Molecular Soil Biology 2018, Vol.9, No.2, 12-17
http://msb.biopublisher.ca

Research Report **Open Access**

Quantification of Cyanide and Major Nutrients of Soil around Cassava (*Manihot esculenta C.*) Processing Industries within Akure, Ondo State, Southwest Nigeria

Olufemi Samson Salami ✉, Akomolafe Olatunji Modupe, Olufemi-salami Folasade Kemisola
Department of Biology, Federal University of Technology, Akure P.M.B. 704, Akure Ondo state, Nigeria
✉ Corresponding author email: olufemisalami25@yahoo.com

Molecular Soil Biology, 2018, Vol.9, No.2 doi: 10.5376/msb.2018.09.0002
Received: 07 Dec., 2017
Accepted: 25 Dec., 2017
Published: 05 Jan., 2018

Preferred citation for this article:
Salami O.S., Akomolafe O.M. and Olufemi-Salami F.K., 2018, Quantification of cyanide and major nutrients of soil around Cassava (*Manihot esculenta C.*) processing industries within Akure, Ondo state, Southwest Nigeria, Molecular Soil Biology, 9(2): 12-17 (doi: 10.5376/msb.2018.09.0002)

Abstract The research work exploited the extent of cyanide pollution and major nutrients (elements) distribution in soils within three cassava processing industries in Akure metropolis, Ondo state Nigeria. The result of the research revealed that the top soil of cassava processing industries are richer in soluble cyanides than subsoil: the highest amount (118.85 mg/l) of soluble cyanide was obtained in the top soil of Igbatoro cassava processing industry while the subsoil of Aba-oyo cassava processing industry had the least soluble cyanide content of 82.906 mg/l. Trace of cyanide was also noticed in the well water of Igbatoro cassava processing industry that was sampled. The pH of the soils sampled followed a pattern that revealed that cyanide content determines the pH value of the soil to a large extent. The major nutrients distribution in the top and subsoils of the cassava processing industries revealed that nitrogen (N), phosphorus (P) and potassium (K) content of the cassava processing topsoils and subsoils were very high; nevertheless, the subsoils in the three industries are richer in N, P and K than the topsoils. Effluents from cassava industries increase soil nutrients and reduce pH.

Keywords Cyanide; Soluble cyanide; Soil nutrient; Effluent and pollution

Introduction

Industrial wastes constitute hazard to the ecosystem, nevertheless, some benefits are obtained from the decomposition of some of these wastes as they tend to improve the nutrient composition of the soil. Wastes such as cyanide have been found in soils in industrial area such as former manufactured gas plant sites in the USA (Shifrin et al., 1996). Cyanide has been detected in the air near large-scale cassava processing facilities in Nigeria at levels ranging between 20 and 46 mg/m^3 (Okafor and Maduagwu, 2000). This pollution was presumed to be due to the richness of cassava in cyanide and cyanogenic compounds (Bokanga, 1994). Cassava is an edible food and it is also used as raw material in cassava processing industry for the production of garri, starch, tapioca e.t.c (Idible, 2006). During the processing of cassava, cyanide leach into the soil and surrounding water hence, serving as pollutants to the surrounding soil and water. Despite the detrimental effects of this waste on human health, its decomposition in the soil should improve soil nutrients. This research is aimed at investigating the effects of waste effluent of cassava processing industries on the soil nutrients as well as cyanide pollution of the soil and water around cassava processing industries in Akure metropolis, Ondo State, Nigeria.

1 Results and Discussion

1.1 Quantification of soluble cyanide and pH of soil and water within cassava processing environments

Table 1 shows the calibration for soluble cyanide. It was observed that absorbance and potassium cyanide (KCN) concentrations were directly proportional to each other (Figure 1).

Table 2 shows the distribution of soluble cyanide within cassava processing industries. The well water of Igbatoro cassava processing industry has soluble cyanide content of 28.09 ± 0.22 mg/l. The soluble cyanide in the effluent from Igbatoro and Road block cassava processing environments were 61.81 ± 7.14 and 52.81 ± 5.66 mg/l respectively, values which were significantly different at $P< 0.05$. Igbatoro top soil had the highest amount of soluble cyanide of 118.85 ± 8.17 mg/l, while the least (95.72 ± 1.20 mg/l) for the topsoils was observed in Aba-Oyo cassava processing industry. Igbatoro subsoil also took lead in the amount of soluble cyanide.

Table 3 shows that the pH of the water, effluents and soils around the three cassava processing industries. The pH ranges between 5.79 ±0.08 and 7.62 ±0.03. The pH (7.553 ±0.02) of the only well water sampled was slightly alkaline. The effluent pH of Road block and Igbatoro cassava processing industries were 6.02 ±0.02 and 5.79 ±0.08 respectively. The pH of the top soil of Roadblock cassava processing industry has a value of 6.89 ±0.07, showing that it was slightly acidic. Other top soils show slight alkalinity.

Table 1 Calibration table for soluble cyanides

Conc. (mg/l)	Absorbance
0	0
10	0.002
30	0.004
50	0.006
70	0.008
90	0.01
110	0.012
130	0.013
150	0.014
170	0.016
190	0.017

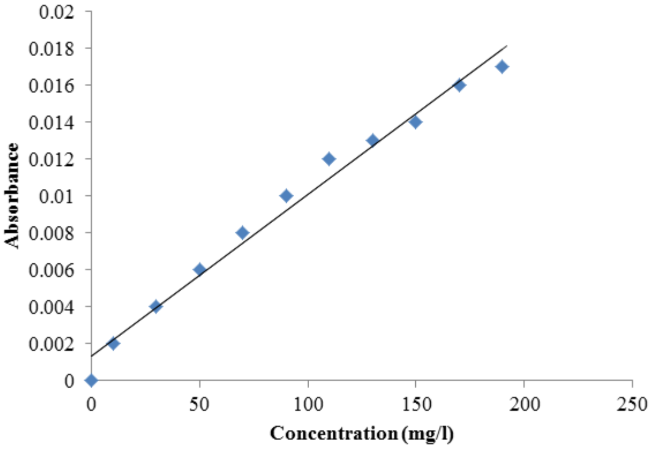

Figure 1 Calibration curve

Table 2 Quantity of soluble cyanide within cassava processing industries

Environment	Soluble cyanide (mg/l) in A	Soluble cyanide (mg/l) in B	Soluble cyanide (mg/l) in C
Well water (within industry)	28.09 ±0.22^b	Not Sampled	Not Sampled
Effluent from pressing unit within industry	61.81 ±7.14^b	52.81 ±5.66^a	Not Sampled
Topsoil around pressing unit	118.85 ±8.17^b	111.43 ±2.86^b	95.72 ±1.20^b
Subsoil	111.43 ±2.86^d	97.14 ±5.72^c	82.91 ±2.79^b

Note: A= Igbatoro cassava processing industry; B = Road block cassava processing industry and C = Aba-Oyo cassava processing industry; Each value is Means ± Standard deviation of three replicates. Values followed by the same letter in the same row are not significantly different using Turkey's HSD Test at $P < 0.05$

1.2 Major elements and organic matter content of the soils in Igbatoro, Roadblock and Aba-Oyo cassava processing industries

Table 4 shows the distribution of major elements and organic matter in the soil of Igbatoro, Road block and Aba Oyo cassava processing industries. The result showed that, phosphorus and potassium were very high in all the top and subsoils of the cassava processing industries. The higher percentages of soil nitrogen of 0.55 ±0.01 and 0.46 ±0.02% were recorded in the topsoil and subsoil of Igbatoro cassava processing industry respectively. Roadblock cassava processing industry's soil had the least amounts of nitrogen (0.25 ±0.01 and 0.04 ±0.01) in its top soil and sub soil respectively. Phosphorus content of the sub soil of road block cassava processing industry was the highest with a value of 176.75 ± 0.01 mg/kg. Road block subsoil had potassium content of 4.72 cmol/kg, which was also the highest value of potassium recorded among the soils that were examined. However, the percentage organic matter was low in the soils of all the cassava processing industries sampled.

Table 3 pH of water and soil within cassava processing industries

Environment	pH of site A	pH of site B	pH of site C
Well water (within industry)	7.53 ±0.02^{b}	Not Sampled	Not Sampled
Effluent from pressing unit within industry	5.79 ±0.08^{b}	6.02 ±0.02^{a}	Not Sampled
Topsoil around pressing unit	6.53 ±0.02^{ab}	6.29 ±0.02^{a}	7.19 ±0.27^{c}
Subsoil	7.62 ±0.03^{d}	6.89 ±0.07^{a}	7.43 ±0.17^{c}

Note: A= Igbatoro cassava processing industry, B= Road block cassava processing industry and C= Aba oyo cassava processing industry; Each value is Means ±Standard deviation of three replicates. Values followed by the same letter in the same column are not significantly different using Turkey's HSD Test at P<0.05

Table 4 Major nutrients (elements) and organic matter in the soil of Igbatoro, Roadblock and Aba-Oyo cassava processing industries

	Nitrogen (%)	Phosphorus (mg/kg)	Potassium (cmol/kg)	Magnesium (cmol/kg)	Calcium (cmol/kg)	Carbon (%)	Organic Matter (%)
Igbatoro Top soil	0.55 ±0.01*	68.78 ±0.02*	0.81 ±0.01*	1.81 ±0.01	0.70 ±0.02	0.63 ±0.01	1.08 ±0.01***
Igbatoro Subsoil	0.46 ±0.02*	176.75 ±0.01*	0.71 ±0.02*	2.00 ±0.01	0.89 ±0.02	0.62 ±0.02	1.12 ±0.01***
Road block Top soil	0.25 ±0.01*	64.85 ±0.07*	1.39 ±0.34*	0.40 ±0.01	3.40 ±0.01	0.37 ±0.01	0.63 ±0.01***
Road block subsoil	0.04 ±0.01*	66.76 ±0.01*	4.72 ±0.03*	4.80 ±0.01	4.10 ±0.01	0.48 ±0.01	0.22 ±0.01***
Aba-Oyo Top soil	0.29 ±0.01*	65.10 ±0.00*	1.18 ±0.03*	0.80 ±0.01	3.20 ±0.01	0.48 ±0.01	0.83 ±0.01***
Aba-Oyo Sub soil	0.36 ±0.01*	75.33 ±0.01*	1.51 ±0.03*	2.30 ±0.01	3.36 ±0.17	0.43 ±0.01	0.55 ±0.18***

Note: *= High quantity, **= Medium quantity and ***= Low quantity (Accordance with UNESCO standard); Each value is Means ± Standard deviation of three replicates

2 Materials and Methods

2.1 Determination of pH, cyanide content and nutrient composition of the top and sub soil around the press units of cassava processing industries

The top soils (between 0-5 cm below the soil surface) and sub soils (between 5-10 cm below the soil surface) not exceeding 2 meters around the press units of Igbatoro, Roadblock and Aba-Oyo cassava processing industries were collected, air dried, and sieved with 2 mm metal sieve, before analyzing the nutrients composition and other properties of the soils.

2.2 Determination of pH and cyanide content of soil

Ten grams of soil sample in 20 ml of distilled water. The mixture was stirred for 1 minute and the setup was left for 30 minute after which the pH of soil was determined by dipping the tip of Jenway 3015 pH-meter into the mixture.

One gram of the soil sample in 10 ml of distilled water was stirred for 1 minute and allowed to settle for 30 minutes the supernatant was decanted, filtered (using Whatman 1 filter paper) and centrifuged at 34,000 rpm for 1 minute. The cyanide content of the clear solution was then determined on the calibration curve using Mihaescu and Drochioiu (2009) Procedure. Calibration curve was drawn by plotting absorbance values of the following concentrations: 10; 30; 50; 70; 90; 110; 130; 150; 170 and 190 mg/L of KCN solution against concentration at 490 nm wavelength, using UV-1100 Spectrophotometer Mapada model.

2.3 Determination of organic carbon (O.C) and organic matter (O.M) in the soils

Potassium dichromate ($K_2Cr_2O_2$) and concentrated H_2SO_4 were added to 0.5 g of soil. The solution was swirled and allowed to cool after which distilled water was added to halt the reaction (extraction phase). Upon completion of the sample extraction phase, the quantity of organic carbon present in the soil was determined through manual titration. An indicator solution ortho-phenanthroline ferrous complex (commercially available as "Ferroin") was used. The excess $Cr_2O_7^{2-}$ was then titrated with ferrous ammonium sulphate $[Fe(NH_4)_2(SO_4)_2*6H_2O]$ or ferrous sulphate ($FeSO_4$) until color change occurs from green to reddish brown (Walkley and Black, 1934).

The % Organic Carbon (O.C) was then determined using the formula:

$(B-T) \times M \times 0.003 \times 1.333 \times 100/wt$

Where

M = Molarity of ferrous ammonium sulfate

B = Blank Titre

T = Titre value for each sample

wt = Weight of the soil sample

% Organic Matter (O.M) was determined with the formula:

$\%\ O.M = \%\ O.C \times 1.724$

2.4 Determination of organic nitrogen

The Kjeldahl method was used for this determination. The method was carried out in three steps. The first step involves digestion, a process where by about 0.6 g of each soil sample was digested with concentrated H_2SO_4 (10 ml) in a dry 500 ml Kjeldahl digestion flask together with on tablet of digestion catalyst (Selenium catalyst). The mixture was then swirled together and the flask was filtered with a loose pear stopper in an inclined position. It was then placed in a fume cupboard and heated gently at first but later increased. The mixture was swirled and shaken from time to time in order to wash down any charred material adhering to the flask. The mixture was heated until a clear solution was obtained. The flask was allowed to cool after which the solution was diluted with tap water to 100 ml out of which 10 ml was transferred into the Kjeldahl distillation flask. The second step was the distillation stage where 40% NaOH solution was added to cooled and diluted digestion sample to make it alkaline. The cloudy nature of the sample solution after the addition of 40% NaOH indicates that NaOH was in excess. To the receiving flask, 25 ml of 2% Boric acid solution was added and few drops of screened methyl red indicator were also added to produce a pink colour solution. The distillation was carried out with the joints tightened with the end of the delivery tube dipping below the Boric acid solution. As the distillation proceeds, the pink colour solution of the receiver turned light green indicating the presence of NH_3. Distillation continues until the distillate was 50 ml after which the delivery end of the condenser was rinsed with distilled water into the receiver.

Equations: - Sample + concentrated $H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$(NH_4)_2SO_4 + 2NaOH_2 \longrightarrow NH_3(g) + Na_2SO_4 + 2H_2O$

The received NH_3 forms a complex with Boric acid as:

$HBO_3 + NH_3 \longleftrightarrow NH_4{:}BO_2$

The final stage involves titration in which NH_3 received in the acid solution was titrated with 0.01 M HCL solutions.

A blank titration was also carried out.

$NH_4 + BO_2^- + HCL \longrightarrow NH_4CL + HBO_2$

Colour changed from light green to pink.

Calculations: % Nitrogen= Volume of acid used × 0.0014g × 100/Weight of sample

2.5 Determination of soil phosphorus

Five gram of soil sample was mixed thoroughly with 35 ml of ammonium fluoride and the mixture was allowed to stand for 30 minute. The extract (filtrate) was then collected by filtering with filter paper. Four milliliter of Murphy and Riley reagents was added to the filtrate and made up to 25 ml with distilled water. The setup was allowed to develop colour. A blank solution was also prepared. The colour developed was then read on Unico UV-2100 spectrometer at 660 nm wavelength.

The amount of phosphorus was then determined using the formula:

Phosphorus (P) in mg/kg = $R \times 35/0.4$

Where R = UV spectrometer reading.

2.6 Determination of soil Potassium (K^+), Calcium (Ca^{2+}) and Magnesium (Mg^{2+})

Ten grams of soil sample was mixed thoroughly with 100 ml of ammonia acetate and it was allowed to standing for 30 minute before filtering. The filtrate (extract) was used to determine the potassium, calcium and magnesium content of each soil sample.

2.6.1 Determination of soil Potassium ion (K^+) only

1 ml of the extract was loaded into JENWAY PFP7 flame photometer and the value read photometrically.

The amount of K^+ was determined using the formula：

K^+ (mol/kg) = R/39

Where R = Flame photometer reading.

2.6.2 Determination of soil Calcium ion (Ca^{2+}) and Magnesium (Mg^{2+}) only

To ten milliliter of the filtrate, 50 ml of distilled water was added. 5 ml of concentrated ammonia solution (buffer) was also added after which 2-3 drops of potassium cyanide, 2-3 drops of 5% Hydroxyammonium Chloride and then a small quantity of Eriochrome Black T (indicator). EDTA of 0.01 M was then titrated with the mixture until the colour changes from light blue to purple. The titre value gives the combined value of Mg^{2+} and Ca^{2+} in cmol/kg.

2.6.3 Determination of soil Calcium ion (Ca^{2+}) only (cmol/kg)

The same procedure was repeated but potassium hydroxide (buffer) and Murexide indicator were used instead of ammonia solution and Eriochrome Black T indicator respectively.

2.6.4 Determination of soil Magnesium ion (Mg^{2+}) (cmol/kg)

{(Mg^{2+} and Ca^{2+} in cmol/kg)} – {Calcium (Ca^{2+}) only (cmol/kg)} = {Mg^{2+} in cmol/kg}

3 Conclusion

The soluble cyanide levels in all the soil of the cassava processing industries were very high. There was also a corresponding decrease in the pH of the top and sub soil investigated. As the cyanide content of the soil increases, the pH of the soil become more acidic, indicating that cyanide pollution of soil might have a link with the soil pH. The effluent released during cassava processing has been reported to be rich in cyanogen (WHO, 1994; Aro et al., 2010). The high level of cyanide in the soils can also be traced to the effluent released during the processing of cassava. Igbatoro cassava processing industry had the highest amount of soluble cyanide in its soil; this might be due to the fact that more cassava was processed there.

Most of the major elements needed by plants for optimum performance are richly abundant in the soil of cassava processing industries that were sampled. The relative abundance of these elements might be as a result of the soils being left to fallow over a long period of time. Furthermore, the effluents might have added to the nutrients composition of the soils, because potassium and sodium cyanides are predominant in the effluent released during processing of cassava (Aro et al., 2010).

Authors' contributions

Akomolafe, Olatunji Modupe helped in the planning of the project, Salami, Olufemi Samson fine tuned the planed project, executed the project, collected data, analysed the data and drafted the manuscript. Olufemi-salami, Folasade Kemisola helped in data collection and editing the drafted manuscript.

Acknowledgments

My sincere gratitude goes to the chief Technologist of Forestry and Wood Technology (FWT) department, FUTA, Mrs. H.B Dafiwhare for making most of the material available for the research and for putting me through in the procedure. I also appreciate Ms Iyagin Faithful (Ph.D. student in FWT) for her assistance in the drying of the samples and releasing some of her chemicals for the research.

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