

Heavy Metals in Soils Associated with Fertilizers in Trinidad

Rosanna Beharry^{1*}, Andrea Joseph¹, Andre Gordon², Mitko Voutchkov²

¹Department of Physics, The University of the West Indies, St. Augustine, Trinidad and Tobago ²Department of Physics, The University of the West Indies, Mona, Jamaica Email: *rosanna.beharry@sta.uwi.edu

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Abstract

Heavy metals in agricultural soil pose human health risks through food consumption. In a novel study for Trinidad, concentration and pollution index levels of heavy metals were assessed from 18 agricultural farms using the X-Ray fluorescence technique, then to evaluate the Geo-accumulation and Nemerow's Integrated Pollution indexes. Toxic elements Pb and As were present but soil quality due to anthropogenic input was found as unpolluted. Overall heavy metal pollution was classified at a precautionary level for 33% of farms, slightly polluted for 61% and moderately polluted for 6% of the farms assessed, thus, regular monitoring and mitigation measures are important for food safety and human health in Trinidad.

Keywords

Heavy Metals, Pollution, Toxicity Level, Pollution Index, Agricultural Soil, Health Effects

1. Introduction

Agricultural soil requires essential micronutrients and macronutrients for efficient plant growth and development (Imran & Gurmani, 2011; Reddy et al., 2013). However, over time, continuous farming depletes nutrients in soil and as a result, fertilizers are used by farmers worldwide. One type of commonly used fertilizer is a nitrogen-phosphorus-potassium (N-P-K) fertilizer. Its composition combines primary macronutrients that are important for the metabolic functions of a plant.

In spite of this, improper use of fertilizers and pesticides can contaminate agricultural soil with potentially toxic heavy metals causing agricultural soil a source of pollution (Reddy et al., 2013). This is because phosphate fertilizers are

manufactured from phosphate rocks (Hassan et al., 2018; Sahu et al., 2019) that contain toxic heavy metals, such as Cd, Pb, Hg, Cr and As (Dissanayake & Chandrajith, 2009). Since heavy metals do not undergo any ecological processes, these elements accumulate within the soil over time (Adedeji et al., 2019; Huang & Jin, 2008; Shifaw, 2018) and can be transferred from plants to humans through the food chain (Dissanayake & Chandrajith, 2009; Reddy et al., 2013). Consumption and exposure to these elements owing to polluted agricultural soil can cause potential health risks to humans (Todorović et al., 2014). At-risk humans include farmers who are in frequent contact with phosphate fertilizers, and persons who consume these food products as they may be susceptible to acute or chronic heavy metal toxicity (Giuffré et al., 2012; Sahu et al., 2019). Around the world, the presence of heavy metals in soil is of great concern. Studies have been done to assess how the accumulation of heavy metals can impact soil quality and human health. For instance, a study was done to review heavy metal pollution in China owing to agriculture, rapid urbanization and industrialization (Shifaw, 2018). Recognising this as a potential problem, nationwide surveys were conducted over 70% of China's land area between 2005 and 2013 to assess soil quality (Shifaw, 2018). Based on Nemerow's integrated pollution index (NIPI), almost 53% of China's provinces were moderate to heavily polluted resulting in polluted green plants and grain products.

Another study conducted in China in 2019 analysed and evaluated heavy metal pollution in agricultural soils in six cities of Hunan Province. This is one of the most important rice-producing areas in China, but it is located along the polluted Xiangjiang River. Heavy metal assessment was done on soil and rice using a Potential Ecological Risk Index (PERI) and Nemerow's comprehensive pollution index. The area of interest was ranked as highly polluted using NIPI and at medium-level risk according to the PERI evaluation based on the high levels of Cd in the soil. This affected the quality of the rice and it was suggested that increased monitoring should be done in that location (Yu et al., 2019).

In Nigeria in 2019, Adedeji et al. (2019) examined the spatial distribution of seven heavy metals, and conducted a health risk assessment of soil pollution by these metals in Ijebu-Ode. This was done because it was found that there was insufficient research that examined potential health impacts of polluted soil in Nigeria (Adedeji et al., 2019). This study estimated human health risks based on heavy metal (Cd, Cr, Cu, Mn, Ni, Pb and Zn) concentrations using GIS and multivariate statistics. Soil samples were taken randomly from various land types to represent the entire city and elemental analysis was determined using an atomic absorption spectrometer. Pollution analysis was done using Enrichment Factor (EF) and Geo-accumulation index (I_{geo}) and it was found that most of the land use area in Ijebu-Ode was substantially contaminated except for Ni. It was also noted that soils found with a low pH had the potential to increase heavy metal mobility. Unlike the other heavy metals assessed, a potential cancer risk was found for Cu, Mn, Pb and Zn.

Within the Caribbean, limited research has been done to assess heavy metals in agricultural soil, Jamaica being the only island that has assessed the levels of radioactivity and heavy metals in soil (Lalor et al., 1995). A geochemical atlas of Jamaica was created by analysing 35 elements using neutron activation, X-ray fluorescence (XRF), and optical emission spectrometry in 1995 (Lalor et al., 1995). This was done because little geochemical mapping had been done in Caribbean islands and Jamaica has a large land area covered with limestone that contains traces of heavy metals.

In other parts of the Caribbean, heavy metal contamination is commonly assessed in coral reefs, fishes, and marine sediments (Fernandez-Maestre & Johnson-Restrepo, 2018; Guzmán & Jiménez, 1992) but no studies were found on heavy metal assessment in agricultural soil.

This study aims to assess the heavy metal pollution of agricultural soils associated with fertilizers from selected farming areas in Trinidad, and to discuss the potential food safety and health issues.

2. Method

Agricultural soil samples were taken from 18 registered farmers located in eight zones in Trinidad as shown in **Figure 1**. A questionnaire was used at each farm to collate information on farming practices, types of crops grown, personal protective equipment customarily used, and any health effects farmers may have experienced as a result of their farming practices.

2.1. Soil Sampling

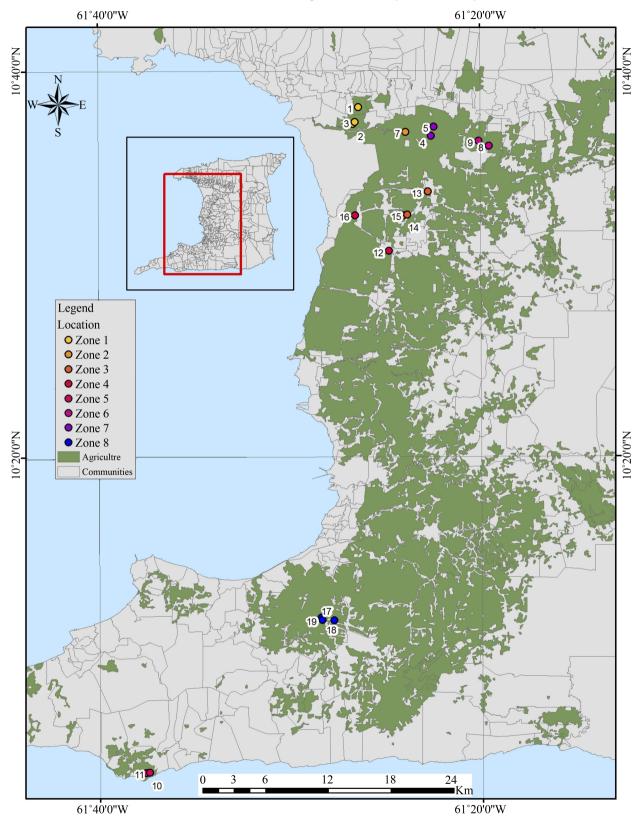
Soil samples were taken from two soil layers at each farm: the topsoil layer and subsoil layer (Adedeji et al., 2019; Mirecki et al., 2015) and GPS coordinates were recorded using a GARMIN GPSmap 62 GPS. Each subsample was properly packaged and labelled to indicate the date, county, farm number, depth of soil, subsample number, and subsample GPS coordinates. One control soil sample was taken from the subsoil layer at the centre of each farm (Lalor et al., 1995).

2.2. Soil Preparation and Elemental Analysis

Agricultural soil subsamples from each farm were mixed to create a homogenous composite sample (IAEA-TECDOC-1415, 2004). This mixed sample was oven dried at 80°C until a constant weight was obtained. The dried sample was then ground and sieved at 2 mm (Mueller, 2013). This process was repeated for the control soil samples. All soil (agricultural and control) and fertilizer samples were analysed using an X-Ray Fluorescence (XRF) Thermo Fisher Scientific Niton Analyzer XL3 Analyzer for the following elements: Pb, As, Zn, Cu, Fe, Mn, Cr and V.

2.3. Statistical Data Analysis

Soil pollution was assessed using Geo-accumulation Index (I_{geo}), Equation (1)



Location of Farms in relation to Agriculture areas (Landuse 2007)

Figure 1. Eighteen agricultural locations in Trinidad. Farms identified using the same colour are listed within the same farming zone.

(Müller, 1979; Nowrouzi & Alireza, 2015) and Nemerow's Integrated Pollution Index (NIPI), Equation (2) (Shifaw, 2018; Yu et al., 2019).

$$I_{geo} = \log_2\left(\frac{Cn}{1.5Bn}\right) \tag{1}$$

where *Cn* is agricultural soil concentration and *Bn* is control soil concentration.

$$NIPI = \sqrt{\frac{PI_{avg}^2 + PI_{max}^2}{2}}$$
(2)

where PI is Pollution Index (Shifaw, 2018),

$$PI = \frac{Cn}{Bn}$$
(3)

Elemental concentrations were normalized between 0 and 1 using Equation (4) (Lakshmanan, 2019).

Normalization =
$$\frac{\text{conc. Of element} - \min. \text{ conc of element}}{\max. \text{ conc. of element} - \min. \text{ conc of element}}$$
 (4)

Before normalizing, the outlier concentrations were removed for each heavy metal.

2.4. Classification of Heavy Metal Assessments

Percentiles were used to categorize the elemental concentrations. Less than the 25th percentile was categorized as Low (<0.25), between the 25th and 75th percentile was Medium (0.25 \leq Toxic Index \leq 0.75), and greater than the 75th percentile was High (>0.75). Classification for I_{geo} was Low for $I_{geo} < 0$, Medium 0 < $I_{geo} < 1$ and High $I_{geo} > 1$. Classification for *NIPI* was Low for *NIPI* < 1.00, Medium 1.00 \leq *NIPI* \leq 1.25 and High *NIPI* > 1.25.

3. Results and Discussion

Data collected came from Farms 1 - 5 and Farms 7 - 19. From the questionnaires, all farmers participating in the study were males and within the age range from 26 years to greater than 60 years. Farms were in agricultural use for a period of 1 - 10 years to greater than 50 years, with 32% in agricultural use for a period of 11 - 20 years.

A full spectrum analysis using XRF found fifteen elements in the 36 soil samples (18 control soil samples and 18 homogenous composite agricultural soil samples). This included toxic elements, micronutrients, macronutrients, and other elements. Toxic elements found were Pb and As. The essential micronutrients and macronutrients identified were Zn, Cu, Fe, Mn, Cr, Ca, and K. Other elements found were Mo, Zr, Sr, Rb, V, and Ti. For this study, eight heavy metals were used to assess the level of soil pollution: Pb, As, Zn, Cu, Cr, Fe, Mn and V. The XRF limit of detection used for the heavy metals were Pb < 5.00 mg·kg⁻¹, As < 4.00 mg·kg⁻¹, Cu < 10.00 mg·kg⁻¹, Mn < 35.00 mg·kg⁻¹, Cd < 10.00 mg·kg⁻¹ and Hg < 6.00 mg·kg⁻¹.

Average concentrations were found for each heavy metal in agricultural and control soils, respectively (see **Table 1**). As noted in the table, the average concentrations of Pb, Cu, Zn, Fe, Mn and Cr were found to be lower in the agricultural soil when compared to the control soil except for As where the average was slightly higher in the agricultural soil.

Soil has three main layers, the topsoil (A horizon), subsoil (B horizon), and bedrock or parent rock (C horizon). Agricultural soil samples were taken from the topsoil layer which can often be prone to flooding and weathering due to atmospheric deposition, such as rain, aerosols, dust fallout, and gas movement from the atmosphere to the earth. Also, topsoil can be loose and porous allowing movement of water and air; as a result, this layer of soil can be dynamic, causing the concentration of elements to continuously change. These characteristics in agricultural soil (topsoil) may be the reason the average concentration values were lower in the agricultural soil. However, the control soil samples were taken from the subsoil layer which is more compact, thus, limiting continuous changes in soil concentration. This layer can represent the accurate elemental concentration of the soil (Lalor et al., 1995).

As seen in **Figure 2**, the highest concentration for toxic element Pb was found to be 107.57 mg·kg⁻¹. This was an outlier value found in the control soil of Farm 1 which was higher than the World Health Organization (WHO) recommended value of 85 mg·kg⁻¹. There were four additional outlier values for Pb found in Farms 1, 2, and 3. Although these values were within the WHO's acceptable limits, they were numerically higher than other values from the data set, see **Figure** 2. These elevated values were found in farms from a zone which was located close to a major highway in Trinidad. For many years, leaded gasoline was used in Trinidad until legislation was passed in 2004, after which it was phased out (Enill, 2003). As a result, fumes from the leaded gasoline may have contributed

Table 1. Comparison of average values for agricultural and control soil in Trinidad anddesirable maximum levels of elements in unpolluted soils (Osmani et al., 2015; Toth et al.,2016).

Element –	[†] Average (^{††} Assess as (mag log-1)			
	Agriculture Soil	Control Soil	— ^{††} Average (mg·kg ⁻¹)		
Pb	7.63	7.83	85.00		
As	11.74	11.71	20.00		
Cu	29.06	33.93	36.00		
Zn	116.14	119.66	50.00		
*Fe (%)	2.48	2.87	3.80		
*Mn (%)	0.02	0.03	0.08		
Cr	61.09	68.60	100.00		
V	135.97	148.13	100.00		

*Fe and Mn (%)-concentration divided by 10,000; [†] This Study; ^{††} WHO/EU/World.

☐ Fe	□ Zn	□ Cr	🗆 Cu
60000.00	250.00	250.00	120.00
50000.00	200.00	200.00 °	100.00 <u> </u>
40000.00	150.00	150.00	80.00
30000.00			60.00
20000.00			40.00
10000.00	50.00	50.00	20.00
0.00	0.00	0.00	0.00
🗆 Mn		□ As	🗆 РЬ
1400.00	250.00	40.00	120.00
°	200.00	35.00	°
1000.00		30.00	80.00
800.00	150.00	20.00	60.00 °°
600.00	100.00	15.00	40.00
	50.00	10.00	20.00
200.00		5.00	
0.00	0.00	0.00	0.00

Figure 2. Box and whisker plot for concentrations of heavy metals Fe, Zn, Cr, Cu, Mn, V, As and Pb.

to residual Pb accumulation in these farms as compared to the other selected farms in Trinidad. Similarly, high Pb concentration was also linked to traffic emissions in Nigeria indicating that these emissions were a potential source of contamination (Adedeji et al., 2019). Additionally, in Trinidad, farms in this zone have been in agricultural use for more than 40 years. Since Pb can be a toxic impurity found in phosphate fertilizers, usage over time can cause accumulation of Pb in the soil. Also, over the years, this zone has become urbanized with the development of a lot of businesses. Studies have shown higher levels of heavy metals, such as Pb, in urban soil (Adedeji et al., 2019; Shifaw, 2018). Pb can be a mobile heavy metal that moves from a plant's roots to its leaves (Nowrouzi &

Alireza, 2015) and can be ingested via food and drink. Once absorbed into tissues of the body, Pb can cause various adverse health effects to humans. Pb toxicity affects the gastrointestinal, renal, and haemopoietic organs as well as the nervous system. Acute signs of Pb poisoning include anorexia, dyspepsia, constipation, and paroxysmal abdominal pain. It is also known that Pb can be transferred from mothers to the foetus through the placenta and if a person has a calcium or iron deficiency, Pb uptake can be favoured (Smith & Steinmaus, 2009). Pb can accumulate and be stored in bones over time, where it can be redistributed into the human body. Pb ions can also interfere with the DNA repair system and disrupt the transcription process by replacing the Zn ions necessary for these processes to take place (Engwa et al., 2019).

Arsenic, another toxic element, was found to be higher in concentration than the acceptable limit of 20 mg·kg⁻¹ (Toth et al., 2016) in 5 soil samples from the agricultural and control soil samples for Farms 1 and 2, and the control soil sample for Farm 13. However, from the box and whiskers plot (Figure 2), three values were considered outliers. Farms 1 and 2 have been in agricultural use for over 40 years and farmers have used fertilizers and pesticides routinely over the years for plant growth and development. According to Atafar et al. (2010) and Huang and Jin (2008), As is a toxic impurity found in phosphate fertilizers. Some pesticides also contain levels of As, therefore, continuous use of these products may cause an accumulation in soil, resulting in higher than average values. Arsenic pollution can occur through air, water, and soil; and ingestion of As can affect early child development resulting in stillbirths, reduced birth weight, congenital birth defects, repress mental development of children and cancer (Murphy et al., 2019; Smith & Steinmaus, 2009). Adult exposure to As can cause lung cancer, acute myocardial infarction, skin lesions, and keratosis. Information obtained from questionnaires showed that 10.5% farmers experienced acute symptoms of skin lesions after handling fertilizers and pesticides. This may be due to levels of As in the products used, therefore, monitoring of fertilizer composition is recommended.

Cu is a heavy metal and an essential micronutrient needed for human consumption but in minimal amounts (Reilly, 2002). However, overexposure to Cu over time can cause health effects, such as irritation to the nose, mouth and eyes, headaches, dizziness, nausea, and diarrhea (ATSDR, 2004) because Cu can destroy red blood cells. Cu has also been found to cause DNA strand breaks with oxygen free radicals (Engwa et al., 2019). As shown in **Table 1**, the average Cu concentration in agricultural and control soils in Trinidad was within the acceptable, desirable level for unpolluted soil set by the WHO of 36 mg·kg⁻¹. However, 13 soil samples recorded higher than the acceptable Cu concentration, only one of which (96.80 mg·kg⁻¹) was considered an outlier from the box and whiskers plot seen in **Figure 2**. Farms 1, 2, 3, 11, and 13 recorded concentration values between 41.31 to 96.80 mg·kg⁻¹.

From fertilizers tested, it was found that the N-P-K (12-12-17) and potash contained a substantial Cu concentration (see Table 2). Thus, use of these fertilizers

Element Concentration of Fertilizer (mg·kg ⁻¹)											
Fertilizer	Pb	As	Hg	Zn	Cu	Ni	Fe	Mn	Cr	Cd	V
N-P-K (R)	<lod< td=""><td>10.92</td><td><lod< td=""><td>307.84</td><td><lod< td=""><td>32.58</td><td>6938.35</td><td>203.49</td><td>87.78</td><td><lod< td=""><td>40.33</td></lod<></td></lod<></td></lod<></td></lod<>	10.92	<lod< td=""><td>307.84</td><td><lod< td=""><td>32.58</td><td>6938.35</td><td>203.49</td><td>87.78</td><td><lod< td=""><td>40.33</td></lod<></td></lod<></td></lod<>	307.84	<lod< td=""><td>32.58</td><td>6938.35</td><td>203.49</td><td>87.78</td><td><lod< td=""><td>40.33</td></lod<></td></lod<>	32.58	6938.35	203.49	87.78	<lod< td=""><td>40.33</td></lod<>	40.33
Potash	33.27	12.18	20.53	122.72	59.79	200.51	1035.9	312.53	15.41	46.59	<lod< td=""></lod<>
N-P-K (F)	<lod< td=""><td>9.93</td><td><lod< td=""><td>42.22</td><td><lod< td=""><td><lod< td=""><td>3972.77</td><td>38.91</td><td><lod< td=""><td><lod< td=""><td>15.21</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	9.93	<lod< td=""><td>42.22</td><td><lod< td=""><td><lod< td=""><td>3972.77</td><td>38.91</td><td><lod< td=""><td><lod< td=""><td>15.21</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	42.22	<lod< td=""><td><lod< td=""><td>3972.77</td><td>38.91</td><td><lod< td=""><td><lod< td=""><td>15.21</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>3972.77</td><td>38.91</td><td><lod< td=""><td><lod< td=""><td>15.21</td></lod<></td></lod<></td></lod<>	3972.77	38.91	<lod< td=""><td><lod< td=""><td>15.21</td></lod<></td></lod<>	<lod< td=""><td>15.21</td></lod<>	15.21
N-P-K (12-12-17)	<lod< td=""><td>5.25</td><td><lod< td=""><td>1088.43</td><td>214.94</td><td>60.8</td><td>680.65</td><td>327.78</td><td><lod< td=""><td>18.17</td><td>8.31</td></lod<></td></lod<></td></lod<>	5.25	<lod< td=""><td>1088.43</td><td>214.94</td><td>60.8</td><td>680.65</td><td>327.78</td><td><lod< td=""><td>18.17</td><td>8.31</td></lod<></td></lod<>	1088.43	214.94	60.8	680.65	327.78	<lod< td=""><td>18.17</td><td>8.31</td></lod<>	18.17	8.31
N-P-K (YM)	<lod< td=""><td><lod< td=""><td><lod< td=""><td>143.7</td><td>22.65</td><td>41.65</td><td>2027.33</td><td>365.37</td><td>99.22</td><td>10.09</td><td>102.4</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>143.7</td><td>22.65</td><td>41.65</td><td>2027.33</td><td>365.37</td><td>99.22</td><td>10.09</td><td>102.4</td></lod<></td></lod<>	<lod< td=""><td>143.7</td><td>22.65</td><td>41.65</td><td>2027.33</td><td>365.37</td><td>99.22</td><td>10.09</td><td>102.4</td></lod<>	143.7	22.65	41.65	2027.33	365.37	99.22	10.09	102.4
Calcium Nitrate + Boron	<lod< td=""><td><lod< td=""><td><lod< td=""><td>6.26</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>6.26</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>6.26</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	6.26	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Calcium Nitrate	<lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>

Table 2. Elemental concentration of seven fertilizers commonly used in Trinidad.

may have contributed to Cu accumulation in agricultural soil resulting in elevated concentrations. Also, according to Huang and Jin (2008), the use of manure can cause Cu concentrations to be higher in some farms because trace amounts of Cu may be present in feed used in livestock diets. Based on the questionnaires, Farm 1 used the 12-12-17 (N-P-K) fertilizer and Farm 13 used pen/chicken manure as fertilizers.

Zn is a commonly used heavy metal in the composition of fertilizers, and it is an essential element needed for both plant development and human nutrition. According to Shifaw (2018), water irrigation, manure and chemical fertilizers are anthropogenic sources that can increase Cu and Zn in agricultural soil. From **Table 1**, the average concentration of Zn in Trinidad exceeded the recommended limit set by the WHO of 50 mg·kg⁻¹. Only 4 soil samples had concentrations below 50 mg·kg⁻¹. Zn was present in six of the seven fertilizers analysed, with the highest concentration of 1088.43 mg·kg⁻¹ found in the N-P-K (12-12-17) fertilizer (see **Table 2**). It can, therefore, be inferred that use of this type of fertilizer in agricultural soil can contribute to the increased Zn concentration observed. According to the Food and Agricultural Organization (FAO), although Zn is beneficial to human health, consumption at high concentrations of 4 - 8 g could lead to adverse health issues. Toxicity signs include nausea and vomiting, fever, and lethargy (FAO/WHO, 2001). Excess Zn can be excreted through bile and other intestinal secretions to maintain homeostasis (Roohani et al., 2013).

Cr, a potentially toxic element, has a high penetrating power and exposure can be through inhalation, absorption through the skin, and ingestion, therefore, personal protective equipment is essential when handling products that include this element (Were et al., 2014). The average Cr concentration in agricultural and control soils were found within the acceptable limit set by the WHO of 100 mg·kg⁻¹ (see **Table 1**). However, seven soil samples in Farms 2, 3, 17, and 18 exceeded this limit. As noted in **Table 2**, fertilizer analysis showed that N-P-K (YM), N-P-K (R) and the potash fertilizers contained levels of Cr. Farms 2, 17 and 18 used the fertilizers N-P-K (YM) and a composition of N-P-K (R) fertilizer. It can, therefore, be inferred that use of these types of fertilizers may have contributed to higher Cr concentration in agricultural soil in these farms. Long-term exposure to Cr can affect the liver and kidney (Toth et al., 2016) but according to the WHO, although Cr is considered carcinogenic, there has been no evidence to support that Cr in food is dangerous to human health (Reilly, 2002).

Fe and Mn are common elements found in the earth's crust and play an important role in functions of the human body. There were no acceptable limits set by the WHO for these elements. As such, concentrations of Fe and Mn in Trinidad were compared with world averages and were found to be lower than acceptable limits. The human body has developed a mechanism to keep the Fe levels balanced and to prevent Fe deficiency or too much Fe in the body, such as loss of dead skin or mucosal cells and loss of menstrual blood in women. This mechanism is also determined by the degree to which red blood cells are produced in the body (Means, 2014). Mn is an essential micronutrient for human consumption as it functions as an enzyme activator. It is necessary for enzymes, such as arginase, hexokinase, superoxide dismutase, and xanthine oxidase. Mn toxicity can affect humans mainly through inhalation rather than ingestion and the WHO has indicated that only a few cases of Mn toxicity have occurred due to ingestion. However, when Mn is inhaled, the heavy metal may reach the central nervous system causing neurological disorders such as tremors, difficulty walking, and facial muscle spasm (WHO, 2000). This may be because Mn has been found to accumulate in the mitochondria neuron disrupting adenosine triphosphate (ATP) synthesis that can cause oxidative stress by generation of free radicals. Oral intake of Mn can often be excreted through bile and not linked to health effects (Reilly, 2002). Both Fe and Mn concentrations were present in 5 fertilizer samples. They were found in all the N-P-K and potash fertilizers, but they were not present in the calcium nitrate fertilizers.

V is not an essential nutrient for human health (Harland & Harden-Williams, 1994). It can be found in fossil-fuel combustion and exposure can be through air, drinking water and ingesting food. The significant entry of V is through the lungs, but its rate of absorption depends on its chemical nature. From **Table 1**, average concentration levels of V in agricultural and control soils in Trinidad were found to be higher than a world average of 100 mg·kg⁻¹. Acute and chronic symptoms of V are linked to bronchitis, pneumonia, cancer and heart disease (WHO, 2000). V has a similar structure to phosphates, and when absorbed into the body, it can simulate phosphate metabolism by replacing phosphate in the process. V can also cause direct and indirect damage to DNA and interfere with DNA repair due to oxidovanadium hydroxide formation of an oxygen species (Rehder, 2013; WHO, 2000). V was found in all N-P-K fertilizers tested but none in the potash and calcium nitrate fertilizers, as seen in **Table 2**.

Soil pollution was assessed using I_{geo} and NIPI (see **Table 3**). I_{geo} values ranged from -2.59 to 0.82 for 18 farms in Trinidad. This is equivalent to uncontaminated to moderately contaminated soil quality based on the classification index

	I_{geo}							NIDI	
Location	Pb	As	Zn	Cu	Fe	Mn	Cr	V	NIPI
Farm 1	-0.98	-0.89	-0.83	-0.95	-0.93	-1.38	-1.25	-0.82	0.80
Farm 2	-0.48	-0.72	-0.44	-0.65	-0.63	-0.58	-0.58	-0.49	1.06
Farm 3	-2.59	-1.29	-2.33	-0.39	-2.63	-0.58	0.15	-2.14	1.27
Farm 4	-0.77	-0.56	-0.32	-1.32	-0.63	-0.95	-0.70	-0.66	1.07
Farm 5	-0.58	-1.03	-1.18	-0.78	-1.05	-1.14	-1.28	-1.06	0.88
Farm 7	-0.78	-0.64	-0.56	-0.63	-0.60	-0.62	-0.59	-0.62	0.99
Farm 8	-0.58	-1.03	-0.65	-1.00	-1.04	-0.58	-0.85	-0.91	0.93
Farm 9	-0.58	0.55	-0.59	-0.96	-0.86	-0.58	-0.20	-0.98	1.74
Farm 10	-0.83	-0.47	-0.51	-1.46	-0.56	-0.72	-0.75	-0.52	1.01
Farm 11	-0.44	-0.69	-0.41	-0.81	-0.75	-0.58	-0.67	-0.58	1.06
Farm 12	-0.28	-0.88	-0.69	-0.58	-0.72	-0.81	-1.01	-0.79	1.09
Farm 13	-0.58	-1.00	-0.61	0.02	-0.89	-1.01	-0.80	-0.93	1.26
Farm 14	-0.58	-0.28	-0.46	-0.58	-0.58	-0.02	-0.57	-0.40	1.31
Farm 15	-0.58	-0.82	-0.88	0.82	-0.71	-2.85	-0.59	-0.51	2.01
Farm 16	-0.58	-0.53	-0.66	-0.48	-0.74	-1.20	-0.98	-0.77	1.00
Farm 17	-1.02	-0.82	-0.29	-0.35	-1.07	-2.29	-0.20	-0.28	1.14
Farm 18	-1.01	-0.09	-0.54	-0.89	-0.61	-0.58	-0.46	-0.54	1.22
Farm 19	-0.46	-0.45	-0.39	-0.20	-0.43	-0.32	-0.65	-0.60	1.21

Table 3. *I*_{geo} values for eight heavy metals Pb, As, Zn, Cu, Fe, Mn, Cr, and V for 18 farms in Trinidad.

for I_{geo} (Müller, 1979; Shifaw, 2018; Yu et al., 2019). Some of the lowest I_{geo} values were discovered in Farm 3. This farm was located alongside a river tributary and was affected by a major flood in 2018. As a result, the topsoil may have been washed away during the flood which resulted in minimal anthropogenic contribution at the time of sampling. The lowest Cu I_{geo} was discovered in Farm 10, where it was observed that the Cu concentration in the control soil was higher than in the agricultural soil. This farm was located in a zone that experienced a major earthquake in 2018, causing significant land movement. This occurrence may have contributed to the anomaly observed. The lowest Mn I_{geo} was found in Farm 15. Here, it was observed that the concentration of Mn was below the limit of detection in the agricultural soil but not in the control soil, resulting in the low value calculated. The lowest Cr I_{geo} was found in Farm 5. It was also observed that Cr levels were higher in the control soil when compared with the agricultural soil, resulting in the low value calculated. All I_{geo} values for Pb, Zn, Fe, Mn and V were below zero, this led to an uncontaminated classification for these metals based on the I_{geo} classification index (Müller, 1979; Shifaw, 2018; Yu et al., 2019). However, based on the I_{geo} values for As, Cu, and Cr, the soil quality classification for these metals was found to be uncontaminated to moderately contaminated.

The highest As Igeo was discovered in Farm 9, but all other farms were found with Igeo values less than zero and were classified as uncontaminated (see Table 3). A wide range of fertilizers, including rooting spray, seaweed fertilizer, N-P-K fertilizer, and liquid fowl litter was used in Farm 9. The fertilizers input amounted to approximately 200 kg/acre every 1 - 2 weeks for a 2-month crop cycle. Based on questionnaires, farmers from this location experienced nausea, headaches, nervousness (trembling), and muscle cramps after handling pesticides. These are some symptoms that can potentially be related to acute As poisoning and exposure. As a result, the large amounts of fertilizers and pesticides used at this farm may have contributed to the moderate pollution index found. Also, while Farms 15 and 13 were uncontaminated to moderately contaminated for Cu, the highest Cu Igeo was found in Farm 15. These farms used chicken manure/pen manure and other salt and spray fertilizers. As noted before, manure has been found to contain traces of Cu which is known to be used in animal feed. Therefore, the inclusion of manure at these farms may have contributed to the higher Cu concentration than other unpolluted farms (Huang & Jin, 2008). Farm 3 was found to be moderately contaminated with respect to Cr. This farm used several types of organic fertilizers. No testing was done on these fertilizers but according to Ciavatta et al. (2012), Cr can be present in organic fertilizers derived from tannery industries. Other commonly used fertilizers with levels of Cr included N-P-K (R), potash, and N-P-K (YM). It was also possible that previous flooding in this location may have caused topsoil with higher Cr concentrations to settle in this farm, causing an elevated Cr concentration.

NIPI assessed the overall pollution of heavy metals at each farm (Kowalska et al., 2018; Shifaw, 2018). From **Table 3**, the NIPI values ranged from 0.80 to 2.01. Based on Nemerow's classification, six farms were ranked at a precautionary domain, 11 farms were slightly polluted, and one farm was moderately polluted (Müller, 1979; Shifaw, 2018; Yu et al., 2019). The lowest NIPI value of 0.80 was found for Farm 1, indicating a precautionary level for this farm. Although Farm 1 recorded some relatively high heavy metals concentrations, these values were higher for both the agricultural and control soil causing the NIPI value to be lower than other farms. The highest value was found in Farm 15 with an NIPI value of 2.01, indicating a moderate level of pollution for this farm. This is observed as a result of a high Cu concentration in that farm.

Overall pollution levels varied throughout the country and a disparity in farming practices may have contributed to this finding. Farmers in Trinidad all have different farming techniques based on experiences gained over the years, and on knowledge gleaned from mentors and older family members. Two farmers indicated that they were certified by a local corporation which educates farmers on trade protocols and keeps them informed of fair agricultural production regulations. As a result, those farms must be inspected for pest and disease concerns before a recommendation can be made to obtain a farm certificate. However, this is not necessary for farmers selling crops locally, therefore, the lack of standards and protocols may impact the quality of farming practices. Other factors which may have contributed to the variation in pollution levels include farming practices being utilized at the time of soil sampling, the types of soil used for farming, the location of farms, the quality of fertilizers, and the types of crops planted.

Table 4 compares the average toxic index for elemental concentration between agricultural and control soil samples. It was found that toxicity levels were comparable for both types of soils. However, from the I_{geo} analysis, based on the anthropogenic input into the soil, 77.8% of the farms were assessed to be at a low toxicity level and 22.2% of the farms at medium toxicity level. No farms were found to have a high toxicity level. From the NIPI analysis, which is based on an overall heavy metal assessment, 27.8% of Trinidad's farms were found to have a high toxicity level, 44.4% a medium toxicity level, and 27.8% a low toxicity level. This trend was also observed in Shaifaw's study where NIPI levels highlighted higher risk levels than I_{geo} (Shifaw, 2018). This can show a clear insight into the quality of agricultural soil because the index considers both average and maximum elemental concentrations.

Farmers in Trinidad typically use multiple fertilizers, with toxic heavy metals being present in more than one of them. From the questionnaires, farmers stated that they commonly use an N-P-K fertilizer together with potash and a Ca fertilizer for plant growth and development. This practice can cause the accumulation of heavy metals in, and, thus, potential contamination of, agricultural soil. These findings can suggest a growing risk of heavy metals entering the body if agricultural pollution continues. In addition, there is no formal assessment in Trinidad of the quality of fertilizers imported into the country, and commercial resellers often repackage fertilizers and sell without a safety sheet or a content of elements present in the fertilizer.

Table 4. Summary of three heavy m	tal assessments:	elemental ana	lysis for agricultural
and control soil, <i>I</i> geo and <i>NIPI</i> .			

Percentage (%) of farms ranked as Low, Medium, and High for toxicity levels								
Low Medium High Outlier								
Toxic Average (Agricultural Soil)	34.72	47.22	14.58	3.47				
Toxic Average (Control Soil)	28.47	52.08	14.58	5.56				
I_{geo}	77.8	22.2	0.0	-				
NIPI	27.8	44.4	27.8	-				

4. Conclusion

Overall soil pollution levels in farms were found to be at a precautionary level to moderate pollution in all farms, thus reducing the quality of food safety. Continuous exposure and consumption of these heavy metals can lead to adverse acute and chronic health effects over time. The concentration of toxic elements Pb and As appeared to be high in Farms 1, 2, and 3, this was related to high traffic in that area and the high extent of agricultural use. In addition, Pb concentration in Farm 1 was higher than the acceptable limit set by the WHO, while Farms 1, 2, and 3 had As concentration higher than the limit set by the European community for agriculture. Cr concentration was higher than the acceptable limit set by WHO in Farms 2, 3, 17 and 18 and Zn concentrations were higher than the acceptable level set by WHO for all farms. An average toxic index presented showed approximately one-third of the farms had a low toxicity level, approximately half had a medium toxicity level, 13.5% had a high toxicity level, and 4.0% exceeded acceptable limits for agricultural soil. The Igeo, for As, Cu, and Cr, indicated that soil quality was classified as uncontaminated to moderately contaminated in 22.2% of the farms while an overall pollution index indicated a precautionary level to moderately polluted levels. Concentration values varied for individual farms which reflected farming practices, types of crops grown, and soil geology at each location.

It is extremely important to monitor levels of heavy metal in agricultural products and soil; the following are recommendations to be considered:

1) Continuous soil monitoring for heavy metals: Government ministries should monitor heavy metal concentration over time to assess how heavy metal may accumulate in agricultural soil.

2) Assessment of quality of fertilizers imported: It is important to assess the quality of fertilizers entering the country since fertilizers manufactured in some countries can contain toxic by-products.

3) Education and Training: Farmers should be educated on fertilizer usage and soil remedial strategies.

4) Development of permissible levels for unpolluted soil: To ensure food safety, permissible heavy metal concentrations should be developed for Trinidad and Tobago. This will allow a limit for levels of heavy metal concentration in soil.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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