: potential ecological risk factor and potential risk index of heavy metals in spent oil contaminated soil.

Sampling Spots	Potential ecological risk factor						Potential risk index
	Cd	Cu	Cr	Ni	Zn	Pb	
1	0.00	2.50	0.20	0.45	0.65	48.10	51.9
2	0.00	1.60	0.16	0.10	0.57	41.80	44.23
3	0.00	2.15	0.18	0.25	0.63	47.10	50.31
4	0.03	2.05	0.18	0.45	0.60	48.60	51.91
5	0.00	2.00	0.16	0.40	0.56	45.70	48.82
6	0.00	2.35	0.16	0.30	0.65	47.60	51.06
7	0.00	2.25	0.18	0.30	0.65	47.30	50.68
Minimum	0.00	1.60	0.16	0.10	0.56	41.80	44.23
Maximum	0.03	2.50	0.20	0.45	0.65	48.60	51.91