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A decade's (2014-2024) perspective on cassava's (*Manihot esculenta* Crantz) contribution to the global hydrogen cyanide load in the environment

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ABSTRACT

In recent years, developing countries have increased their cassava (*Manihot esculenta*) production for food security. Cassava contains cyanogen glycosides, mainly as linamarin, which through bio-catalysis, i.e. enzyme hydrolysis, results in hydrogen cyanide (HCN). HCN is released into the environment through numerous ways with subsequent volatilisation. Thus, the HCN released during the period 2002–2013 was estimated between 0.025×10^{-3} to 6.71 ppq (African), 0.012×10^{-3} to 1.01 ppq (Asian) and 0.007×10^{-3} to 0.920×10^{-3} ppq (South American). Furthermore, a decade's (2014–2024) projection of HCN volatilisation displays increases of 60.5% (Africa), 57.7% (Asia) and 50.5% (South America) when compared with the current production. Furthermore, gas released during cassava plants' growth, i.e. HCN, NH_3, and NO_2, was quantified in healthy plants. Varying concentrations of HCN were released. These further indicated the presence of a pseudo-halogenic gas in the environment – a contributor to climate change.

KEYWORDS

Cassava (*Manihot esculenta*); hydrogen cyanide; GIS; environment

Introduction

Cassava (*Manihot esculenta*) is a tropical crop used daily in many impoverished commu- nities, particularly in Africa, Asia and South America [1,2], with an estimated billion tons being produced from 2002 to 2013. The continental contribution of Africa (55% for food), Asia (32% for food/biofuel), and South America (13% for food/biofuel) (see Figure 1), indicates sub-Saharan Africa as the highest cassava producer in the world [3]. The leaves, stems and tubers of cassava contain cyanogenic compounds [4,5]. The glycosides, mainly linamarin, produce hydrogen cyanide (HCN) through enzymatic hydrolysis [5,6], of which the deglycosylation generates acetone cyanodrin, which in turn decomposes into HCN and acetone, largely at slightly acidic pH values and moderate temperature (30 °C) suitable for HCN volatilisation [6].

The concentration of cyanogenic compounds differs from tubers to leaves, with leaves having a higher cyanogen concentration during the early growth stages of the cultivar [7].

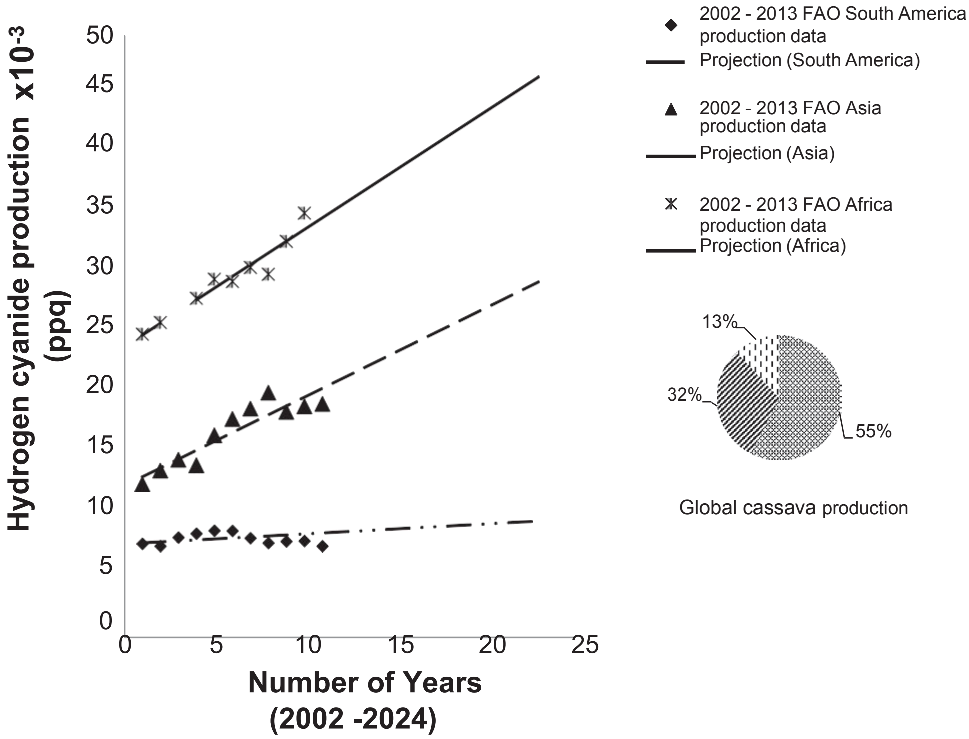

Figure 1. Global hydrogen cyanide load (2002–2013), including a linearised projection (2014–2024).
note: Inset: Global cassava production for Africa, Asia and South America.

An HCN estimated at 250 mg HCN per kg dry weight cassava tubers (DWCT) in mature plants [7] suggested an astronomical quantity of HCN, i.e. 0.25 parts per quadrillion (ppq) were released into the atmosphere between 2002 and 2013 [8,9] – a consequence of limited use of genetically modified cultivars [10]. Previous studies revealed that genetically modified cultivars have low cyanogen content (<1%) in comparison with the wild-type cultivars [11]. t hus, even if genetically modified cultivars were cultivated, an estimated 0.006–0.01 ppq of HCN production was predicted between 2002 and 2013.

Research on genetic modification of cassava occurred in the mid-1990s [12]. Some sub-Saharan countries were unenthusiastic. Only Nigeria, Kenya, Ethiopia, Ghana and the Democratic Republic of Congo piloted the genetically modified cassava project [12]. Environmental activists and non-governmental organisations (NGOs) from those countries argued that genetically modified organisms (GMOs) negatively impact communities by: (1) socio-cultural and economic losses of local cassava production and conservation knowledge, (2) high input costs to procure genetically modified cultivars. The objectors also argued that there are (3) health and food safety concerns as GMO food and products may be allergenic and toxic, and (4) the invasion of genetically modified genes can affect non-target organisms, resulting in a loss of biodiversity [13,14]. Consequently, there has been restricted acceptance of GMOs, for which there are no regulatory frameworks and/ or strategies [14].

There are several pathways through which cyanides in general and HCN in particular enter the environment. The HCN from cassava harvesting and processing, usually in the form of contaminated wastewater and volatilised gas, can result in bio- and physico-chemical modification of the receiving soil, water and air [15]. In addition, metal cyanides and other forms of anthropogenic cyanide can decompose to HCN, resulting in complexation with free reactive metallic species in soil and water, which in the long term, facilitates prolonged deposition, dissolution and leaching into the environment.

Previous studies on cassava cultivation and cyanogen proliferation in the environment show a relationship between continuous cassava cultivation and a decrease in soil mineral content and other parameters such as potassium, magnesium, organic carbon, organic matter and bulk density [15]. Some of these chemical elements may play an essential role for plant growth, so that their depletion in soil will lead to poor yield, thus affecting communities whose staple food has been cassava, for instance, sub-Saharan communities.

Therefore, it is judicious to assess the spatial and temporal distribution of cassava, in particular its cyanogens and HCN production, since HCN is a pseudo-halogen that contributes to agricultural land deterioration and ozone layer degradation, which in turn is associated with global warming and consequent climate change [16]. HCN decomposition leads to the production of CN^- (free cyanide) and OCN^- (cyanate), which are additional sources of nitrogen oxides (N_yO_x) – contributors to global warming [17], with nitrous oxide in the troposphere being nearly 300 times higher than it was a century ago [18]. Since 2007, the UNEP and WHRC estimated the global atmospheric N_2O concentration to be 18% higher than in pre-industrial times, with its increase at a rate of about 0.3% per year since 1980 in comparison with the 1.2 petagrams of carbon (pg C) increase of CO_2 per annum reported in the same period [19].

Furthermore, a reaction of N_yO_x from HCN and other forms of reactive nitrogen by-products, i.e. ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), nitric acid (HNO_3), nitrous oxide (N_2O), and nitric oxide (NO) in a liquefied carrier can contribute to acidification and eutrophication when they enter water bodies [20]. The intention was to assess cassava's contribution to HCN release during the period 2002–2013 in order to project an estimate up to 2024.

Hence, this study focused on the global spatial and temporal distribution of cassava and its contribution to HCN release into the environment. Additionally, HCN, NH_3, NO_2 gases volatilised from cultivated young cassava plants were also quantified.

Furthermore, the plants' chlorophyll content and photosynthetically active radiation (PAR) were also assessed, since they indicate plant health, particularly as HCN can be easily volatilised in dying diseased leaves. The chlorophyll content and PAR enabled assessments of the cassava plants' wellbeing during which HCN is created and released through volatilisation [21]. In young plants, HCN, mostly in leaves, decomposes via UV to NH_3 and NO_2 [22].

Materials and methods

Mapping of cassava production and estimated HCN release from cassava production

Geographic Information System software (ArcGIS, ESRI Pty Ltd, Italy) and Quantum GIS (QGIS, Open Source Geospatial Foundation) were used to map cassava production,

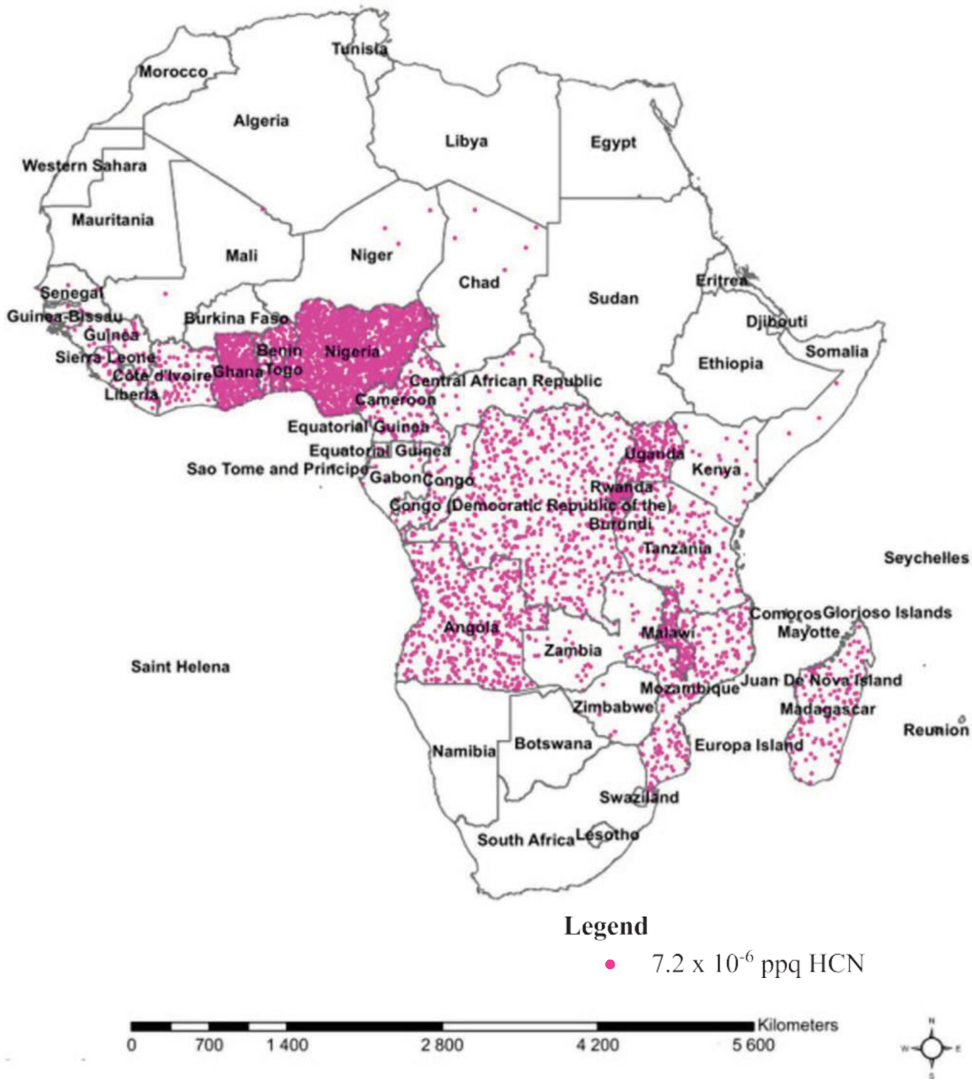

Figure 2(a). africa's cassava production and estimated hydrogen cyanide concentration.

including global distribution. The geospatial analysis used in GIS mapping enables the visualisation of maps giving information on a specific commodity using historical data for analysis [23]. The study focused on the highest cassava producers, i.e. Africa, Asia and South America. hus, cassava-growing countries were shaded using a key marker, whereby a single key marker is equivalent to 72×10^{-5} ppq (Africa), 36×10^{-5} ppq (Asia) and 41×10^{-5} ppq (South America); the countries that do not have records of producing cassava were let blank (Figures 2(a)–(c)). Overall, most cassava-producing countries are inland, with the highest cassava producers being within the inter-tropical convergence zone (ITCZ), where it is relatively hot and rainy throughout the year [24,25].

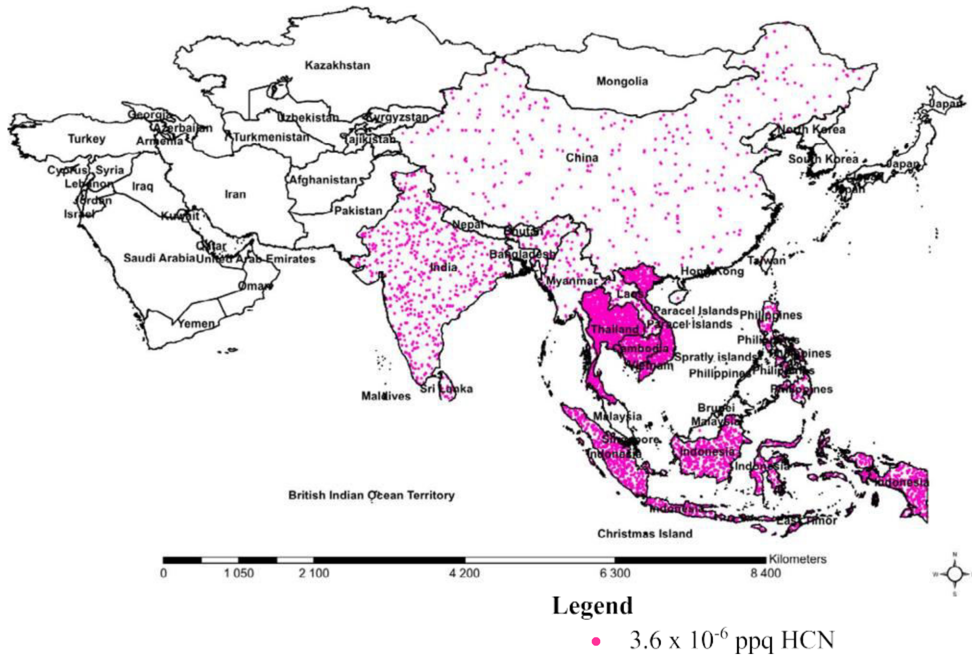

Figure 2(b). asia's cassava production and estimated hydrogen cyanide concentration.

Reliability of Food and Agriculture Organization data

The Food and Agriculture Organization (FAO) data raise concerns. Firstly, there is not full coverage of the FAO country members: many developing countries have remote areas difficult of access because of poor infrastructure; this affects the recording of cassava production. Secondly, the collection and recording of data in many developing countries is not adequate; data collection is often done manually before being computerised at the nearest data-logging site. In the case of missing data, statistical methods can be used to minimise errors [26]. Statisticians oten determine (by estimation) the national, regional, continental and world aggregates to compile secondary derived statistics by using supply and actual use accounts from the database to check the consistency of particular data sets [27].

Thus, statistical methods such as average yield or average production, estimation of mean values, etc., have to be used to minimise errors as far as possible.

Model development and HCN load projection

Global cassava production data were obtained from the FAO statistical database. A decade (i.e. 2002–2013) was considered for the projection (2014–2024) of corresponding HCN load (ppq) into the environment, by using a linear projection (Equation 1) with correlation coefficients (R2) being; Africa – 0.93, Asia – 0.84, and South America – 0.92:

$$P_x = P_b + kt \tag{1}$$

$$\text{whereby } k = \left(P_b - P_{ref}\right) \big/ \left(t_b - t_{ref}\right) \tag{2}$$

Figure 2 (c). South america's cassava production and estimated hydrogen cyanide concentration.

where P_x (ppq) is the projected HCN load at time t (yr), k (ppq/yr) – projected incremental rate of HCN load, P_b(ppq) is the estimated HCN load projection at t_b, P_{ref} (ppq) is the start of the projection, t_b is the estimated time of the projection and t_{ref} is the reference (initial) year.

Table 1. HCn content in cassava.

Type: non GMO	Non-bitter	Bitter	Very bitter	references
tubers & leaves	100 mg HCn/kg fW*	100–450 mg HCn/kg fW*	450 mg HCn/kg fW*	[41]
		10–500 mg HCn/kg dW*		[4]
		6–250 mg HCn /kg fW*		[7]
		420 mg HCn/kg fW*		[41]
		200–1300 mg HCn/kg dW*		[5]
type: Gmo	non-bitter			[11]
tubers & leaves	10–50 mg HCn/kg fW*			[42]
	6–50 mg HCn/kg fW*			[7]

notes: HCn estimated at an average of 250 mg HCn per kg dry weight cassava tubers (dWCt) in mature plants [7].
*dW: dry weight, fW: fresh weight.

Statistical analysis of FAO data

A statistical analysis of FAO data (2002–2013) [28] and the estimated projection trend up to 2024 was done using MS Excel® v2010. For modelling HCN load into the environment, 250 HCN (mg) per mass (kg) was used as per FAO data (Table 1). For data presentation, 1 quadrillion was represented as HCN concentration divided by 10^{15}. The mean absolute deviation (MAD) between the model and the actual data was calculated Equation (3).

$$\mathrm{MAD} = \frac{\sum |\mathrm{errors}|}{n} \tag{3}$$

where Σ |errors| is the absolute value of errors between the projection and actual HCN load values (ppq), while n is the number of periods (yr) under consideration.

Cassava plant health studies

The overall plant health of cassava under greenhouse conditions, characterised by PAR and chlorophyll content measurements, was assessed. These two processes are important for plant growth under normal and controlled environments to assess developmental functions such as leaf lifespan, nitrogen content, hydraulic conduction, chlorophyllfluorescence and relectance [29]. Although chlorophyll and PAR fluorescence wavelength range is between 400 and 700 µmol/m^{2}s [30], a healthy plant under a controlled environment has a relative photosynthesis efficiency range between 380 and 780 µmol/m^{2}s [30], while its chlorophyll content can range between 15 and 200 µmol/m^2 [31,32]. Plants' leaves contain pigments (chlorophyll) that react with photochemical energy (photons) during the photosynthesis process. During the process CO_2, water molecules and photons are used to produce plant's growth elements (e.g. glucose) while; the hydrogen atom is removed and replaced by oxygen which is released in the air [32].

The physical characteristics of the cassava plants used for analysis were: Plant 1: 63.5 cm long; the two branches were 53, 44 and 37 cm long; the length of the leaves on each branch was approximately 31 cm. Another plant (Plant 2) was 1.05 cm long with minimal sprouting of branches; the leaves were 43, 38, and 30 cm long.

Finally, cassava cuttings of 15 cm were placed into rectangular plastic trays for 6–10 days, depending on the plants' growth, then transferred into 4 kg black plastics bags with soil and placed on top of a warm bed to allow growth for 2–3 months. The plants were water sprinkled for 2–3 min periodically, with the temperature in the greenhouse ranging from

19 to 25 °C. At five months, plants were transferred into 10 kg bags for rooting development and further growth.

Determination of plant's chlorophyll content and PAR

A chlorophyll content meter (CCM, Model-200 plus, ADC BioScientiic Ltd) and a PAR meter (AccuPAR PAR/LAI Ceptometer, Model LP-80, Decagon Devices, Inc., USA) were used to assess the chlorophyll content and PAR from cassava leaves according to the manufacturers' instructions. During measurements, three (3) readings from three different leaves of each plant were taken. Each leaf reading was averaged and the readings were repeated thrice. Finally, a standard deviation for each reading was calculated (Equation 4):

$$\text{Standard Deviation} = \frac{\sum (x - \bar{x})}{n} \tag{4}$$

where x – measure value (µmol/m^{2}s); $\bar{x}$ – average of the reading (µmol/m^{2}s); n – number of times the measurements were taken.

The PAR actual signal was obtained using the following Equation 5:

$$S_{act} = S_{obs} + S_{dev} \tag{5}$$

where S_{act} – *is the* Actual signal, S_{obs} – Observed signal and S_{Dev} – Signal deviation.

Determination of gases (NH_3, HCN, NO_2) volatilised from cassava plants

A gas analyser device was constructed (see Figure 2(a)–(c)) using rectangular plastic containers (ADDIS® clear storage) of 56 L each. The containers were sealed using silicon glue. ATI Gas analysers (Wire Gas Transmitters, Models: B12-22-1-0200-1, range: 0–200 mg/L/HCN; B12-15-1-2000-1, range: 0–500 mg/L ammonia; B12-26-1-0200-1, range: 0–200 mg/L nitrogen dioxide) were placed on the inside of the constructed device at about 80 cm height, and an air pump (Resun® AC-9906) was placed at the bottom. A paperless recorder – Fiji Model PHF61B11-E1OYV-F (N & Z Instrumentation & Control Pty Ltd, South Africa) was used to determine the quantity of HCN, NH_3 and NO_2 volatilised from the cassava plants. Gas analysis was recorded at 24 h intervals.

Results and discussion

Cassava production and estimated HCN load in the environment

The results of the yearly cassava production revealed variation from one region to another: Africa (55% for daily consumption), Asia (32% for daily consumption/bioenergy), and South America (13% for daily-consumption/bioenergy) (Figure 1). This suggests that sub-Saharan Africa is the largest region in cassava production globally [33,34]. The quantity of HCN released per continent from 2002 to 2013 ranged from: 0.025×10^{-3} ppq to 6706×10^{-3} ppq (African), 0.012×10^{-3} ppq to 1010×10^{-3} ppq (Asian) and 0.007×10^{-3} ppq to 0.920×10^{-3} ppq (South American).

Africa's production of cassava during the ten years of study (2002–2013) is the highest in the world [35]. This may be owing to rapid population growth as well as the population's daily dependence on this cultivar, which constitutes a staple crop. During 2009 the production of cassava per ton for each region was: Africa: 1.21×10^8 tons, Asia: 8.1×10^7 tons and South America: 3.1×10^7 tons, while the estimated production of HCN released during the period under consideration was estimated at: 31.93×10^{-3}, 18.49×10^{-3} and 8.44×10^{-3} ppq, respectively [35] (Figure 2(a)–(c)).

The MAD was 10.48, 0.86, 0.05 for African, Asian and South American continents respectively, when the projections were compared against computed data.

Recently, cassava production has increased for several reasons: Africa (55%, self-nourishment only), Asia (32%, for self-nourishment and renewable energy (biofuel), South America (13%, self-nourishment and renewable energy production) [36–39]. In most cases the cultivar is used as a staple for the population. Manually processed products such as foufou, gari, manioc, etc., are sold [40]. Increased industrial activity, with high energy demand in Asia and South America, has resulted in production of the cultivar for biofuel [38,39,41]. Thus, the trend of cassava production globally has increased by 13% to 55% between 2002 and 2013, representing increases of 0.1×10^7–0.19×10^8 tons with a further

projected increase to 23.9×10^{-4} and 23.4×10^{-5} by 2024 (see Figure 1). The corresponding estimated HCN load in the environment would thus increase by 9.2×10^{-3}–47.1×10^{-3} ppq HCN from the smallest to the largest continental cassava producers, respectively.

This indicates the overall increase in HCN load in the environment per continent for the next decade (2014–2024) to be 60.5% (Africa), 57.7% (Asia) and 50.5% (South America). It has been previously determined that there is a direct relationship between increased cassava production and the concentration of cyanide released into the environment [40–43]. These increases in cassava production, and thus cyanide and/or cyanogen loading in the environment, necessitate the proper management of cassava cultivars, including the introduction of GMOs, particularly for Africa, to mitigate the increasing HCN loads, which eventually result in residual ammonium nitrogen (NH_4–N), nitrate (NO_3–), nitrite (NO_2–), nitric

acid (HNO_3), nitrous oxide (N_2O), NO and other sources of nitrogen oxides (N_yO_x).These releases contribute to global warming [17,18].

Changes in global weather patterns resulted in reduced casava production during the warmest years, i.e. 2005, 2010 and 2014, with global temperature anomalies of 0.53, 0.67 and 0.70 °C respectively [44–46]. This does not necessarily correspond with reduced cyanide loading in the environment. This is because higher global temperatures and the warmest years resulted in spoillage of crops and reduced the amount of agricultural produce, including cassava, reaching the market [42,43].

Global warming and higher temperatures could result in previously colder parts of the world having favourable weather conditions for cassava growth. Thus, in the past, South Africa, generally and the Western Cape province, particularly, did not have a record of producing cassava or even growing cassava plants because of cold weather conditions. Recently, cassava plants have been grown in the north-eastern [47,48] and south-western regions of the country which were previously known as cold areas, owing to changes in weather conditions.[1] Thus, favourable growth conditions will lead to an increase in production, resulting in an increase in HCN load release into the environment through volatilisation [46–49].

Determination of cassava plant volatilised gases (HCN, NH_3, NO_2), chlorophyll content and PAR

Plant gases (HCN, NH_3, NO_2) volatilised from healthy cassava plants (1 and 2) which were 8–10 months old with a height range of 55–170 cm, showed varying concentrations of gases being produced. he gases released from both plants (1 and 2) measured using 12 h intervals were 4.7 mg/L (HCN), 10.1 mg/L (NH_3), 3.6 mg/L (NO_2) and 40.7 mg/L (HCN); and 67.9 mg/L (NH_3) and 1.9 mg/L (NO_2), respectively. The chlorophyll content of the cassava leaves ranged from 26.55 to 29.5 μmol/m^2 for Plants 1 and 2, respectively. Irradiance PAR on both plants' leaves showed that it ranged from 169.67 to 399.67 μmol/m^2s (Table 2). The readings indicated that the cassava plants were healthier.

A comparative analysis of the averaged cassava plant gas analyses revealed discrepencies between both plants as well as the two readings of each plant. The initial readings for Plant 1 for HCN and NH_3 were lower than the second set of readings, while NO_2 values were nearly identical. In contrast, Plant 2 showed higher values for the irst readings for all three gases (HCN, NH_3, NO_2) than for the second readings (Table 3). The difference of the values is caused by: (1) the transformation of volatilised HCN into NH_3 and NO_2; (2) a decrease in or insufficient CO_2 in the gas analyser device and insufficient solar radiation for photosynthesis; and (3) the length and size of plants as well as their leaves.

Analysis of the chlorophyll content and PAR for each plant showed minimal differences between the two plants: chlorophyll readings were 28.75 μmol/m^2 with a standard deviation of ±2.32 (Plant 1 before being in the gas analyser device) and 29.52 μmol/m^2 with a standard deviation of ±0.69 (after 12 h in the gas analyser device). Additionally, Plant 2 readings revealed chlorophyll levels of 26.55 μmol/m^2 and 29.8 μmol/m^2 with a standard deviation of ±1.45 and ±1.13 respectively, which are in the range of 15–200 μmol/m^2 for a healthy plant [21,22,30]. Both plants' chlorophyll content after 12 h in the device was nearly identical (Table 2).

The PAR value of both plants showed a discrepancy, with Plant 1 having a higher PAR prior and ater gas analyses (Table 2). The discrepency was attributed to the decrease of the

Table 2. Chlorophyll and photosynthetically active radiation (Par) readings of cassava plants.

	Chlorophyll content (μmol/m2)			
	Plant 1		Plant 2	
	A	B	A	B
average	28.75	29.52	26.55	29.8
Stand. dev.	±2.32	±0.69	±1.45	±1.13
	Par (μmol/m^2s)			
average	399.67	260	169.67	88
Stand. dev.	±16.8	±3.3	±26.8	±0.7

*a – plant readings prior to being placed into the gas analyser device and B – plant readings taken 12 h after volatilised gas analyses.

Table 3. average cassava plant gas readings using gas transmitter devices (mg/l).

Sampling regime/time	Plant 1			Plant 2			Control		
	HCN	NH_3	NO_2	HCN	NH_3	NO_2	HCN	NH_3	NO_2
t: (16:00, 19:00, 22:00)	4.7	10.1	3.6	40.7	67.9	1.9	0	0	0
t: (07:00, 10:00, 13:00)	31.5	53.1	3.1	5.3	7.8	1.1	0	0	0

t*: time intervals for the cassava plants' gas analyses.

cassava plants' photosynthesis activity, which affected radiant power during measurements in the laboratory, as well as to the lack of sufficient solar radiation.

Conclusion

The production of cassava contributes to an increase of the HCN in the environment through volatilisation. The increase in cassava production to feed communities can alleviate poverty and improve biofuel production for energy. The use of genetically modified cassava will reduce the high concentrations of HCN released/volatilised into the environment. This will eventually contribute to the reduction of environmental pollution and mitigate climate change. The plants' data for chlorophyll content and PAR showed that there are discrepancies prior to and after the analyses. Plants' chlorophyll content and PAR readings were in the range of healthy plants, thus indicating healthy plant leaves.

Glossary

CCM	chlorophyll content meter
CN^-	cyanide
DW	dry weight
DWCT	dry weight cassava tubers
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
F-CN	free cyanide
FW	fresh weight
GIS	geographic information system
GMOs	genetically modified organisms
HCN	hydrogen cyanide
HNO_3	nitric acid
MAD	mean absolute deviation
NGOs	Non-Governmental Organisations
NH_3	ammonia
NH_4^+	ammonium
NH_4-N	ammonium nitrogen
NO	nitric oxide
NO_3^-	nitrate
NO_2^-	nitrite
N_2O	nitrous oxide
NOB	nitrite-oxidising bacteria
NyOx	nitrogen oxides
OCN^-	cyanate
PAR	photosynthetically active reaction
Pg C	petagrams of carbon
ITCZ	intertropical convergence zone
UN	United Nations
UNEP	United Nations Environment Programme

UNCTAD	United Nations Conference on Trade and Development
WHO	World Health Organization

Note

1. For example, on Wednesday, 4 March 2015, Cape Town (in the Western Cape) recorded a temperature of 40 °C, the highest in 100 years.