Heavy Metal Analysis in the Vegetable Farm Soil in the Kingdom of Bahrain

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Abstract
Soil serves as deposits and filters all substances. It has limitless size and capable of absorbing all harmful and deadly materials washed and flushed in it so careful determination on what are thrown and absorb should be taken into consideration. This study aimed to determine the presence of heavy metals and to assess the physico-chemical properties of vegetable farm soil in Budaiya, Kingdom of Bahrain and the results on the physicochemical analysis were compared against the environmental standard composition of farm soil. The physico-chemical analysis on the soil samples was done in the biochemistry laboratory while the analysis of heavy metals and macronutrients was done in an ISO certified laboratory. Atomic Absorption Spectroscopy was done in assessing the amount of Lead, Cadmium, $S0_4^{-2}$, $N0_3^{-1}$and $P0_4^{-3}$ while the spectrophotometer was used to determine the amount of Ca^{+2} , Mg^{+2}, K^{+}, and $Fe^{+2}$and have been found out through T-test that there is no significant difference on these components thus, they are comparable to the normal composition though $Mg^{+2}$and $N0_3^{-}$ is quite higher when compared to the normal composition of vegetable farm soil indicating the soil is slightly acidic and has that ability to absorb most of the micro-nutrients. Further, the determination of pH was carried out with an average pH of 6.87 which is still within the standard pH for garden soils ranging from 6.5 to 7.5. This value is attributed to the organic fertilizer applied and to nature of the soil in an area. However, this value must be monitored since the amount of dissolved carbon dioxide in soils may lead to decrease in pH making it acidic. Extreme pH values can result from depletion of some micronutrients and some plants may suffer from iron chlorosis at basic soil pH. It was also analyzed that the vegetable farm soil was found to be positive with heavy metal lead and found negative with heavy metal cadmium. As such, it is recommended that soil samples in other sites be done and subjected for parallel study to monitor the same parameters included in the study.
Keywords: Heavy metals, physic-chemical properties, elemental composition, Polyatomic ions, micronutrients, macronutrients, Atomic Absorption Spectroscopy

1. Introduction

In the manufacturing sector today, human capital is still essential for most factories to carry out a variety of There are attention-arresting concerns that trigger the stimulation of soil pollution: human activities, industry, attrition and the continuous spread of urbanization. The soil properties and composition plays the role of a filter that can retain and deposit toxic substances in it. The most common contaminants of soil are heavy metals and mineral oil. Heavy metals are toxic to all forms of organisms and have approximate density of 5.0 g/ml or higher like lead, copper, mercury and cadmium that may react chemically in the environment [1]. As a result, human health is in peril due to toxic substances that enter the crops and the ground water.

Solly (2014) explains that heavy metals like Arsenic (As), Lead (Pb), Cadmium (Cd), Chromium (Cr) although only the form Cr(VI) is toxic, Nickel (Ni), Zinc (Zn), Copper (Cu) and Mercury (Hg) rank prevalent in the list of heavy metals. On the other hand, some of these elements are essential to human health. They are likewise advantageous when taken as supplements properly at low levels. Other elements like, cadmium, lead and mercury are always toxic in all forms to humans since they do not have any biological function [2].

These heavy metals can undergo chemical change and can form bioavailability [2]. Biodegradation of any organic matter are prevented with the presence of heavy metals in the soil. Avoiding biodegradation will sustain a healthy environment; thus, lessening problems and risks to humanity as well. The soils, water, and the environment should be free from lead, cadmium, mercury and arsenic due to their hazardous effects to human health and to the community [3].

Brigdes and Burnham (2006) in their study on Soils of the State of Bahrain mentioned said that soil formation in Bahrain is influenced by different factors like solonchaks, regosols, yermosol and fluvisols other than the effect of climate. The Solonchaks include unique amounts of gypsum that cannot undergo leaching (which leads to increase in different morphological features). The physiographical location throughout the country could be the cause for the circulation of fluvisols, yermosols and regosols in the different areas. Aside from this factor, the original material or topography is also considered [4].

A study done by Stefan et al., (2010) on the influence of traditional agricultural practices on mobilization of arsenic on soil also stated that the sewage and sludge level used and the type of industrialization where the soil samples were taken can affect the presence of heavy metals in soil [7]. It is for this reason that this study was conducted considering all these possibilities that may lead to soil contamination. This endeavor aims to help the farmers harvest produce which are free from heavy metals.

1.1 Statement of the Problem

This study was conducted to determine the presence heavy metal and limited to lead and cadmium only in the vegetable farm soils in Budaiya, Kingdom of Bahrain.
Specifically, it aims to answer the following questions:

1. Are the vegetable farm soils in the Budaiya, Kingdom of Bahrain contaminated with heavy metals like lead and cadmium?
2. What are the concentrations of lead and cadmium from the said soil samples?
3. What are the other physico-chemical properties in the vegetable farm soils in the aforementioned sites?
4. Is the concentration of the assessed physico-chemical properties of soil under study comparable to the Environmental Standard for Normal Garden Soil?

1.2 Significance of the Study

The presence of heavy metals in soil can be dangerous for human health because the toxic substances can enter the crops, soil and ground water. The soils have a property which plays the role of a filter that can retain and deposit toxic substances in it.

Soil analysis is important in determining the fertility of a garden soil. The analysis can determine the required nutrients to maintain the soils' productivity- this can be done at least once every after 4 to 5 years as recommended by soil experts for the farmers to know and to improve the necessary possible growing environment for plants to attain maximum growth. It also includes the determination of pH level and micro nutrients content like Magnesium, Calcium, potassium and iron. Similarly with the macronutrients that include the nitrates, $N0_3^-$, sulfates, SO_4^{-2} and phosphate, PO_4^{-3} [6, 7].

The heavy metals like lead, cadmium and arsenic should not be found positive from the garden soil. Plants that grow in infected areas cause health problems to the locality [8].

This research is beneficial to the following entities:

Future researchers. This could serve as guide in monitoring the composition of the garden soils of the area in the future and assessing the presence of toxic metals in the conduct of other studies.

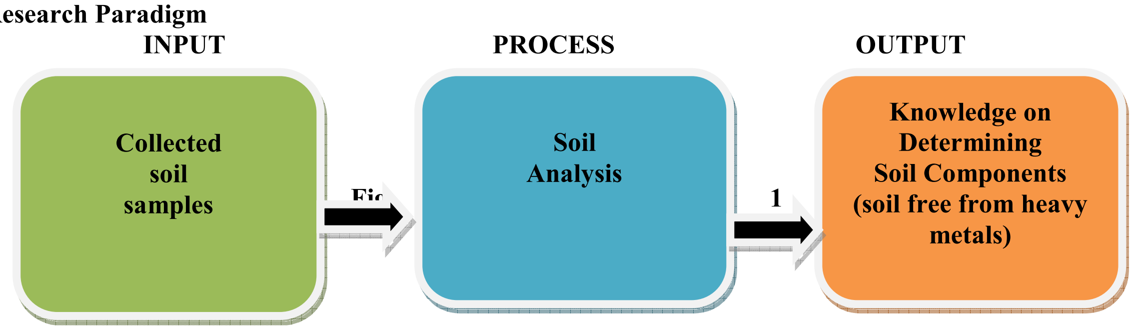
Farmers and consuming public. This study can provide information on the present characteristics of the farm soil. The consuming public will be aware on the quality of the agricultural produce that they consume.

This study can also help authorities, health workers, gardeners and housewives to become aware on the effects of heavy metals to their health and environment.

1.3 Scope and Limitation

This study focused on the determination on the level of heavy metals like lead and cadmium while the physico-chemical determination concentrated on the elemental analysis of Calcium (Ca^{2+}), potassium (K^{+1}), Magnesium (Mg^{+2}) and Iron(Fe^{+3}) likewise, the polyatomic ion sulfates (SO_4^{-2}), nitrates (NO_3^{-1}) and phosphate (PO_4^{-3}) were also determined. Soils samples were collected from a vegetable farm in Budaiya, Kingdom of Bahrain. The amount of heavy metals, phosphates, nitrates and sulfates from soil samples was analyzed at the Department of Science and Technology, Regions 02- Philippines when the researcher took her annual vacation last December 2014 while the other analysis was done in the biochemistry laboratory of AMAIUB from May-July 2015.

1.4 Research Paradigm



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2. Literature Review

Heavy metals are by nature toxic in particular stages. Immoderation of heavy metal deposit in soils is lethal to all living things. Heavy metal contamination of urban and agricultural soils could be traced from the manufacturing and using of synthetic materials. Garbage in open dump sites is composed of 5% heavy metals and 1% special hazardous materials according to solid waste management program on the Environment and Natural Resources [10, 11].

Most common cationic metals are nickel, copper, zinc chromium, mercury, cadmium, lead, and manganese. These heavy metals from locally produced toxic and hazardous wastes if not properly handled and disposed will come in contact with soils posing some dangers not only to siltation and flooding but infection and epidemic [11]. Indeed, heavy metals which are left uncheck would be lethal to all forms of living organisms.

Relatively, excess accumulation of heavy metal in soils is toxic to all animals. Long period exposure to heavy metals is normally chronic due to food chain transfer. There are occasional cases of severe or direct poisoning from heavy metals; however, it is likely to happen through intake or dermal contact [11].

Amer, S. A. (2006) discussed in his research which he included 47 sites specifically in Budaiya, the management on soil and water management in the farming activity. This research is about the demonstration of protected vegetable production in Bahrain using brackish water in Budaiya for irrigation purposes. It was found out that the pH level was still within the normal range. The amount of sodium (Na^{+}) and chlorine (Cl^{-}) was also monitored in both water and soils and found out to be toxic to some extent in some sensitive crops because it exceeded the maximum amount. The toxicity of sodium in the soils and waters of Bahrain can be modified and decreased because soils in the country is rich in calcium carbonates and also gypsum in the soil [4, 13]. They also monitored the absorption of boron to some crops though they suggested that boron can be monitored in the future.

Potassium (K) is one of the basic macro-nutrients needed for plant growth. This is absorbed in the root zone of the plants needed for the production of most agronomic crops. Extension soil scientist Rehm and Schmitt (2002) explained that the role of potassium (K) in plant growth has not been clearly characterized. They said that potassium is associated with the movement of water, nutrients and carbohydrates in plant tissue [14]. Growth is undersized if potassium (K) is deficient they added.

Soil pH can affect the accessibility of nutrients to plants and the activity of soil microorganisms. At pH above 7, free uncombined Calcium begins to accumulate in the soil making it basic and sensitive to some plants. The Iron (Fe^{+2}) content of the soil becomes less stable making the free calcium of the soil in amending the acidic loving plants like blueberries, azaleas, and rhododendron. [10, 15]. Likewise, there are also some plants which are affected in acidic soil; consequently; it leads to reduction of micronutrients available in the soil making it crucial to some plants at pH of 4.5; hence, soil pH must be monitored.

This study was conducted after considering possible factors that can cause contamination of soils due to heavy metals and their physico-chemical properties.

Research Methodology

Materials, Equipment and Glass ware

The materials used were clean plastic containers, bucket, shovel, prewashed bottle, hot plate, beakers, watch glass, petri dishes, micropipets of different volumes, 0.1 mL (units) graduated cylinder, 6 oz. (160 ml) dilution bottles, Erlenmeyer flaks, rubber stoppers or plastic screw caps, bunsen burner, pH meter, refrigerator, water bath, digital weighing scale and Atomic Absorption Spectra which was used in determining the heavy metals of lead and cadmium, $P0_4^{-3}$, SO_4^{-2-}, NO_3^{-1} and NO_2^{-1}.The following regents were use in the study: deionized water, reagent blanks and standard reagents of calcium, potassium, magnesium and iron.

Experimental Design

This study used experimental design and T-test was utilized to test the difference in the physico-chemical properties against the normal elemental composition of normal garden soil and further check it these properties are related thru Pearson-correlation test.

Procedures on Physico – Chemical Parameter

l. Collection of Soil Samples for the Study

Random sampling was used in gathering soil samples.

2. Methods

A. Heavy Metal Determination

1. Analysis of Lead Using Atomic Absorption Spectrometry Method

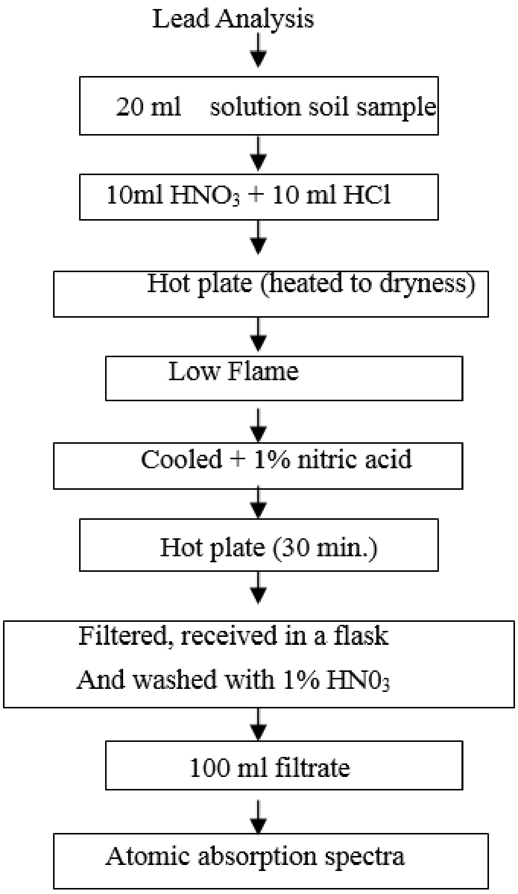

Fig. 2. Flow Chart on Lead Analysis Using Atomic Absorption Spectrometry

2. Extraction of Cadmium for **Atomic Absorption Spectrometry Method**

B. Determination of Anion Phosphate (PO_4^{-3}), Sulfates (SO_4^{-2}) , Nitrates (NO_3^-) and Nitrites ((NO_2^-)

Analysis of nitrate, (NO_3^-)

Determination of Phosphate, **(PO_4^{-3})**

Determination of Sulphate, (SO_4^{-2})

C. Elemental Determination of Soil Samples

Thirty grams of the soil composite were homogenized with the use of a magnetic stirrer which was utilized for the elemental determination with the use of the spectrophotometer available in the Biochemistry laboratory in AMA-IUB. The following were the macro-elements analyzed.

1. Determination of Calcium (Ca^{+2})
2. Determination of Potassium (K^{+1})
3. Determination of Magnesium (Mg^{+2})
4. Determination of Iron (Fe^{+3})

D. pH

Results and Discussion

Soil samples were collected from a vegetable farm in Budaiya, Kingdom of Bahrain in December 2014 and last May 2015. Samples were placed in a zip-lacked plastic containers and these were kept in cooler box then transported to the Biochemistry Laboratory of AMA – International University of Bahrain for analysis and same was done on the samples which were brought to the Philippines last December 2014 for the analysis of heavy metal cadmium and lead. The determination of anions like nitrate and nitrites, sulfates and phosphates was also conducted. The spectrophotometer was used to determine the amount of sodium, calcium, iron and magnesium while pH meter was used to determine the acidity and alkalinity of the soil. The following are the results of the study;

4.1 . That the vegetable farm soil in Budaiya is contaminated with heavy metal lead and found negative with cadmium.

4.2. That there are traces of lead with concentration of 14 ppm through Atomic absorption spectra determination and found negative with cadmium.

Table1. **Result of the Atomic Absorption Spectroscopy analysis of Heavy Metals**

Heavy Metals	Result
Lead	14 µg/g or ppm
Cadmium	Not determined

4.3. That the other physico-chemical properties in the aforementioned sites were found to contain PO_4^{-3}, SO_4^{-2}, NO_3^-, Ca^{+2}, K^+, Mg^{+2}, Fe^{+3} and found to be slightly acidic.

Results on PO_4^{-3} is shown in table 2 reveals that the garden soil is low in PO_4^{-3} as compared to the allowed PO_4^{-3} which is 0.01% by mass composition indicating that Budaiya vegetable farm soil is quite acidic. With this result, indicates that the absorption of macro-nutrients like Fe, Zn, K and Ca is more absorbed in the soil.

Results on the analysis of SO_4^{-2} as seen in table 2 showed 2900 ppm as compared to 2000-3000 ppm or 0.2 percent by mass as soluble sulfate in soil indicates that the Budaiya vegetable farm soil is still within soluble sulfate threshold to safe acceptable risk. Maher (2013) said that at about 0.2 to 0.3 percent is at low risk SO_4^{-2} and more advantageous on the absorption of macro-nutrients like Fe, Zn, K and Ca in the soil [17, 18].

Table 2 below shows the analysis of NO_3^- which is found to be higher in composition with a percent composition by mass which is 0.207 % mass composition as compared to 1500-1800 ppm or 0.15- 0.18 % composition by mass as soluble nitrate in soil indicating that the Budaiya vegetable farm soil is quite high in nitrate content. Though this was the result when the assessment was done, the life of fixed nitrogen in the soil is short. Both nitrate and ammonium ions are bound weakly by ion-exchange processes, so they are both leached out by rainwater, and finish up in ground water. Nitrate and ammonium ions encourage the growth of weeds. Nitrogen is also lost from the soil by the activities of denitrifying bacteria that convert the nitrate and ammonium ions back to dinitrogen, or more usually, to nitrous oxide (N_2O). This is a greenhouse gas and so increasing the amount of fixed nitrogen in the soil indirectly increases the amount of nitrous oxide in the atmosphere and potentially contributes to the raising of the temperature of the earth. Farming practices which lead to high levels of nitrogen in the soil can therefore contribute to environmental problems [19, 20].

Table 2. Result on the Analysis of polyatomic ions PO_4^{-3}, SO_4^{-2} and NO_3^- on Vegetable farm soil

Anions	Result
PO_4^{-3}	596 ppm
SO_4^{-2}	2900 ppm
NO_3^-	2068 ppm

Note : 10,000 ppm or 10,000 mg/kg is equal to 1 percent by mass [14,20].

The occurrence of calcium in soil exists in tolerable amounts. It is an element deposited as mineral in the soil which are insoluble in some agricultural considerations. Calcium is also one of the elements present in soil in moderately soluble forms, as a cation (Ca^{+2}) adsorbed as colloidal complex. The ionic form is considered to be available to crops. George Rehm and Michael Schmitt (2013) in their study on the nature of Phosphorous, Potassium and Nitrogen in Soil mentioned that calcium functions as essential for many plants like cell partition and elongation, cell growth and expansion, absorption of nitrate and starch metabolism and enzyme activity among others [14].

As seen in table 3, results on Ca^{+2} analyzed was 923.33 mg/L which is within the required amount of calcium in soil as compared to the standard composition of normal garden soil which ranges from 700 – 1300 mg/L.

Potassium (K^+) is a basic nutrient needed for plant development. Because large amounts are absorbed from the root zone in the production of most agronomic crops, it is classified as a macronutrient. Potassium affects the size, shape, color, taste and other measurements needed for development of a plant [16].

Results on the analysis of potassium (K^+) showed that it is comparable to the standard amount of potassium found in garden soil which was found to be 436.67 mg/L against 510 mg/L.

Magnesium is essential for plant metabolic processes, particularly in chlorophyll production and in the uptake of phosphorous. Too much magnesium can compel your soil leading to less penetration of water and nutrients. Excessively high magnesium can also trigger increase in pH [16, 20].

Exchangeable calcium and magnesium are attracted to the negatively charged part of the clay and other organic material in the soil where they are not totally leached to soil but are available to plants [20].

Results on the analysis of magnesium (Mg^{+2}) as seen in table 2 showed that it is quite high when compared to the standard amount of magnesium found in garden soil which was found to be 316.66 mg/L against 270 mg/L.

Results on the analysis of iron (Fe^{+2}) showed that it is comparable to the standard amount of iron found in garden soil which was found to be 60.33 mg/L against 100 mg/L.

The pH is significant because it affects the accessibility of nutrients in the soil that are necessary for plant development. Water can dissolve CO_2 which results to being little acidic to dissolve the presence of calcium in the soil when water evaporates from it. This happens when rainwater reacts with limestone or dolomite in caves causing the melting of limestone which will react with CO_2 forming weak carbonic acid in soil [16, 22]. The acid can be maintained at a consistent level, but due to global warming like increased amounts of carbon dioxide in the environment, the absorption from vegetation and soil surrounding the area pH is sometimes difficult to maintain hence, monitoring of soil pH is required. El-Meligi (2014) in his research on Effect of Global warming on the Ice Cap Melting of Poles mentioned the effect of CO_2 in Global warming is greatly affecting the pH on soils and water [22, 23]. When the pH is higher, micronutrients such as iron (Fe), manganese (Mn), boron (B), copper (Cu) and zinc (Zn) become less available. This is because soil pH affects the solubility of plant nutrients in the soil becoming more soluble as pH increases while other nutrients are absorbed as the pH decreases [24].

Result on pH as shown in the table below found to be 6.87 in average which is slightly acidic and found to be comparable to the standard pH for vegetable farm soil which ranges from 6.5- 7.5. This may be due to the organic fertilizer applied and may also be due to nature of the soil in an area. Dr. J. Floor (2007) said that the acidy is due to too much dissolved $C0_2$ in the soil. Further, he said that this must be monitored because it may harm the other vegetation planted in the soil [27].

Table 3. Physico– Chemical Composition of Garden Soil when Compared to the Standard Composition of Garden Soil

Detected Parameters On Garden Soil	**Results**				**Standard Composition of Elements in soil in mg/L or ppm** Environmental Garden Soil Standards (2007)
	Trial 1 Conc. in mg/L or Ppm	Trial 2 Conc. in mg/Lor ppm	Trial 3 Conc. in mg/L or ppm	Average Conc. in mg/Lor ppm	
Ca^{+2}	910	920	920	923.33	700-1300
K^{+2}	450	430	430	436.67	120-510
Mg^{+2}	350	300	300	316.66	140-270
Fe	61	60	60	60.33	100
pH	7.0	6.8	6.8	6.87	6.5-7.5

4.4. Concentration of the assessed physico-chemical properties of soil under study is comparable to the Environmental Standard for Normal Garden Soil

T-test (two tailed) was used to compare if there is significant difference on the physico-chemical properties against the normal composition of garden soil. Results of the comparison reveal that there is no significant difference as seen in the table below.

Table 4. Test of Difference between Physico-Chemical Properties and Standard Composition of Vegetable Farm Soil

Detected Parameters On Coastal Water	**Average Conc. in mg/Lor ppm**	**Standard Composition of Elements in soil in mg/L or ppm** Environmental Garden Soil Standards	**Sig. (2-tailed)**
Ca^{+2}	923.33	700-1300	0.590 *no significant difference
K^{+2}	436.67	120-510	
Mg^{+2}	316.66	140-270	
Fe	60.33	100	
pH	6.87	6.5-7.5	

Further, Pearson test for paired correlation was also used (as seen in table 5) below to compare linear association and found to be high positive in correlation and statistically significant at 0.05 level. Hence, there is sufficient evidence that the average concentration in mg/L or ppm in terms of elemental composition and pH under study is comparable to the concentration in mg/L or ppm elements found in the garden soil. It is conclusive that the site where the samples were collected is within its ideal physico-chemical properties.

Table 5. Paired Correlation between the Concentration on Physico-chemical Properties and Standard Composition of Vegetable Farm Soil

Paired correlations		Correlations	Interpretation
Average Conc. in mg/Lor ppm and the Standard Composition of Elements in soil in mg/L or ppm	Pearson Correlation	.975	High positive correlation and statistically significant
	Sig. (2-tailed)	.005*	

*correlation is significant at 0.05 level

Conclusions

The following conclusions were derived from the findings:

1. The vegetable farm soils in Budaiya contain minimal amount of heavy metal lead and found free from cadmium in the area.
2. The result on the analysis of Mg +2, and NO3- is quite higher than the standard composition of garden soil. The result corresponds to the observation that the increase may be due to petroleum refilling station, excessive application of organic matter and to the industrial nature of the area where the samples were taken.

3. The vegetable farm soils in Budaiya, Kingdom of Bahrain where the samples were taken are not yet polluted as seen in the result of the micronutrients Ca^{+2}, K^{+} , Fe^{+2} and macronutrient SO_4^{-2}, and PO_4^{-3} and so with pH. Although it was observed that there is a minor increase on the micronutrient Mag^{+2} and macro-nutrient NO_3^{-1} on the soil samples.

Recommendations

The following recommendations are given based on the findings of the study:

1. Collection of the soil samples in other sites should also be done and be subjected to analysis.
2. Monitoring should be done at least every after 3 -4 years so to monitor the trend on the physico-chemical components as recommended by soil experts.
3. Environmental campaign on the effects of untreated waste should be given emphasis since oil spills may present long-term ecological effects and may even lead to worst on all individuals consuming produce gathered from the site.
4. Microbial test should also be conducted on the organic matter applied in the garden soil to check on the presence of e-coli on the manure that are applied in the area.
5. Parallel studies should be conducted to test other parameters.

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