

# Evaluation of Heavy Metal Pollution on Soil in Vanderbijlpark, South Africa

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**Abstract:** In this study, inductive coupled plasma-optical emission spectroscopy (ICP-OES) is employed for the evaluation of soil pollution for selected metals in the Vanderbijlpark area of South Africa. Soil samples investigated were collected from five different sites in the city based on their proximity to the industrial areas of Vanderbijlpark. Soil samples were collected from close to traffic robots, farms, township schools, Iemas garage and central East 5 (CE5) suburbs. The results obtained show metal levels at the robot decrease in the order Pb > Zn > V > Bi > Ni > Li > As > Sn > Co > Cu > Mo > Sb > Hg > Se; at the farm they decrease in the order Pb > Zn > Bi > Li > Sn > As > V > Cu > Mo > Sb > Ni > Co > Cd > Se > Hg; in the township school they decrease in the order Pb > Zn > Cu > Li > V > Sn > As > Ni > Bi > Mo > Sb > Co > Cd > Se > Hg; at the Iemas garage the decreasing order is Pb > Zn > V > Li > Sn > As > Bi > Cu > Ni > Mo > Co > Cd > Se > Hg > Sb and in the CE5 suburb the decreasing order is Pb > Zn > V > Li > As > Cu > Sn > Ni > Mo > Co > Bi > Cd > Sb > Se > Hg. In all the sample points, the levels of lead (Pb) was found to be high, particularly at the farm and the township school area. However, the concentrations of all other metals at all the sampling points were within the US-EPA maximum allowable limits.

**Keywords:** Inductive Coupled Plasma, Optical Emission Spectroscopy, Soil, Heavy Metals

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## 1. Introduction

Soil contamination by heavy metals is a major concern because at high concentration they can harm human life and the environment [1]. Some of the contributors to soil contamination include mining, steel and iron industry, smelting procedures, chemical industries, traffic, agriculture and domestic activities [2]. Once heavy metals are deposited in the soil, they are not degraded and persist in the environment for a long time and cause serious environmental pollution [3-5]. They accumulate in soils and plants and would have a negative influence on physiological activities of plants such as photosynthesis, gaseous exchange and nutrient absorption which result in plant growth reduction and dry matter accumulation [6-7]. There is a growing concern about the possibility of soil contamination resulting in uptake by plants and the introduction of elements in vital food chains affecting food safety [8]. Animals that graze on such contaminated plants and drink from polluted waters, as well as marine lives that breed in heavy metal polluted waters also accumulate these metals in their tissues and milk if lactating [9]. In small concentrations, traces of heavy metals

in plants or animals are not toxic except that cadmium, lead and mercury are toxic even at low concentrations [10-11].

Metals exist in a number of different soluble and particulate forms which influence their mobility and bioavailability [12-13]. Since their toxicity is related to their existing species, their speciation is increasingly attracting more attention [14]. To monitor soil contamination by heavy metals, the Environmental Protection Agency of the United States (USEPA) [8, 15], recommends that concentrated nitric acid be used as an extractant for the determination of total contents in soils even though the results do not often represent a good indication of bioavailability to plants [16]. Open beakers heated on hot plates, digestion tubes in a block digester and digestion bombs placed in microwave ovens are the most commonly used equipment to digest solid sample matrices [17]. Digestion of solid samples for elemental analysis is an established routine sample preparation method with the usage of nitric acid in a closed system under elevated temperatures and pressure and it has been used since 1860 [18]. The increasing improvement for element

determination in an extract, together with the evidence that exchangeable metals correlate better with plant uptake, has led to the development of single extraction methods which use less aggressive solutions [19-20]. Microwave-assisted sample digestion technique has been used since 1980s and is adopted by the EPA under EPA Methods 3051 and 3051a for extraction of metals from sludge, soil or sediments [18]. This method provides rapid, safe, and efficient digestion and is not prone to losses of volatile metals [21].

In the present study, five soil samples were treated by microwave assisted digestion and the resulting solutions were analysed by Inductive coupled plasma-optical emission spectroscopy (ICP-OES). This is due to the fact that ICP-OES has low detection limits, large dynamic range and high precision [18]. The objective of the present study is to provide information regarding accumulation of heavy metals in the soil of heavily industrialized Vanderbijlpark area of South Africa. Furthermore, information about heavy metal content in this area is scarce.

## 2. Experimental

### 2.1. Study Area

Vanderbijlpark (26°70S, 27°85E) is a classic example of an industrial township of the 20<sup>th</sup> century. It falls under Sedibeng municipality and is an industrial city next to the Vaal River in Southern Gauteng, South Africa. The economy of Sedibeng District Municipality has for the largest part of its existence been dominated by heavy manufacturing and still is the dominant feature of regional economy. There are two main subsector of manufacturing divided into fabricated metal and chemicals. In the metal sector, the Arcelor-Mittal (formerly ISCOR) steel plant, the Cape Gate Davsteel wire and steel plant and the ferromanganese plant of Samancor, are the three main large baseline plants in the District, while DCD-Dorbyl Heavy Engineering is the biggest manufacturer of massive engineered products in Southern Africa. SASOL, of which the primary plant in the District is based in the Metsimaholo Local Municipality in the Free State, is the major player in the chemical industry sector in the District [22].



Figure 1. Map showing study areas in Vanderbijlpark.

### 2.2. Sampling

The soils investigated in this experiment were sampled from Vanderbijlpark area of South Africa, which is known to be highly industrialized as shown on the map in Figure 1. At each sampling point, about 2 kg of soil at surface level (0-10

cm in depth) were collected. Three samples were collected in each point, thoroughly mixed in a clean container made of perfluoroalkoxy polymer (PFA) to obtain a representative sample. Collected soils were crushed and passed through a 2 mm sieve before stored in a labeled polythene bags prior to analysis.

### 2.3. Sample Preparation and Heavy Metal Determination

Samples were dried at 105°C for 3 hours. About 0.2 g of sample was accurately weighed into a container made of PFA which was then placed in a microwave pressure vessel. Sample preparations were done according to the method described by Moore et al. [23] without minor improvements. The digested samples were analysed for metals using an iCAP 6000 Perkin Elmer Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) from Thermo Electron Corporation (Cheshire, United Kingdom). Pump rate = 45 rpm, Nebuliser argon pressure = 0.3 L.min<sup>-1</sup>, Centre tube = 2 mm, RF forward power = 1150 W, Coolant gas flow = 12 L.min<sup>-1</sup>, Auxiliary gas flow = 0.5 L.min<sup>-1</sup> and Integration time = 15 sec. European soil certified reference material (EURO876-1 from Industrial Analytical in S.A.) was used to prepare a 1.000 g/L stock solution from which a series of standard solutions were prepared under the same experimental conditions as the samples to validate the method. Acceptable linear calibration graphs were produced and detection limits of the elements were determined from the averages of three repeat (3 times) analyses. In order to test the accuracy of the method, one gram of each soil sample was diluted with one gram of As, Bi, Cd, Co, Cu, Hg, Li, Mo, Ni, Pb, Sb, Se, Sn, V and Zn salts in separate beakers and digested. Glassware was soaked for 24 h in dilute (5% v/v) nitric acid, rinsed with distilled water and dried in an oven before use. A Consorte C862 benchtop conductivity/pH/DO meter with separate beakers was used to determine soil pH

using soil-water ratio of 1: 5

### 2.4. Data Analysis

Data obtained were analysed using Analyse-it® v.22, which is the statistical software for Microsoft Excel. Results are presented as  $\pm$  standard deviation. Statistical variations were considered significant at  $p < 0.05$ .

## 3. Results and Discussion

Limit of detection (LOD) and limit of quantification (LOQ) were calculated by using equations 1 and 2 respectively.

$$\text{LOD} = \frac{3 \times \text{SD}_{\text{blank}} \times \text{Conc.}_{\text{sample}}}{I_{\text{sample}} - I_{\text{blank}}} \quad (1)$$

$$\text{LOQ} = \frac{3 \times \text{SD}_{\text{blank}} \times \text{Conc.}_{\text{sample}}}{I_{\text{sample}} - I_{\text{blank}}} \times 10 \quad (2)$$

Where  $\text{SD}_{\text{blank}}$  is the standard deviation for the signal recorded on the blank for the element studied

Quality control study for the metals studied using the microwave assisted digestion method was obtained as percentage recoveries and are presented in Table 1. The percentage recoveries of these elements ranged from 43.5% to 112.3% with mercury being the lowest and nickel being the highest.

**Table 1.** The Limit of detection, Limit of quantification and average % recoveries of different elements.

Element (mg/L)	European soil certified reference material (EURO 876-1)				
	Limit of detection (LOD) (ppm)	Limit of quantification (LOQ) (ppm)	Experimental value (SD)	Theoretical value (SD)	Average % recovery
As	<0.00869	0.0674	0.13 (0.12)	0.16 (0.03)	92.8
Bi	<0.0093	0.0918	0.009 (0.01)	0.011 (0.005)	54.3
Cd	<0.0002	0.0018	0.88 (0.09)	0.89 (0.1)	95.9
Co	<0.0017	0.0137	9.96 (0.7)	9.98 (1.3)	100.76
Cu	<0.0017	0.0225	0.425 (0.04)	0.420 (0.2)	99.28
Hg	<0.0022	0.024	0.006 (0.001)	0.007 (0.001)	43.5
Li	<0.0013	0.0108	0.09 (0.01)	0.10 (0.04)	98.9
Mo	<0.0011	0.008	0.002 (0.003)	0.002 (0.001)	88.9
Ni	<0.0012	0.0106	2.44 (0.06)	2.46 (0.2)	112.3
Pb	<0.0032	0.0355	8.8 (0.14)	8.7 (1.6)	100.2
Sb	<0.0046	0.0387	0.003 (0.001)	0.0027 (0.002)	97.9
Se	<0.0088	0.0758	0.0001 (0.02)	0.0003 (0.0001)	89.4
Sn	<0.0133	0.0968	0.67 (0.1)	0.67 (0.01)	90.8
V	<0.0011	0.0116	0.11 (0.05)	0.12 (0.6)	99.8
Zn	<0.0031	0.0232	20.0 (0.04)	20.9 (4.8)	105.9

The results of the pH values and the total mean metal concentrations from five sampling points are presented in

Table 2 while the correlation of the metals is given in Table 4.

**Table 2.** Metals results of soil from 5 selected areas.

	Robot (mg/kg) n = 3, pH = 7.8	Farm (mg/kg) n = 3, pH = 6.9	Township school (mg/kg) n = 3, pH = 6.8	Iemas garage (mg/kg) n = 3, pH = 7.4	CE-5 (mg/kg) n = 3, pH = 7.1
As	0.0555 (0.002)	0.085 (0.009)	0.0658 (0.007)	0.0664 (0.007)	0.060 (0.02)
Bi	0.0896 (0.005)	0.169 (0.06)	0.0536 (0.01)	0.0578 (0.005)	0.0075 (0.004)
Cd	0.0103 (0.001)	0.0085 (0.0001)	0.0085 (0.001)	0.0159 (0.009)	0.0072 (0.003)
Co	0.0340 (0.003)	0.0112 (0.006)	0.0255 (0.008)	0.0188 (0.004)	0.0184 (0.009)
Cu	0.104 (0.02)	0.0631 (0.009)	0.172 (0.005)	0.0559 (0.005)	0.0557 (0.01)
Hg	ND	ND	ND	ND	ND
Li	0.0683 (0.004)	0.151 (0.007)	0.142 (0.06)	0.0924 (0.01)	0.0724 (0.02)
Mo	0.0174 (0.06)	0.0479 (0.008)	0.0414 (0.009)	0.0263 (0.004)	0.0243 (0.008)
Ni	0.0751 (0.005)	0.0366 (0.004)	0.056 (0.001)	0.0428 (0.002)	0.0417 (0.008)
Pb	1.15 (0.09)	5.261 (1.36)	2.922 (0.11)	2.577 (0.8)	2.388 (0.09)
Sb	0.0079 (0.0008)	0.0374 (0.007)	0.0371 (0.009)	ND)	ND
Se	ND	ND	ND	ND	ND
Sn	0.0466 (0.007)	0.0865 (0.008)	0.0890 (0.009)	0.0796 (0.008)	0.0538 (0.02)
V	0.0905 (0.005)	0.0659 (0.004)	0.104 (0.008)	0.132 (0.01)	0.0774 (0.07)
Zn	0.246 (0.09)	0.268 (0.09)	0.2784 (0.07)	0.245 (0.09)	0.195 (0.05)

ND = Not detected

In general, Table 2 shows that the metal levels at the robot decrease in the order Pb > Zn > V > Bi > Ni > Li > As > Sn > Co > Cu > Mo > Sb > Hg > Se; at the farm they decrease in the order Pb > Zn > Bi > Li > Sn > As > V > Cu > Mo > Sb > Ni > Co > Cd > Se > Hg; in the township school they decrease in the order Pb > Zn > Cu > Li > V > Sn > As > Ni > Bi > Mo > Sb > Co > Cd > Se > Hg; at the Iemas garage the decreasing order is Pb > Zn > V > Li > Sn > As > Bi > Cu > Ni > Mo > Co > Cd > Se > Hg > Sb and in the CE5 suburb the decreasing order is Pb > Zn > V > Li > As > Cu > Sn > Ni > Mo > Co > Bi > Cd > Sb > Se > Hg. The difference in the trend may be attributed to the fact that environmental dependent parameters are never static due to changes in temperature, pH and nature of human perturbation on the natural ecosystem [24]. The concentration of lead (Pb) was found to be high in all the sampling points compared to other studied metals. Its concentration was found to be 5.261 (1.36) ppm on the farm and lowest at the robot at 1.15 (0.09) mg/kg (Figure 1 and Table 3). The farm is not used for farming but as dumping site by a steel producing company in the area. The high levels of mercury might be due to these dumping activities. What is also noticeable from these results is that, soils with high pH values show high concentration of metals as can be noticed with the farm and the nearby school soils as shown in Table 2. Qishlaqi *et al.*, 2007 in their studies observed that soil samples with alkaline pH and high organic

matter content accumulate significant high concentrations of heavy metals compared with other soil samples [25]. However, metal such as lead have low solubility at pH range of 5.5-7.5 [24]. This might mean that the concentrations of lead obtained in this study might not be the true reflection of the actual concentration in the soil sample studied since the pH's of the soil samples were in the range 5.5-7.5 and above. The concentrations might be higher. All metals studied are below the minimum allowed concentrations in the soil from different countries and USEPA as can be seen in Table 3. Anthropogenic sources of Cu, Zn and V include coal burning in residential areas for cooking and space heating as well as burning during industrial alloy and smelting processes [26]. High levels of V can harm lungs, throat and eyes or cause death whilst Ni can affect the urinary tract, especially the kidneys and may lead to paralysis if not managed [27]. Lead has no known biological role [28]. Lead poisoning can cause learning disability, sterility and growth inhibition [29]. Sources of Pb includes paint in old houses, metal scrap yards and soil contaminated by leaded petrol since Pb is not biodegradable and stays long in the environment [30]. The presence of lead on the school grounds is of concern because learners play with the soil and some eat it. Continuous monitoring of metals, particularly those that are toxic in the soil is important since they can affect the health of people and animals if they enter the food chain.

**Table 3.** Value of Maximum Allowable limits for heavy metals in soil (mg/kg) from different countries [6].

Chemical element	Australia	Canada	Poland	Japan	Great Britain	Germany	US-EPA
Cd	5	8	3	-	3	2	85
Co	50	25	50	50	-	-	0.3-200
Cr	100	75	100	-	50	200	
Cu	100	100	100	125	100	50	4300
Ni	100	100	100	100	50	100	75
Pb	100	200	100	400	100	500	450
Zn	300	400	300	250	300	300	7500
As							75

**Table 4.** Correlation between metals.

	As	Bi	Cd	Co	Cu	Hg	Li
As	1	0.16	0.747	-0.9	-0.193	0	0.774
Bi	0.16	1	-0.12	-0.313	-0.098	0	0.475
Cd	-0.0553	-0.0208	1	-0.362	-0.268	0	-0.361
Co	-0.898	-0.299	-0.362	1	0.564	0	0.591
Cu	-0.1934	-0.0983	-0.289	0.564	1	0	0.301
Hg	0	0	0	0	0	0	0
Li	0.692	0.58	0.298	-0.591	0.301	0	1
Mo	0.799	0.524	0.317	-0.652	0.213	0	0.995
Ni	-0.915	-0.0909	-0.726	0.973	0.558	0	-0.511
Pb	0.829	0.96	0.385	-0.854	-0.192	0	0.867
Sb	0.422	0.686	-0.0635	-0.229	0.556	0	0.897
Se	0	0	0	0	0	0	0
Sn	0.794	0.743	0.665	-0.552	0.259	0	0.856
V	-0.0579	-0.308	0.575	0.26	0.156	0	-0.292
Zn	0.178	0.561	0.0827	0.039	0.598	0	0.624

**Table 4.** (Continue)

	Mo	Ni	Pb	Sb	Se	Sn	V	Zn
As	0.799	-0.915	0.829	0.611	0	0.794	-0.058	0.178
Bi	0.524	-0.0909	0.657	0.484	0	0.369	-0.398	0.627
Cd	-0.351	-0.0037	-0.221	0.395	0	0.157	0.844	0.124
Co	-0.652	0.973	-0.667	-0.408	0	-0.552	0.26	0.039
Cu	0.212	0.558	-0.192	0.235	0	0.259	0.156	0.598
Hg	0	0	0	0	0	0	0	0
Li	0.995	-0.511	0.867	0.698	0	0.856	-0.292	0.624
Mo	1	-0.562	0.911	0.691	0	0.844	-0.333	0.594
Ni	-0.562	1	-0.738	-0.349	0	-0.519	0.134	0.165
Pb	0.911	-0.738	1	0.616	0	0.731	-0.415	0.41
Sb	0.877	-0.349	0.616	1	0	0.945	0.375	0.815
Se	0	0	0	0	0	0	0	0
Sn	0.843	-0.519	0.731	0.945	0	1	0.221	0.713
V	-0.333	0.133	-0.415	0.374	0	0.221	1	0.156
Zn	0.594	0.165	0.411	0.815	0	0.713	0.156	1

The correlations between metals were evaluated to establish possible common sources. Positive correlations were established between Mo and Li ( $r = 0.995$ ); Pb and Mo ( $r = 0.911$ ); Ni and Co ( $r = 0.973$ ); Li and Pb ( $r = 0.867$ ); Sb and Sn ( $r = 0.945$ ); Zn and Sb ( $r = 0.815$ ); V and Cd ( $r = 0.844$ ); Bi and Pb ( $r = 0.96$ ); As and Pb ( $r = 0.829$ ) which suggests similar sources. However, some elements have positive correlation but their correlations were poor and suggested different sources (Table 4). Local anthropogenic sources linked to these elemental distributions include steel and metallurgical alloy making processes, road transport, industrial chemical reactions, coal and oil burning activities and windblown dust<sup>26</sup>.

## 4. Conclusion

Monitoring of elements in the soil provides an efficient way to assess their qualitative and quantitative concentrations at distinct locations. The distribution of different metal concentrations in the soils of the selected areas indicated that

these areas have been affected by the anthropogenic activities and some are from the same source as shown by the correlations of some metals. Furthermore, the experimental results indicate that the concentrations of the studied metals decrease with the distance far from the industrial area. Of all metals studied, lead (Pb) was found to be high but less than US-EPA allowable limits, particularly on the farm and the township school. This is of concern since lead has been reported to be harmful to humans and also affect the intelligence of children. As a result, more intensive sampling is necessary to monitor any change or increase of the studied metals in the investigated areas over time.

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