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Pollution

Elixir Pollution 58 (2013) 15238-15242

ISSN: 2229-712X

Heavy metals and health risk assessment of selected vegetables on display for sale along the Haatso – Atomic High way in Accra, Ghana

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ARTICLE INFO

Article history:

Received: 13 March 2013;
Received in revised form:
15 May 2013;
Accepted: 29 May 2013;

Keywords

Metals,
Atomic,
Vegetable,
Vehicles.

ABSTRACT

This work assessed the heavy metal pollution impacts of vehicular and other human activities on vegetables such as lettuce and cabbage on display for sale along some busy roads in Accra using instrumental neutron activation analysis and atomic absorption spectrometry. The background levels of Ni, Cr, Cd and Pb 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, Cr (4.06) > Ni (2.93) for lettuce and Ni (2.59) > Cr (2.32) for cabbage. The levels of Cd and Pb in both exposed and unexposed samples were below the detection limits of the analytical instruments used. The levels of the elements detected 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, Ni (1.87) and Cr (1.16) for lettuce and Ni (2.38) and Cr (1.8) for cabbage. Rates of contamination of the vegetables by metals in mg/kg/day were, Ni (0.62) > Cr (0.56) for lettuce and Ni (0.79) > Cr (0.6) for cabbage. The estimated daily intakes of the elements through consumption of the contaminated vegetables were all below the upper tolerable intake levels of the elements and pose no health risk.

Introduction

Heavy metal pollution is one of the main ecological problems in most parts of the world (Claus *et al*., 2007; Gardea-Torresdey *et al*., 2005). Heavy metals are found in farmlands, plants as well as various food chains, which normally cause serious ecological and human health problems (Zheljazkov *et al*., 2006; Malik, 2004). Heavy metal pollutants are of significant ecological and environmental concern because unlike the organic pollutants, they are not biodegradable and have long half–lives in the soil. They therefore impose far reaching effects on biological systems including soil microorganism and other soil biota (Ram *et al*., 2000; Adeniyi, 1996). Majority of heavy metals are toxic to the living organisms and even those considered as essential can be toxic when present in high concentrations. Heavy metals can impair important biochemical processes posing a threat to human health, plant growth and animal life (Silva *et al.*, 2005; Jarup, 2003; Michalke, 2003). Pollution by heavy metals is a problem usually associated with areas of intensive industralization. However, roadways and automobiles are now considered to be one of the largest and primary sources of heavy metals (Aribike, 1996). It is now well established that a variety of motor vehicles introduce a number of toxic metals into the environment, most of which are released adjacent to roadways (Atiemo *et al*., 2010; Nabulo *et al*., 2006; Othman *et al*., 1997; Golow, 1993a, 1993b; Moore and Moore, 1976; Williamson, 1973). These metals are released during different operations of the road transport such as combustion of fuel and lubricating oil, component wear, fluid leakage and corrosion of metals. Copper is released by the wear of ball bearings, engine and brake parts. Zinc is released by tire wear, motor oil, grease, brake emissions and corrosion of galvanized parts while leaded gasoline, tire wear, bearing wear, lubricating oil and grease release Lead. Smaller amounts of many other metals, such as Manganese, Iron, nickel, chromium and cadmium are also released into the environment by automobiles. Manganese, now used in place of lead as a fuel additive in Ghana and in many countries, is released by combustion of fuel. Iron is released by auto body rust and engine parts. Cadmium is released by tire wear, fuel burning and batteries. Chromium is released by air conditioning coolants, engine parts and brake emissions, and Nickel is released by diesel fuel and gasoline, lubricating oil, and brake emissions. Iron, Manganese, Lead, Copper, Zinc, Nickel, Cadmium and Chromium are released by combustion of Engine oil by weak engines with worn out piston rings. The metals when released into the environment, contaminate foods such as vegetables sold along busy roads

Estimated daily intake (EDI) of metals through the consumption of these vegetables by humans can be calculated using the equation below (Zhuang *et al*, 2009).

$$EDI = \frac{C_{metal} \times W_{food}}{Bw}$$

EDI is the estimated daily intake (milligram/kilogram body weight)

C_{metal} is the concentration of the metal in the medium (milligrams per kilogram)

W_{food} is the daily average consumption (kilograms)

Bw is the body weight (kilograms)

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The EDI values can be compared with Upper tolerable intake level (UL), the level beyond which an adverse effect may occur.

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 Dangme 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. 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.

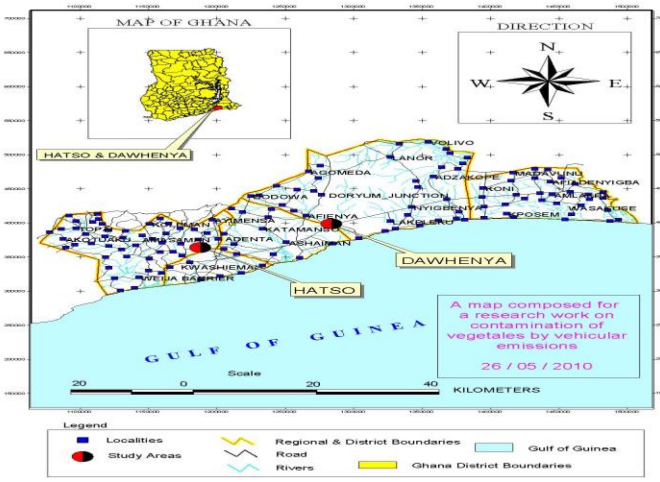

Fig 1: A map of Greater Accra showing Haatso and Dawhenya

Sample collection:

Forty pieces each of Lettuce and cabbage were harvested from the vegetable farms 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.

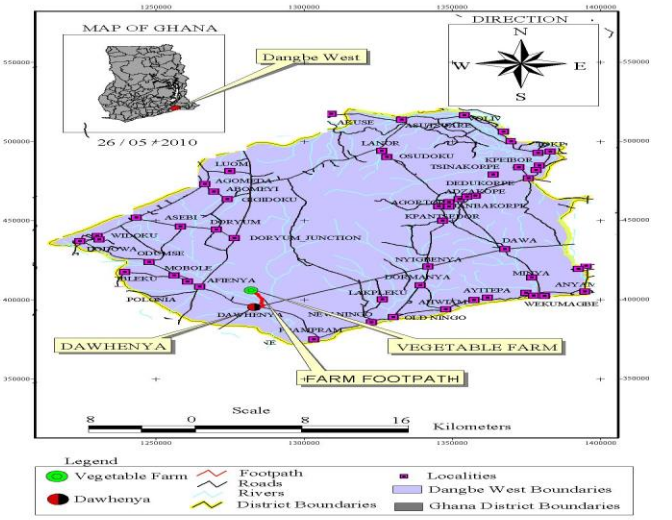

Fig 2: A map of Dangbe West District showing the position of a vegetable farm at Dawhenya

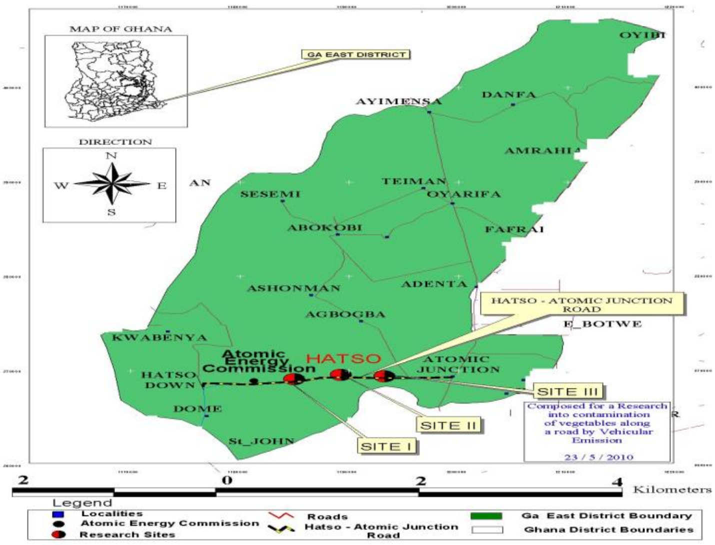

Fig 3: A map of Ga East District showing Haatso – Atomic junction road

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:

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 (%)
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 (%)
Ni	0.65 ± 0.08	0.69 ± 0.09	5.8
Pb	0.90 ± 0.03	0.87 ± 0.03	3.4
Cr	0.9 ± 0.02	(1)*	10

( )* Non certified / recommended / information values.

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 are 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 and 5 give graphical representation of the average situation. Results for Cd and Pb have not been shown because their levels were found to be below the detection limits of the analytical instruments used (0.001mg/kg for Pb with AAS and 0.01mg/kg for Cd with INAA).

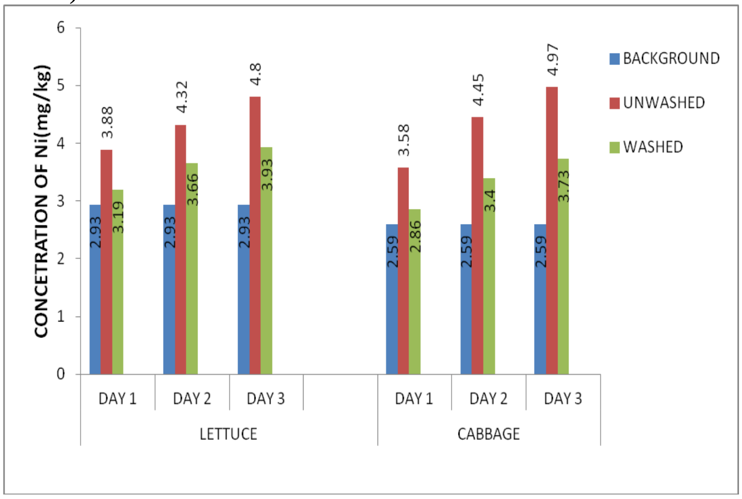

Fig. 4: Levels of Ni in vegetables exposed for three days compared with unexposed

From figures 4 and 5, 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 levels present before the exposure. 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 contamination process.

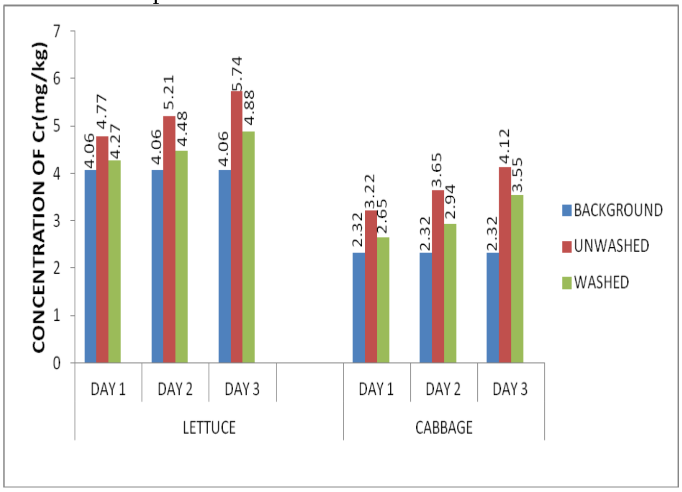

Fig.5 Levels of Cr in vegetables exposed for three days compared with unexposed

Total contamination (measured in mg/kg) and rate of contamination (measured in mg/kg/day) of the vegetables with the metals were determined and the results are as shown in table 3 below.

Table 3: Total and Rate of contamination 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)
Ni	1.87	0.62	2.38	0.79
Cr	1.16	0.56	1.8	0.6

Human Health Risk Assessment

Estimated daily intake (EDI) of metals through the consumption of vegetables by children and the aged were calculated using the model provided by (Zhuang *et al*, 2009).

EDI values have been compared with UL values (tables 4 and 5). In the calculations, the total concentration of elements (background concentration plus the total contamination) of each metal obtained after three days exposure was used. The minimum recommended daily consumption of vegetables by WHO is 0.4 kg/person/day and the average daily intake of vegetables in Ghana is estimated to be 0.137 kg/person/day (50.1 kg/person/year) (Ruel *et al*, 2004). Results of the calculations using the minimum recommended value are shown in tables 4 and 5 below.

Table 4: Estimated daily intake of metals from consumption of lettuce

ELEMENT	EDI(mg/kg body weight)		UL(mg)
	CHILD	AGED	
Ni	0.14	0.03	1
Cr	0.17	0.04	ND

Table 5: Estimated daily intake of metals from consumption of cabbage

ELEMENT	EDI(mg/kg body weight)		UL(mg)
	CHILD	AGED	
Ni	0.15	0.03	1
Cr	0.12	0.03	ND

The estimated daily intake of the heavy metals using the minimum recommended daily consumption of vegetables which is even higher than the actual average daily intake in Ghana gave values which are all below the upper tolerable intake levels. This indicates that the current rate of contamination on the road and the background levels of heavy metals in the vegetables, poses no risk of adverse health effect. However, vegetables may be harvested either contaminated or not with heavy metals depending on the soil on which they grow. Exposure of these vegetables for sale by busy roads can cause further contamination. The extent of contamination depends on the traffic density, the duration of exposure and wind current among other factors. This work did not record excessive levels of heavy metals but the possibility of the metals reaching excessive levels cannot be ruled out. This is especially possible if the vegetables are grown on heavily polluted soils and exposed along busier roads with more intense human and vehicular activities than the road chosen for this study.

Conclusion

The levels of 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 Ni (1.87) and Cr (1.16). Total deposition for cabbage was Ni (2.38) and Cr (1.8). Levels of Cd and Pb were below the detection limits of the analytical instruments. The results indicate that heavy metal contamination also takes place when vegetables are exposed along busy roads and the extent of exposure 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 contamination of the vegetables was by adsorption and absorption

The rate of contamination of the vegetables by the heavy metals were determined in mg/kg/day to be Ni (0.62) > Cr (0.56) for lettuce and Ni (0.79) > Cr (0.6) for cabbage.

The estimated daily intake of each of the metals from the consumption of the vegetables was below the upper tolerable intake level and poses no health risk.

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