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Enrichment of some vegetables on display for sale along busy roads, with some essential elements due to vehicular emissions – A Case Study of the Haatso – atomic junction road in Accra, Ghana

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ABSTRACT

This work assessed the enrichment of lettuce and cabbage on display for sale along some busy roads in Accra with some essential elements using instrumental neutron activation analysis and atomic absorption spectrometry. The background levels of Fe, Mn, Cu and Zn, in lettuce and cabbage harvested from a vegetable farm were determined. The amount of the metals deposited on the vegetables after deliberate exposure along a busy road for three days were also determined. Background levels of elements in the vegetables in mg/kg were, Fe (162.97) > Mn (58.28) > Zn (10.78) > Cu (4.61) for lettuce and Fe (44.91) > Mn (20.95) > Zn (6.69) > Cu (1.16) for cabbage. The levels of all the elements increased in both vegetables after deliberate exposure with the third day recording the highest levels. The total amount of elements deposited on the vegetables after exposure for three days in mg/kg were Fe (22.27), Mn (11.8), Cu (1.68) and Zn (3.17) for lettuce and Fe (18.76), Mn (12.83), Cu (1.59) and Zn (5.58) for cabbage. Rates of enrichment of the vegetables by elements in mg/kg/day were, Fe (9.09) > Mn (3.93) >Zn (1.06) > Cu (0.56) for lettuce and Fe (6.25) > Mn (4.28) > Zn (1.86) > Cu (0.53) for cabbage.

Introduction

Increasing human population and the quest to make life comfortable have resulted in an intense increase in human activities. Most of these human activities including vehicular transport, burning of fossil fuel, waste disposal and incineration are concentrated in urban areas. The intensity of these activities has led to increased emissions of both organic substances and heavy metals into the urban environment (Wong *et al*., 2006). Heavy metals when present in the human body can either be beneficial or cause serious health problems by interfering with normal body functions. In small quantities, some heavy metals are nutritionally essential for a healthy life. Some of these are referred to as essential trace elements (e.g., iron, manganese, copper, zinc, Nickel, and chromium). Heavy metals get into the atmosphere by way of vehicular emissions and other human activities. Studies have been conducted to assess the heavy metal contamination of roadside soils and vegetation in different parts of the world (Nabulo *et al*., 2006; Temmerman and Hoenig, 2004; Amusan *et al.*, 2003; Jaradat and Momani, 1999; Othman *et al*., 1997; Fatoki, 1996; Golow, 1993a, 1993b). Most of these studies have indicated that the levels of heavy metals in roadside soils and vegetation are higher as compared to their natural background levels. However, not much work has been done to assess the heavy metal enrichment or contamination of food items such as vegetables displayed along busy roads. Previous studies have concentrated on the contamination of food crops such as vegetables, as they grow on heavy metal contaminated soils. When these vegetables are harvested, they no longer absorb heavy metals from the soil but when the harvested vegetables are displayed along busy roads for sale, the questions to answer are, (1) Do the levels increase as a result of adsorption and absorption after atmospheric deposition of particles on them? (2) Does the washing of vegetables reduce the levels of metals not? Answers to these questions will give an idea as to what levels consumers in urban areas are actually exposed to.

Materials and methods

Equipment:

Freeze drier (BETA 1-16), microwave digester (ETHOS 900), VARIAN AA 240FS flame atomic absorption spectrophotometer, Ghana Research Reactor-1 (GHARR-1), a PC-based gamma-ray spectrometer system consisting of a high purity germanium (HPGe) N-type coaxial detector (model GR 2518-7500SL), a high voltage power supply model 3103, a spectroscopy amplifier model 2020 and a multi-channel analyzer (MCA).

Chemicals and reagents:

5 % v/v HNO_3 65 % HNO_3, 30 % H_2O_2, SRM 1571 Orchard Leaves, SRM 1547 Peach Leaves

Study area

The samples chosen for the study were cabbage and lettuce and Figures 3.1 – 3.3 show some details about the study area. The samples were harvested from a vegetable farm in a vegetable growing area, about four (4) kilometers away from the main road in Dawhenya. Dawhenya is located in the Dangbe West District of the Greater Accra Region in Ghana. It is located on the main Tema – Afloa road and is about eleven (11) kilometers from Tema.

The main "Haatso-Atomic Junction" road in Haatso was chosen for the exposure of the samples to vehicular emissions.

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Haatso is located in the Ga East district of the Greater Accra Region in Ghana. As part of this work, a three day study was carried out on the road and the average daily traffic density was estimated to be about 6000 vehicles per day. This road was chosen because, careful observation revealed that the area is not characterized by intense human activities such as biomass burning and refuse dumping which could enhance the concentration of the heavy metals along the road. The road was also chosen for its proximity to the Ghana Atomic Energy Commission where the analysis was carried out.

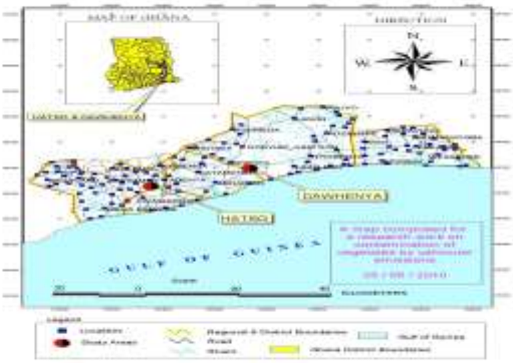

Fig 1: A map of Greater Accra showing Haatso and Dawhenya

Fig 2: A map of Dangbe West District showing the position of a vegetable farm at Dawhenya

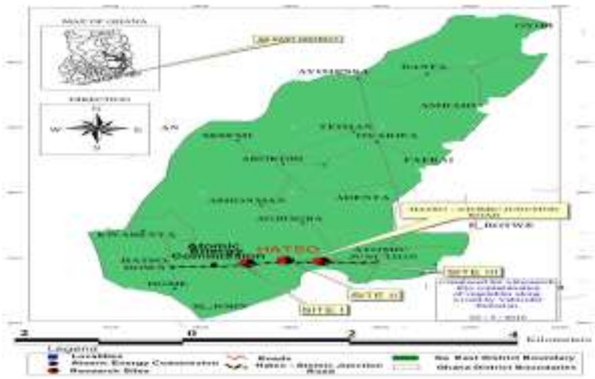

Fig 3: A map of Ga East District showing Haatso – Atomic junction road

Sample collection:

Forty heads each of Lettuce and cabbage were harvested from the vegetable farm with at least five heads each taken at random from each bed. The vegetables were transported in polyethylene bags and on arrival they were washed with doubly distilled water. Six heads each of the washed cabbage and lettuce (making twelve) were selected at random on the same day and labeled unexposed. On the next day the remaining were displayed at three locations along the selected road labeled site 1 (S1), site 2 (S2) and site 3 (S3). The vegetables were displayed from 8 am to 6 pm (10 hours) each day for three days. At the end of each day, three heads each of cabbage and lettuce were selected at random from each of the three sites and sent to the laboratory. The collection was done in such a way that, the last batch of vegetables were collected after they had been exposed for three days (30 hours)

Sample preparation:

The Twelve (12) heads of unexposed vegetables (six each of cabbage and lettuce) were cut separately into pieces. A portion of each of the twelve heads of vegetables after cutting was placed into a separate zip lock and labelled. In all, twelve (12) unexposed samples were prepared and were all placed immediately in a freezer. For the exposed vegetables, the three heads each of cabbage and lettuce (making 6) taken from each of the three sites (making 18) at the end of each day were cut separately into pieces. A portion of each head of vegetable, after cutting, was washed with doubly distilled water and the remaining portion left unwashed.

All portions both washed and unwashed (making 36) were placed in separate zip locks, labelled accordingly and placed immediately in a freezer. In all, a total of hundred and eight (108) exposed samples were obtained for the three days. All the 120 samples (both unexposed and exposed) placed in a freezer, were allowed to freeze at a temperature of 0 ^{o}C for two (2) days. All frozen samples were dried with a freeze drier (BETA 1-16) at a temperature of 23 ^{o}C. The dry samples were pulverized and stored in separate zip locks which had all been pre-cleaned with acetone.

For INAA, About 0.2 g of each of the pulverized samples was weighed into separate clean polythene foil, wrapped with forceps and the foil heat–sealed. Two (2) replicates of each of the samples were prepared.

Two replicates of a standard reference material of peach leaf (SRM 1547) from National Institute of Standards and Technology (NIST) were prepared. The reference materials were packed together with samples as close as possible in the same polyethylene irradiation vial. This was to ensure that samples and standards were activated under the same conditions as possible since any variation can remarkably affect the accuracy. The reference materials were used as a comparator standard for quantitative evaluation using the relative method of standardization for neutron activation analysis (NAA).

For AAS, Digestion beakers, test tubes and volumetric glasswares were cleaned by first soaking them in 5 % v/v trioxonitrate(v)acid for 24 hours and then rinsed with double distilled water for a minimum of six times and oven dried. 0.5 g of each of the pulverized samples was weighed into Teflon vessels of a microwave digester (ETHOS 900). 6 ml of 65 % HNO_3 and 1ml of 30 % H_2O_2 were added to each vessel containing the sample. The vessels were swirled gently to mix well and fitted into the microwave digester (ETHOS 900) and digested for 25 minutes. Replicates of each sample were prepared in a similar manner for digestion.

Upon completion of digestion, the solutions containing the samples were cooled down in a water bath for fifteen (15) - twenty (20) minutes to reduce the high temperature and pressure built up within the vessel.

Each solution was transferred into a measuring cylinder and diluted to 20 ml using deionised water. Blanks were prepared in a similar way but without samples. All the samples and blanks were analysed using VARIAN AA 240FS flame atomic absorption spectrophotometer.

Sample analysis

The samples were analyzed for the heavy metals using the research reactor (neutron activation analysis) and the atomic absorption spectrophotometer all at the Ghana Atomic Energy Commission. Neutron activation analysis was used to determine manganese and copper which have short half-lives and cadmium with a medium half-life. Iron, zinc, nickel and chromium were not determined by neutron activation analysis because they have long half-lives and therefore analysis of the 120 samples can be time consuming. Lead was also not determined by neutron activation analysis because of the inability of the method to do so. Iron, zinc, nickel, chromium and lead were determined using the atomic absorption spectrophotometer.

Results and discussions

Validation of results:

Results of analysis:

Results obtained indicated that all the exposed samples (both lettuce and cabbage) at the three different sites along the road, recorded higher levels of the elements than the unexposed samples. Those collected after being exposed for three days recorded the highest levels of the elements. It was also observed that the values for the exposed samples showed slight variations among the three exposure sites. Analysis of variance (ANOVA) of concentrations by sites gave "P" values of 1.000 for lettuce and 0.998 for cabbage. Since P values are both greater than 0.05 ($P > 0.05$), the variations are statistically insignificant. This could be due to the fact that the three exposure sites were located along the same road and therefore factors such as traffic density and wind current which affect the deposition were similar. High values measured for the third day indicate that the deposition depends on the traffic density as well as the duration of exposure.

Due to the statistically insignificant differences observed for the three sites, mean levels of the metals in vegetables exposed at the three sites were calculated. Figures 4 to 7 give graphical representation of the average situation.

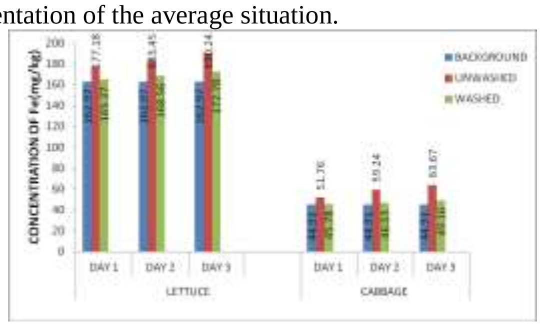

Fig. 4: Levels of Fe in vegetables exposed for three days compared with unexposed

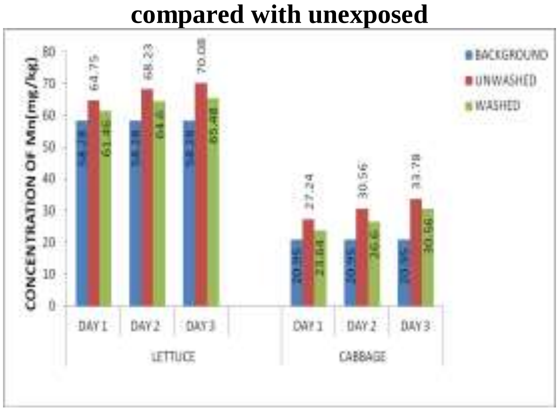

Fig.5 Levels of Mn in vegetables exposed for three days compared with unexposed

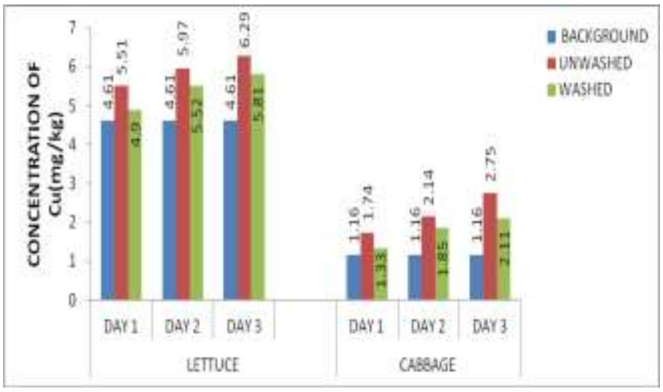

Fig. 6: Levels of Cu in vegetables exposed for three days compared with unexposed

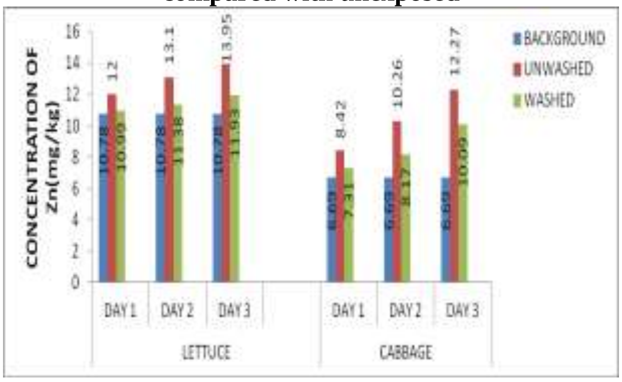

Fig. 7: Levels of Zn in vegetables exposed for three days compared with unexposed

From figures 4 - 7, the concentration of each metal increased with exposure period up to the third day for both vegetables. Washing was observed to reduce the concentration of the metals but could not reduce the concentration of any of the metals to the background level. This is in agreement with the statement made by Temmerman and Hoenig (2004) that there is no adequate method to completely remove all heavy metals originating from the dust deposition. The fact that washing could not remove completely the amount of heavy metals added after exposure suggests that adsorption and possibly absorption are both mechanisms involved in the enrichment process.

The high rate of enrichment of Fe and Mn could be due to their high natural abundance in the earth's crust causing them to be dominant in resuspended dust particles and road dust. The rate of enrichment of Mn was also high probably because of its use as a fuel additive. Zn and Cu follow Fe and Mn and this is also probably because the two elements are components of tyre and brake and they thus form a major part of road dust.

Atiemo, (2009) studied the elemental composition of road dust on some major roads in Accra. The results of enrichment factors showed no indication of anthropogenic contribution to the levels of Mn and Fe. Results for Zn and Cu however showed significant anthropogenic influence. This means that the enrichment by Fe and Mn cannot be avoided even if the vegetables are not exposed because the two elements have a crustal origin and are present in dust everywhere.

Conclusion

The levels of all the elements increased in both vegetables after deliberate exposure with the third day recording the highest levels. Total amount of metals in mg/kg deposited on lettuce for the three days were Fe (22.27), Mn (11.8), Cu (1.68), Zn (3.17), Total deposition for cabbage were Fe (18.76), Mn (12.83), Cu (1.59), Zn (5.58). This indicates that enrichment takes place when vegetables are exposed along busy roads and the extent of enrichment depends on the traffic density and the duration of exposure. Washing of the vegetables was able to reduce the levels of the heavy metals but could not reduce them to the background levels indicating that the enrichment of the vegetables was by adsorption and absorption The rate of enrichment of the vegetables by the heavy metals were determined in mg/kg/day to be Fe (9.09) > Mn (3.93) >Zn (1.06) > Cu (0.56) for lettuce and Fe (6.25) > Mn (4.28) > Zn (1.86) > Cu (0.53) for cabbage.

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Table 1: Measured and certified concentrations of elements in SRM 1571 orchard leaves (INAA)

ELEMENT	MEASURED VALUES(mg/kg)	CERTIFIED VALUES(mg/kg)	PERCENTAGE DEVIATION (%)
Mn	89±4.2	91±4	2.2
Cu	12.7±0.6	12±1	5.8
Cd	0.12±0.02	0.11±0.02	9.1

Table 2: Measured and certified concentrations of elements in SRM 1547 peach leaves (AAS)

ELEMENT	MEASURED VALUES (mg/kg)	CERTIFIED VALUES(mg/kg)	PERCENTAGE DEVIATION (%)
Zn	18.3 ± 0.5	17.9 ± 0.4	2.2
Ni	0.65 ± 0.08	0.69 ± 0.09	5.8
Pb	0.90 ± 0.03	0.87 ± 0.03	3.4
Fe	214 ± 5.1	(220)*	2.7
Cr	0.9 ± 0.02	(1)*	10

Table 3: Total and Rate of enrichment of lettuce and cabbage by elements

ELEMENT	LETTUCE		CABBAGE	
	C_t(mg/kg)	C_r(mg/kg/day)	C_t(mg/kg)	C_r(mg/kg/day)
Fe	27.27	9.09	18.76	6.25
Mn	11.8	3.93	12.83	4.28
Cu	1.68	0.56	1.59	0.53
Zn	3.17	1.06	5.58	1.86