International Journal of Environment and Pollution Research
Vol.9, No.1 pp.45-51, 2021
Print ISSN: 2056-7537(print),
Online ISSN: 2056-7545(online)

ASSESSMENT OF COPPER AND ZINC CONTAMINATION THROUGH VEHICULAR EMISSION ON VEGETABLES GROWING NEAR ROAD SIDE

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ABSTRACT: *Vegetables are important sources of many nutrient, including vitamins, dietary fibre, folate (folic acid), and minerals and have beneficial antioxidative effects. Heavy metals like Cu and Zn can easily enter in our body through consumption of vegetables contaminated with such metals. The toxic levels of the Zinc and Copper in leafy vegetables growing near road side fields were highly dependent on vehicular exhaust and non-exhaust emissions. Industrial emissions and the frequency of brake use and vehicles coming to a complete stop were additional factors that affected the contamination levels of Zn and Cu in leafy vegetables. The concrete highway also had higher contamination levels of such heavy metals than the asphalt highway. Vehicle speed was also a Major factor contributing to the contamination of higher level of Cu and Zn in road side vegetation of heavy traffic areas. The significant level of Cu in vegetables growing in road sides areas may be due to high rate of brake abrasion from the vehicles and the levels of zinc in vegetables is due to tyre abrasion from vehicles as zinc oxide is used as a vulcanizing agent in making tyre rubber. The main aim of this review article is to determine the level of Cu and Zn in leafy vegetables collected from road side (heavy traffic) areas.*

KEY WORDS - vegetables, copper, zinc, heavy metals.

INTRODUCTION

Vegetables are important part of daily diets in many households, forming an important source of vitamins and minerals necessary for human health. The vegetables play an important role in growth and development of the body. Vegetables not only helps in diseases prevention but also helps in strengthening of immunity system. They also help in neutralizing the acidic substance form during digestion. Green leafy vegetables are rich source of vitamins, iron, folic acid, and dietary fibre. Heavy metal contamination of vegetables is a great public health concern. Road traffic involves numerous potential sources of metals, e.g. combustion products from fuel and oil, wear products from tyres, brake linings, bearings and clutches, corrosion products of vehicle components and road construction materials, and resuspension of soil and road dust [1]. Vehicular exhaust and non-exhaust emissions are one of the major sources of accumulation of particulate heavy metal in vegetables. Despite of having biological importance of Zinc and Copper, both these metal cause acute as well as chronic exposure. The manifestation of acute zinc poisoning could include nausea, vomiting, diarrhoea, fever and lethargy. While long term chronic exposure to excessive zinc levels could resulting in metabolic interference with other trace elements. High concentration of Zinc can cause disability of growth and reproduction. Daily intake of 150-450 mg of zinc have been related to reduction of copper utilization, alteration of iron function, reduction of immune function Zinc has been discovered to have an antagonistic relationship with copper. Therefore, zinc has been utilized to treat Wilson disease, an autosomal recessive disorder of copper metabolism [2]. Excessive Cu is humans is toxic and disturbs many biochemical and physiological processes, such as protein metabolism, and membrane integrity. High concentration of copper in human body may cause liver damage, abdominal pain, cramps nausea, diarrhoea and vomiting.

Accumulation of heavy metals in vegetables from vehicular exhaust and non-exhaust emission is a big threat to human dietary system. Zn was the most abundant heavy metal from tire wear. Its high concentrations resulted from the addition of ZnO and ZnS to the tire during vulcanization. [3] The average mass of a new car tire is approximately 8 kg, and during its lifetime, it loses up to 1.5 kg. This means that within 3 years, 10–20 % of rubber enters the environment due to abrasion. The greatest wear occurs during acceleration, braking, and cornering. The significant level of Cu identified in the road dust can be attributed to a high rate of brake abrasion from the increased stopping and the low speed of vehicles [1]. The main aim of this review is the assessment of heavy metal (Cu and Zn) contamination in edible portions of leafy vegetables and deposition rates of heavy metals through vehicular exhaust and non-exhaust emissions. The present review also asses the health risk factors associated by the consumption of heavy metal (Cu and Zn) contaminated leafy vegetables collected from road side areas (heavy traffic).

Vehicular Emission and environmental exposure of Copper and Zinc

The major sources of vehicular emission of Cu and Zn are brake and tyre. During rapid braking brakes undergoes rapid friction which release fine particles of Cu in the atmosphere. During rapid braking, brakes are exposed to extensive heat from friction, which is transmitted to the brake discs and results in the emission of particles. The most intense brake wear occurs at intersections, corners, traffic lights, and through forced braking [3]. As traffic density and traffic structure at all sampling sites were similar, the sources of the variable metal concentration in road dust can probably be found in traffic conditions on individual sections of the road. Copper is one of the most widely used heavy metals in brake pads and has been used in brake systems from a long time. The airborne copper particles produced by brake wear is an important source of metal containing in atmosphere along road sides, especially in heavy traffic areas. The Cu concentrations have confirmed that brake wear emission is the main source of Cu [1]. Tyre wearing release a significant amount of Zn in atmosphere which makes the environment contaminated with Zn. The concentrations of Ni and Zn in road bitumen were higher than in raw bitumen. This suggests that heavy metal concentrations in road dust are significantly affected by vehicle operation and road abrasion [4]. Hence the more tire abrasion occurs when a vehicle runs on a concrete motorway compared with an asphalt surface which tends to release more Zn in the atmosphere. Elements related to brake wear were impacted by enriched road dust resuspension, but correlations between these elements in indicate that direct brake wear emissions are also important. A sub micro-meter particle mode was observed in the emissions of Pb, Ca, Fe, and **Cu** [5]. The metal contents in lubrication oil could play important roles on the emission of metal contents in the engine exhaust, particularly for Ca and **Zn** [6].

Diesel engines operated vehicles also released a significant amount of heavy metals in atmosphere. The top two absolute metals in diesel soot were **Zn** and Cr [6].

Health risk assessment via consumption of vegetables contaminated with Cu and Zn

Despite of having biological importance of copper and zinc in human body, acute as well as chronic exposure may occur in human body by consumption of vegetables highly contaminated with such heavy metals. The manifestation of acute zinc poisoning could include nausea, vomiting, diarrhoea, fever and lethargy. While long term chronic exposure to excessive zinc levels could resulting in metabolic interference with other trace elements [2]. Human subjects supplemented with 300 mg zinc per day has been characterized to have elevated LDL cholesterol and reduced HDL cholesterol [9]. Chronic enriched zinc intakes could result in various chronic effects in gastrointestinal, hematological, and respiratory system along with alteration in cardiovascular and neurological systems of human [8]. Zn concentration in vegetables differs among vegetables that are closely related genetically. The physiological impact of Zn exposure of two related vegetable species Brassica juncea and B. napus was investigated by exposing them to varying Zn concentrations up to 300 µM. This study revealed that in term of root damage, and microelement homeostasis alteration, B. juncea is more Zn tolerant than B. natus. The physiology of their root was also observed. It was discovered that the oxidative components were predominant compared with nitrosative component in root [10]. In last few years, Several studies have been conducted to evaluate the potential human health risks of Zn and Cu in vegetables. The Zn in Bok Choy (Brassica campestris L. ssp. chinensis Makino), Water Spinach (Ipomoea aquatica Forsk.), Shanghai green cabbage (Brassica chinensis L.), leaf lettuce (Lactuca sativa L. var. ramosa Hort.) from Shanghai, China. It was determined that the Zn concentrations in these vagetables were below the food safety limit set in China [11]. The Zn levels in Lettuce (Lactuca sativa var. crispa), Ethiopian mustard (Brassica carinata A. Br) and Beet (Beta Vulgaris var. cicla) from wastewater-irrigated urban vegetable farming site in Addis Ababa, Ethiopia was also investigated for possible human health hazard. There was no Zn hazard discovered [12]. Consumption of vegetables contaminated with Zn and Cu may leads to serious health hazard as these heavy metals are non-biodegradable and may remain in human body tissues for a long time. Another study done on metal contaminated vegetables revealed that Cd and Cu contamination posed a risk to the human population through vegetable consumption. The risk from Cd and Cu due to consumption of vegetables were higher for B. oleracea followed by A. esculentus [13].

Mechanism of zinc and Copper toxicity via consumption of heavy metal

One of the factors that influence the uptake and bioaccumulation of trace metals in vegetables is atmospheric deposition. Trace metals determination in food stuffs is of vital interest because of their essential or toxic nature. Trace metals analyses are important part of environmental pollution studies. The contamination of vegetables with trace metals due to atmospheric depositions poses a threat to its quality and safety. Vegetable plants that are exposed to atmospheric deposits from anthropogenic activities like vehicular emission, industrial emission and burning of all forms of wastes dumped along roadsides may be contaminated with trace metals to such a level that could be detrimental to the consumers of such vegetables.[13] Cultivation areas near highways are also exposed to atmospheric pollution in the form of metal containing aerosols. These aerosols can be deposited on soil and absorbed by vegetables, or alternatively deposited on the leaves of vegetables and then absorbed. Field studies have found positive relationships between atmospheric metal deposition and elevated concentrations of trace metals in plants and top soil. Anthropogenic activities in an area might significantly contributed to the elevated trace metal loads in atmospheric deposits and consequently in the leaves of vegetables grown in the area. Cu with the highest mean level in the Vernonia amygdalina leaves samples obtained from the three roadsides in this work, could be attributed to different forms of anthropogenic activities such as the discharge of domestic waste and forest fire as well as wind-blown dust and decaying vegetation. [13] The level of Zn is the second highest in the Vernonia amygdalina leaves samples analysed in this study. Zn is an essential element needed by humans in trace amount.[13] It is also a neurotoxin which has the ability to chelate and deplete the neuronal concentration of glutathione (GHS) when taken in large amount. Zn could cause neuronal cell death in a dose dependent manner.[16]

FAO/WHO permissible limit of Cu and Zn in foods

Heavy metals	**FAO/WHO permissible level in food (mg/kg)**
Cu	**73.3**
Zn	**99.4**

Data analysis - Calculation of daily intake of heavy metals from vegetable surfaces deposits

The daily intake of heavy metals from vegetable surface atmospheric de- posits via consumption of unwashed vegetables was calculated by multiplying daily vegetable consumption rate (mg person^{-1} d^{-1}) with mean atmospheric depositions on vegetable surfaces. Daily vegetable consumption was obtained from survey conducted in the study area. Mean atmospheric deposits on vegetable surfaces were obtained by subtracting mean concentrations of heavy metals in washed from that of unwashed vegetables.[13]

Element	Wavelength (nm)	Detection limits (mg ml^{-1})
Copper	324.8	0.001
Zinc	213.9	0.0008

Wavelength and detection limits of each heavy metal measured by Atomic Absorption Spectrophotometers (Model 2380 PerkineElmer Inc., Norwalk, CT, USA). [13]

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Health risk assessment

The daily intake of metals was determined using the following equation [17]

EDI (mg/kg bw/day) = $C_{metal} \times C_{factor} \times D_{food\ intake} / B_w$. C_{metal}, C_{factor}, and B_w represent the mean concentration of each metal in vegetables (mg/kg dw), conversion factor, daily vegetable intake (kg/person/day), and body weight (bw, kg), respectively. In order to convert the fresh vegetable weight into dry weight, the conversion factor of 0.085 was used. The total intake of vegetables was obtained through a formal survey, in which a total of 438 healthy adults (199 males and 239 females) aged 18–54 years old were interviewed for their age, body weight, and daily consumption rate of vegetables. The 97.5th percentile (P97.5) of the estimated daily intake (EDI) levels was used to represent the high consumers [18]. To assess the health risk associated with heavy metal contamination of vegetables grown locally, estimated exposure and risk index were calculated. The results showed that both Cu and Cd contamination in vegetables had potential to pose health risk to the local population. Pb, however, may only pose risk through consumption of *B. oleracea*. Zn may not have any risk to the local population through consumption of these vegetables [19]

DISCUSSION

Traffic areas often receive atmospheric depositions of heavy metals resulted in contamination of vegetables growing near road side fields. Consumption of heavy metal contaminated vegetables may posea great risk to human health. Heavy metals determined in different vegetables showed that the concentrations of Cu, Zn and Cd have often exceeded the safe limits of both Indian [20] and FAO/WHO (Codex Alimentarius Commission, 1984) standards. The heavy metals accumulation in vegetables may be ascribed to the heavy metal concentrations of soil and also to the adsorption of heavy metals from aerial depositions released from vehicular emissions. Variations in the magnitude of reductions in heavy metal contamination due to washings of vegetables also depicted the variations in heavy metal depositions at various market sites. Vegetables sold in local markets of the city still looking healthy and fresh, may pose a risk to human health particularly due to Cu and Cd contamination [13]. Zn may not have any risk to the local population through consumption of these vegetables. [19] have reported that local residents of an area near a smelter in Nanning, China have been exposed to Cd and Pb through consumption of vegetables but no risk was found for Cu and Zn. . It can be expected that the environment is, to the largest degree, loaded with copper and zinc, even though the estimated emission intensities of the two metals differ almost 7-fold (according to the German and Danish methodologies). The predicted emission intensities of Cr, Ni, and Pb are very similar, although the amounts of the load of metals estimated in such a way only partially burdens the environment bordering with the traffic route, e.g. the initial dispersion of the emitted pollutants is effectively blocked by the absorbing noise barriers. PM concentration may decrease up to 50% behind the noise barrier [21]. As traffic density and traffic structure at all sampling sites were similar, the sources of the variable metal concentration in road dust can probably be found in traffic conditions on individual sections of the road. The Cu concentrations have confirmed that brake wear emission is the main source of Cu. The Jedlińsk sampling site was situated directly in front of the traffic lights, so the significant level of Cu identified in the road dust can be attributed to a high rate of brake abrasion from the increased stopping and the low speed of vehicles at this site. Zinc accounts for about 1% by weight of tire tread material and its release through tire wear has been often recognized as a significant source of Zn in road dust. Brake wear and fuel combustion also are regarded as important vehicular emission sources of Zn [1]. Non-exhaust emissions are becoming one of the most significant sources of particulate emissions released into the environment by vehicles in recent years [22]. There have been few studies into the toxicological effects of airborne non-exhaust brake particles on human health. The aim of our investigation was to establish whether particles released from four diferent brake pads induce toxicity in vitro in lung cells and whether this efect could be related to the presence of Cu in the brake pads[7].

CONCLUSIONS

From this review, it can be concluded that vehicular exhaust and non-exhaust emissions have elevated the levels of heavy metals (Cu and Zn) in atmospheric deposits, which consequently increased the concentrations of heavy metals in test vegetables during their production. Changes in the magnitude of reductions in heavy metal contamination due to washings of vegetables collected from road side areas in various research also depicted the settlement of heavy metals in vegetables through automobiles emissions. This review can be used to monitor the contribution of heavy metals through vehicular emission on leafy vegetables. This review also demonstrate that proper washing technique can be used as a tool to assess the heavy metals load in vegetables through atmospheric depositions. The present study further suggested that to reduce the health risk of Cu and Zn in vegetables the use of copper in brake pads should be replace from other safer alloys or materials which should not create toxic hazard to atmosphere and safer for vegetables species too. Respectively the use of heavy metal Zn as a vulcanising a agent in the form of ZnO for making tyre rubbers should be replaced by any other safer vulcanising agent to reduce the zinc toxicity in vegetables growing around road side areas. The most effective measure that we put in work to reduce the toxicity of Cu and Zn in vegetables from heavy traffic is that vegetable should grown at least 10 km away from road side (heavy traffic) areas.

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