

EFFECTS OF GAS FLARE FROM UTOROGU GAS PLANT ON BIOCHEMICAL VARIABLES OF CASSAVA LEAVES (*Manihot Esculentum*), DELTA STATE.

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ABSTRACT: Gas flaring is a major contributor to the emission of toxic gases and other gaseous pollutants into the atmosphere. This study investigates the impact of gas flare on leaves of cassava around Utorogu gas plant, Delta State. Three sampling locations were chosen at 1 km , 2km and 3km distance from the gas flare stack and a control location at Ororokpe. Ambient air quality was determined for methane (CH₄) (ppm), oxide of sulphur (SO_x) (ppm) oxide of nitrogen (NO_x) (ppm), carbon monoxide (CO) (ppm), and hydrogen sulphide (H₂S) (ppm). Leaves collected were taken to the laboratory for analysis. Relative Leaf Water Content (RLWC)(%), Total Chlorophyll Content (TCC)(mg/m³), Leaf Extract pH(LEP)(mol/litre) and Ascorbic Acid Content (AAC) (mg) were determined under standard laboratory methods. Ensuing data were subjected to standard statistical analysis . Results showed that CH₄ varied from 38.00-92.00ppm, H₂S from 0.05-1.20ppm, CO from 11.00-26.40ppm, SO₂ from 252.00-340.00ppm and NO₂ from 82.00-190.00ppm. RLWC varied from 30.50-56.33, TCC varied from 1.98-4.66, LEP varied from 4.50-7.00mol/litre and AAC varied from 0.03-0.15. It was revealed that NO_x, SO_x and CO exceeded NESREA's short-term tolerance limits for ambient air pollutants of (40-60) ppm, 100 ppm, and 10ppm respectively. This shows that air pollutants exerted significant inhibitory influence on biochemical activities of the leaf studied. Environmental regulatory agencies and oil exploration companies should help reduce gas flaring to avoid damages to crop production.

KEYWORDS: *Air pollutants, Biochemical variables, Cassava leaves, Crop growth.*

INTRODUCTION

Air pollution deteriorates ecological condition, and it is the alteration in any atmospheric constituent from the value that would have existed without human activity [1] In recent past, air pollutants, responsible for vegetation damage and crop yield losses have been of increasing concern [2]. The increasing number of industries and automobile vehicles are continuously adding toxic gases and other substances to the environment [3]. These toxic pollutants include sulphur and nitrogen oxides, carbon (II) oxide and soot particles, as well as smaller quantities of toxic metals, organic molecules and radioactive isotopes [4]. Effects of air pollutants on vegetation is the best direct determination of toxic effects of air pollutants [5] .

Associated gases are routinely flared in the course of producing and processing oil. Flaring is a means of safe disposal of waste gases through the use of combustion. However, the Nigerian case attracts more attention given the volume of gas flared and its consequences since the beginning of commercial oil production in the country [6]. According to [7] gas flaring is a major contributor to the emission of toxic gases and other gaseous pollutants into the atmosphere. Like the combustion of other carbonaceous fuels, gas flaring produces oxides of carbon (CO_x), sulphur (SO_x) and nitrogen (NO_x), water vapor, volatile and non-volatile forms of trace metals (e.g. Pb, Hg, Cd, As, etc). [8] stated that incomplete combustion of the flared gas also produces greenhouse gases such as methane, other gaseous pollutants as CO and organic elemental particles such as coke.

Common effects of gas flaring are reduction in soil moisture content, thereby reducing its fertility, corrosion of house and other structures as the flare pollutants (SO_x and NO_x) form acids in the presence of rain water. The acidification of rivers and streams could result in reduction in aquatic life.

Other effects of gas flare on vegetation include:

Chlorosis: SO₂ destroys plant tissues and produces gradual yellowing of leaves as chlorophyll production is impeded [9],

Necrosis: (10) observed that plant organs are impacted by air pollutants leading to necrosis (dead areas on leaves)

Epinasty: (downward curvature of leaves and abscission (dropping of leaves), reduction in growth rate and eventual death of plant (10)

Reduction in soil moisture content, in extension reduction in fertility and crop yield.

As inhabitants are agrarians and their farmlands located in the vicinity of the flow station, this research therefore targeted the effect of these pollutants on the biochemical variables of cassava (*Manihot esculentum*) leaf around the area.

Hydrocarbons contained in gas such as methane, ethane, butane, propane, had been discovered around the gas Plant. This research therefore targeted the effect of these pollutants on air quality and cassava leaf biochemical compositions.

METHODOLOGY

Study Area

Utorugo is situated in Ugheli south local government area of Delta State, Nigeria . It is found at longitude 060,01'34.72''E and latitude 050,31' 19.59''N. Data reveal annual rainfall of 2650mm. Temperature is high throughout the year with an annual mean of 26.3⁰C monthly. Relative humidity range from 60-80% with peak values > 80% recorded in July and August between 2100h and 0700h. The surface wind at Utorogu is calm (1.6 – 2.1m/s) with moderate potentials for dispersing air pollutants introduced to them and is predominantly southwest during the wet season and northeast during the dry season [11]. Vegetation is typical rainforest in nature. The area is a flat lying terrain with elevations below 10 meters above the sea level. The entire area is made up of flood plains with recent alluvial accumulation.

The inhabitants are predominantly farmers. The estimated total population figure is projected at 311,970 [12].

Sampling Collection

Leaf sample collection

With the aid of a stainless knife, leaves of cassava (*Manihot esculenta*) were randomly collected in three different locations at a distance of 1km, 2km, and 3km apart (L1, L2 and L3) and a control sample L4 at 10km away. Samples were carefully taken to the laboratory in a stainless container under a space of 1hour.

Air Quality Monitoring

The sampling equipment used include High Volume Sampler (HVS) (testo 350 Flue gas Analyzer) and Digital automatic gas monitors.

High Volume Sampler (HVS): The modified EPA gravimetric high volume method was used. This technique involved drawing a known volume of air through a pre-weighted glass fiber filter (20 X 25cm) by means of heavy duty turbine blower at flow rate of 1.3 m³/min [11]. This collected suspended particulate matter within the size range of 100-0.1µm diameters.

Digital Automatic Gas Monitors (DAGMs). The Crowcon Gasman Air Monitor that had been pre-calibrated using air cylinder standard [11] was used in the direct detection of CH₄, CO, NO_x, SO_x, H₂S and Temperature (0°C) while the Haze dust 10 µm Particulate Monitor was used for the detection of particulate matter (SPM₁₀).

Determination of Biochemical variables

Relative Water Content (RLWC):

With the method as described by Singh [13], leaf relative water content was determined and calculated with the formula:

$$RLWC = \frac{FW - DW}{TW - DW} * 100$$

Where;

FW = Fresh weight

DW = Dry weight

TW = Turgid weight

Fresh weight was obtained by weighing the fresh leaves. The leaves were then immersed in water over night, blotted dry and then weighed to get the turgid weight. The leaves were then dried overnight in an oven at 70°C and reweighed to obtain the dry weight [14].

Total Chlorophyll Content (TCC)

This was carried out according to the method described by [15]. 3 grams of fresh leaves were blended and then extracted with 10ml of 80% acetone and left for 15 minutes for thorough extraction. The liquid portion was decanted into another test-tube and centrifuged at 2,500rpm for 3 minutes. The supernatant was then collected and the absorbance taken at 645nm and 663nm using a spectrophotometer. Calculations were done using the formula below.

$$\text{Chlorophyll a} = 12.7_{DX643} - 2.69_{DX645} X Vmg$$

$$\text{Chlorophyll b} = 22.9_{DX645} - 24.68_{DX665} X Vmg$$

$$\text{TCh} = \text{Chlorophyll a} + \text{b mg/g}$$

D_x = Absorbance of the extract at the wavelength x nm.

V = Total volume of the chlorophyll solution (ml)

W = Weight of the tissue extracted (g)

Leaf Extract P^H

5g of the fresh leaves was homogenized in 10ml deionized water. This was filtered and the pH of the leaf extract determined after calibrating pH meter with buffer solution of pH 4 and 9 [14]

Ascorbic Acid (AA) Content

Ascorbic acid content (mg/g) was measured using spectrophotometric method [14]. One gram of the fresh foliage was put in a test-tube, 4ml oxalic acid – EDTA extracting solution was added; then 1ml of orthophosphoric acid and plus 1ml 5% tetraoxosulphate (VI) acid added to this mixture, 2ml of ammonium molybdate was added and then 3ml of water. The solution was then allowed to stand for 15 minutes. After which the absorbance at 760nm was measured with a spectrophotometer. The concentration of ascorbic acid in the sample was then extrapolated from a standard ascorbic acid curve.

Statistical Analysis

Descriptive statistics that further employed the use of graphical illustrations were used to present requisite data. The Pearson Product Moment Correlation Coefficient (r) was used to investigate the relationships between the parameters measured. The test of equality in mean variances of the parameters measured in air and cassava leaf was conducted with the one-way analysis of variance (ANOVA). A further examination of relationships and model predictions of related variables was explored with the linear regression. A test of normality of error terms was conducted with regression standardized residual plots.

RESULTS

Ambient air Quality

Wide variations were observed in some of the air pollutants measured (CH₄, H₂S, SO_x, CO and NO_x) across the sampling locations. Methane varied from 38.00-92.00 (65.83±6.20), hydrogen sulphide varied from 0.05-1.20(0.52±0.13), carbon monoxide varied from 11.00-26.40(21.12 ±1.62), oxides of sulphur varied from 252.00-340.00(278.33±8.82) and oxides of nitrogen varied from 82.00-190.00(127.42±13.01), and Temperature 26.5⁰C- 35.6⁰C (30.2±0.40)

Table 1. Descriptive statistics of Air Pollutants around Utorogu gas plants (ppm)

Parameters	Minimum	Maximum	Range	Mean	SE	FEPA (1991)
CH ₄	38.00	92.00	54.00	65.83	6.20	NS
H ₂ S	0.05	1.20	1.15	0.52	0.13	NS
CO	11.00	26.40	15.40	21.12	1.62	10
SO ₂	252.00	340.00	88.00	278.33	8.82	100
NO ₂	82.00	190.00	108.00	127.42	13.01	40-60
Temp.(⁰ C)	26.5	35.6	9.1	30.2	0.40	NS

SE = standard error, NS = not specified

Oxides of nitrogen(82-190) ppm, oxide of sulphur (252-340) ppm, and Carbon (11) oxide (11.00-26.40) ppm measured exceeded FEPA (1991) short-term tolerance limits for ambient air pollutants of (40-60) ppm 100 ppm, and 10ppm respectively.

Biochemical Parameter of Cassava (*Manihot esculenta*) leaves

Slight variations were observed in the biochemical variables measured across the sampling locations. RLWC varied from 30.50-56.33 (42.65±2.08), TCC varied from 1.98-4.66(3.49±0.28), LEP varied from 4.50-7.00(5.39±0.20) and AAC varied from 0.03-0.15(0.99±0.11)

Table 2. Variation in biochemical parameters of cassava leaves around Utorogu gas plant (ppm)

Parameters	Minimum	Maximum	Range	Mean	SE
RLWC	30.50	56.33	25.83	42.65	2.08
TCC	1.98	4.66	2.68	3.49	0.28
LEpH	4.50	7.00	2.50	5.39	0.20
AAC	0.03	0.15	0.12	0.99	0.11

SE = standard error, RLWC = relative leaf water content, TCC = total chlorophyll content, LEpH = leaf extract pH, AAC= ascorbic acid content.

Of the biochemical variables, RLWC exhibited the highest range of 25.83 ppm, while AAC recorded the least range of 0.12 ppm. However, TCC and LEpH exhibited comparatively moderate ranges of 2.68 and 2.50ppm respectively.

Relationships between air pollutants and biochemical variables of crop.

At $P < 0.05$, CH_4 and SO_x showed significant negative influence on TCC ($r = -0.683$) and RLWC ($r = -0.652$) respectively. At $P < 0.01$ CH_4 showed significant negative influence on RLWC (-0.815), H_2S showed negative significant influence on RLWC (-0.823) and TCC (-0.776). CO showed significant negative influence on RLWC (-0.740), LEpH (-0.833), AAC (-0.810) while SO_x showed significant negative influence on TCC (-0.841). NO_x showed significant negative influence on RLWC (-0.808) and TCC (-0.733) at $P < 0.01$.

Many of the pollutants measured exerted significant inhibitory influence on the biochemical variables of cassava (**Table 3**)

Table 3. Correlation coefficients (r) between the air pollutants and crop leave variables.

Parameters	CH_4	H_2S	CO	SO_x	NO_x
RLWC	-0.815**	-0.823**	-0.740**	-0.652*	-0.808**
TCC	-0.683*	-0.776**	-0.482	-0.841**	-0.733**
LEP	-0.522	0.387	-0.83**	-0.09	-0.418
AAC	-0.245	0.188	-0.810**	-0.106	0.101

*** = significant at $P < 0.05$, ** = significant at $P < 0.01$, RLWC = relative leaf water content, TCC = total chlorophyll content, LEpH = leaf extract pH, AAC= ascorbic acid content.**

Regression between Biochemical variables and Air pollutants RLWC and Methane

The regression scatter plot showed that relative leaf water content (RLWC) decreased with increasing methane concentration (Fig.1). The multiple correlation, R , is large, $R= 0.815$, indicating a strong relationship. The coefficient of determination, R^2 , shows that more than $\frac{1}{2}$ the variation in RLWC is explained by the regression model. The regression and residual sums of squares (380.718 and 192.75 respectively) in the ANOVA table are unequal, confirming that more than half the variation in RLWC is explained by the model. The significance value of the F statistics (0.01) is less than 0.05, indicating that the variation explained by the model is not due to chance (i.e. is significant at $P<0.05$).

The coefficients table shows that the expected $RLWC = -0.274 \times CH_4 + 60.70$.

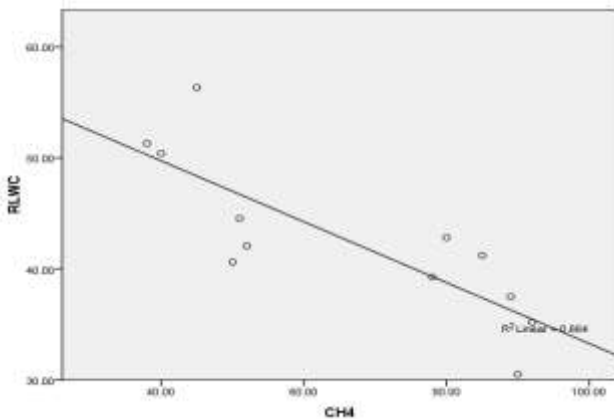


Fig. 1. Regression plot between relative leaf water content and methane concentration.

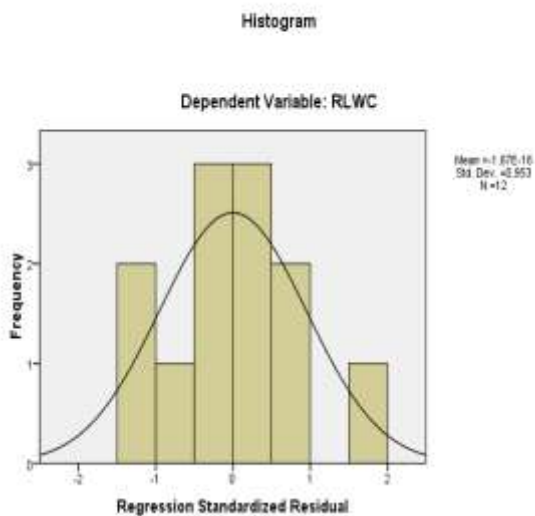


Fig. 2. Regression standardized residual plot between RLWC and CH_4 concentrations.

The test of the normality of the error term, using a regression standardized residual plot (**Fig.2**) revealed a histogram with approximately the shape of the normal curve.

TCC and Methane

The regression scatter plot showed reveals that Total Chlorophyll Content (TCC) decreased with increasing methane concentration (**Fig. 3**). The multiple correlation, R, is large $R=0.683$, indicating a strong relationship. The coefficient of determination, R^2 , shows that more than $\frac{1}{2}$ the variation in TCC is explained by regression model. The regression and residual sums of squares (4.794 and 10.273) respectively in the ANOVA table are unequal, confirming that more than half the variation in TCC is explained by the model. The significance value of the F statistics (0.01) is less than 0.05 indicating that the variation explained by the model is not due to chance (i.e. is significant at $P<0.05$).

The coefficients table shows that the expected $TCC = -0.031 \times CH_4 + 5.521$.

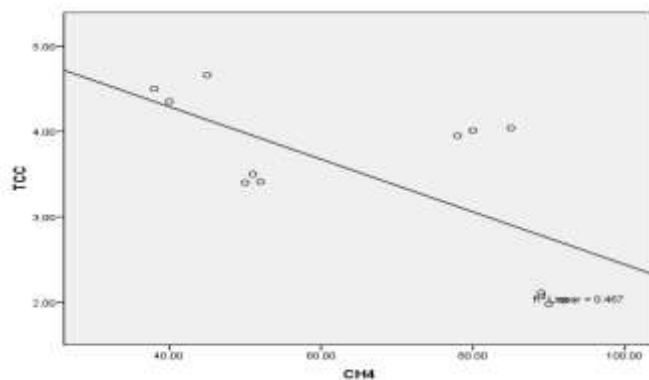


Fig. 3. Regression graph of Total Chlorophyll Content and Methane

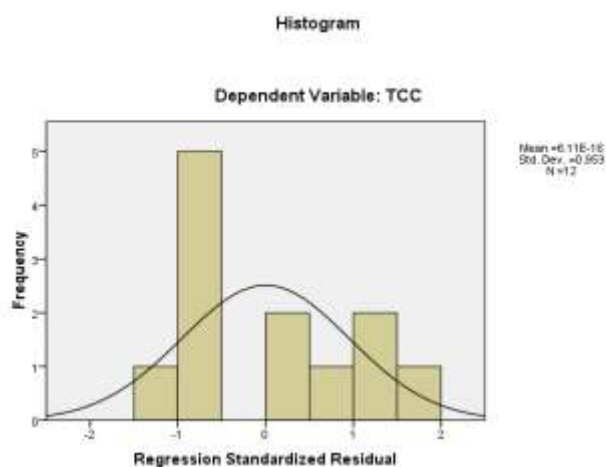


Fig. 4. Regression standardized residual plot between TCC and CH_4 concentrations.

The test of the normality of the error term, using a regression standardized residual plot (Fig.4) revealed a histogram with approximately the shape of the normal curve.

Spatial Variation in biochemical variables and air pollutants.

There existed variations in concentrations of both biochemical and air pollutants variables measured across the sampling locations. Biochemical concentrations in relative leaf water content (RLWC), total chlorophyll content (TCC), and ascorbic acid content (AAC) were highest in sampling locations 3, 2, and 1, respectively from the flare stack respectively. Methane, carbon 11 oxide, oxide of sulphur, hydrogen sulphide and oxide of nitrogen were highest in cassava leaves in locations 1, location 3, location 3, location 2 and location 3 respectively.

The test of equality in mean variances of the trace metals concentrations across the horizontal sampling locations from the flare stack revealed inequalities (heterogeneity) in air variables [$F_{(16.59)} > F_{crit(4.10)}$] and in the biochemical variables, [$F_{(5.23)} > F_{crit(4.17)}$] at $P < 0.05$.

Longitudinal variation of air pollutants and biochemical variables.

The oxides of sulphur IV (SO_2) exhibited maximum concentration; while H_2S was least at all the sampling locations (Figure 5). In the overall, SO_2 concentration was highest (340 ppm) in sampling location 1, while least (257 ppm) in location 3.

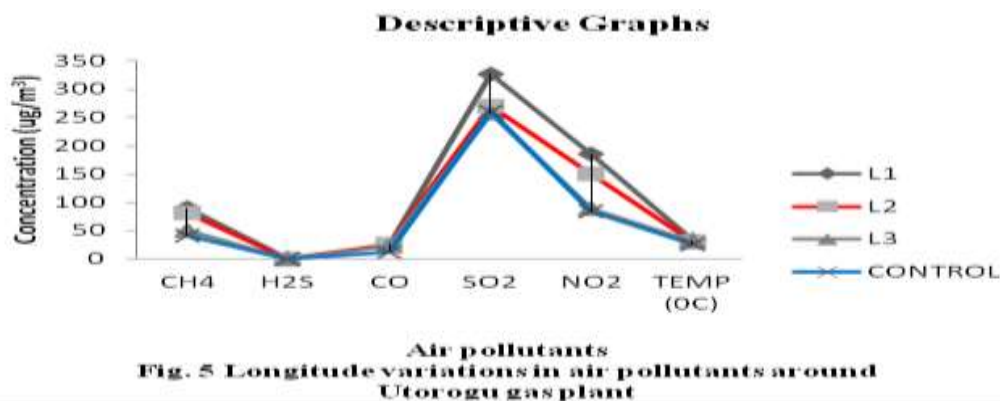


Fig. 5. Graph of Longitudinal variations in air pollutants around Utorogu Gas Plant.

Longitudinal variation of biochemical variables of *Manihot esculenta* around Utorogu gas plant.

The control location recorded comparatively higher concentrations in RLWC (56.33ppm), TCC (4.66 ppm) and LEP (7.00ppm).(Figure 6). However, RLWC in cassava leaves revealed maximum concentrations at all the locations while AAC revealed least concentrations.

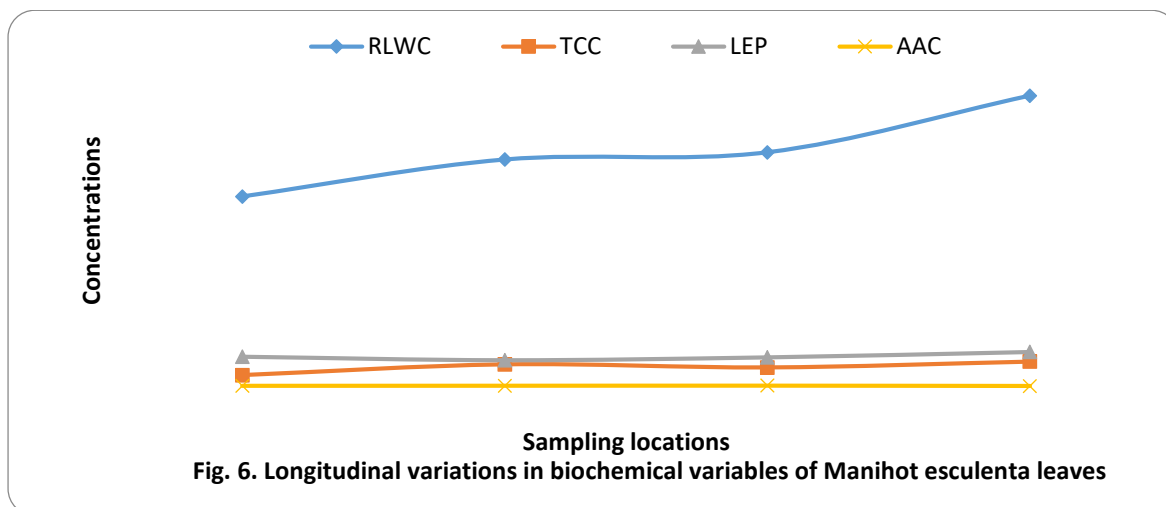


Fig. 6. Graph of Longitudinal variations in biochemical variables of *Manihot esculenta* leaves.

DISCUSSION

We observed that concentration of the pollutant gases in this study area are obviously elevated high above natural ambient levels [16, 12]. However, values recorded are slightly lower than those recorded by [8] in ambient air samples around a gas flare station at Oben community in the Niger Delta of Nigeria. This elevation was obviously contributed by the gas flare source point of pollution. This collaborates the work of [7, 8] that gas flare fallouts contribute pollutants to the air [17, 18].

Polluted air could lead to losses in essential nutrient as well as contribute to toxic components of crop growth in most agricultural villages. Rainwater containing various metals (such as Cd, Pb and Hg) had been identified as a major cause of serious health problems in the Niger Delta area [19]. Some of these health problems include anemia, renal dysfunction, lung cancer and other neo-behavioral effects. Other negative effects are corrosion and tarnishing of metals (including building roofs), erosion and soiling of buildings, as well as discoloration and peeling of paints [7]. The negative effects of air pollutants on plants have been reviewed by [3].

Mean Methane, Oxides of Sulphur, Nitrogen and Carbon concentrations of the current study were higher than values recorded by [14] in gas flare around Sapele gas plant in Delta State. [20].

We equally observed that Values recorded for H₂S by [13], (0.54-2.33 µg/kg) were higher than the current study's (0.05-1.20µg/kg). However, values of the air quality variables were comparable to their own, except for CO and Methane which were higher in the current study.

Observing the relationships between air pollutants and biochemical variables of crop, at $P < 0.05$ and $P < 0.01$, all the air pollutants show significant negative influence on biochemical variables.

In other words, it means that the air pollutants exerted significant inhibitory influence on biochemical variables of the crop studied.

However, the correlations in CH₄ and CO concentrations in cassava leaves indicate high uptakes of these substances through the roots and subsequent contributory translocation to leaves. The several correlations existing between air pollutants in leaves indicates the close relatedness of these plant parts. Nutrients and other substances are usually taken up from root to the leaves via the stem. On the other hand, gaseous exchanges occur in the leaves and are translocated to the other parts of the plant.

The regression between biochemical variables and air pollutants shows decrease in Biochemical variables (RLWC and TCC) with increase in air pollutants which explains the shrinkage observed in cassava and other plants in the area. The test of the normality of the error term, using a regression standardized residual plot revealed a histogram with approximately the shape of the normal curve.

The observed spatial variation in the biochemical variables concentrations has also been documented by other researchers [7; 17; 21, 22; 14, 3]. The consistency in highest concentrations in Ascorbic Acid Content across the sampling location indicates common pollutant source as well as ecological mobility and bioavailability in biotic tissues

Pollutant concentrations were generally highest in sampling location 2, horizontally from the flare stack and least in sampling location spatially, from the stack for air samples. This confirms the dispersal of aerial materials from point sources of pollution to distances in and around its vicinity. Dispersal of pollutants has been stated to be controlled by wind speed, direction as well as topography, and its concentrations affected by dilution effects over distances [23; 24].

CONCLUSION

CH₄ & SO_x showed significant negative influences on TCC and RLWC.

H₂S exerted significant negative influence on RLWC & TCC, while CO showed a significant negative influence on RLWC, LEP & AAC.

NO_x exerted significant negative influence on RLWC and TCC.

Vegetation is therefore an effective indicator of the overall impact of air pollution and the effects observed is a time averaged result that is more reliable than the one obtained from direct determination of the pollutant in air over a short period

The air pollutants exerted significant inhibitory influences on biochemical variables of the crop studied.

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