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BIOAVAILABILITY OF CADMIUM IN SOILS, FERTILIZER SOURCES AND UPTAKE BY LEAFY VEGETABLES: A REVIEW

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ABSTRACT

Due to its ease of bioavailability and transfer within the terrestrial and aquatic environments, it has been widely established in the literature that cadmium is the most absorbed amongst the eight (8) heavy metals that are of scientific concern. This review documents the occurrences and sources of cadmium in soil, fertilizers, vegetables and industrial effluents that are invariably employed as fertilizer for agricultural use. Some research studies have indicated that vegetables have high absorption and accumulation of cadmium while its accumulation in grains is relatively low. Again, its presence in industrial effluent that is often discharged indiscriminately into the environment is equally documented. This current review equally spells out the ease of cadmium uptake in leafy vegetables and proliferation in human food chain, factors affecting its bioavailability in soils, documented toxic effects and symptoms. Numerous studies have shown that chronic exposure of humans through the food chain leads to a selective accumulation of cadmium in the liver and kidneys and in some studies, up to 75% of the total body burden was found in these organs. An understanding of cadmium sources and its occurrences in soils and uptake by vegetables is essential in establishing a framework for its risk assessment.

Keywords: *Cadmium, Bioavailability, Soil, Vegetables, Fertilizer, Industrial effluent*

INTRODUCTION

Increase in industrial and agricultural activities have been accomplished throughout the world by the extraction and distribution of mineral substances from their natural deposits (Ademoroti, 1996). These high levels of industrial and agricultural activities have led to the continuous discharge of effluents containing harmful materials into our environment. Warren (1981) noted that various activities by man in recent years have increased the quantity and distribution of toxic materials in the atmosphere, land and water bodies thus into the food chain, some of which may be carcinogenic.

Generally, pollution of the environment caused by man's industrial and agricultural activities is difficult to characterize and detailed inventory of wastes generated by these activities on a national scale, is practically non-existent (Ademoroti, 1996; Uchimiya *et al*., 2010a). These wastes contain traces of larger quantities of raw materials, intermediate products, final products, co-products and by-products of any ancillary or processing chemicals used. Although it is difficult to give a complete list, some of them include detergents, solvents, cyanide, heavy metals, minerals and organic acids, nitrogenous substances, fats, salts, bleaching agents, dyes, pigments and so on (Ademoroti, 1996). However, many of the aforementioned are toxic and have detrimental effects on the environment.

Indiscriminate discharge of untreated industrial effluent into the river and surrounding land inevitably contaminates agricultural soils, streams and underground water supplies. Heavy metals such as Cd, Cu and Pb frequently co-occur in contaminated soils and their mobility and bioavailability is of global concern (Uchimiya *et al.*, 2010a, b). Elevated heavy metal concentrations in the soil can negatively affect crop growth, sometimes leading to plant death (Baker *et al.*, 1976; Hoffmann, 1983, Schaller and Diez, 1991). Consequently, quality standards establishing the maximum concentrations of certain heavy metals like Lead (Pb) and Cadmium (Cd) allowed in several agricultural crops were enacted into law (Commission of the European Communities, 2002).However, it has been widely established in the literature that cadmium is the most absorbed amongst eight (8) heavy metals of scientific concern and that it is easily transferred within plants (Lin and Chiou 1990; Kabata-Pendias and Pendias 2001).

In view of the above, this review focuses on the reported information on the cadmium sources, occurrences in soil and its uptake by leafy vegetables as influenced by fertilizer and industrial effluents.

Cadmium

The metal cadmium is a relatively rare element and is not found in the pure state in nature (Friberg *et al.*, 1992). According to Benavides *et al*. (2005) and Khan *et al.* (2015), cadmium is extremely carcinogenic and even in low concentration, it has got the capability of causing toxic reactions. Khan *et al.* (2017) reported that Cd is a non-essential micro element that does not play any known part in the developmental growth of human, plants and animals. It exists in low concentration in all soils and usually occurs as inclusions in ores. Through the process of vacuum distillation, Cadmium is sequestered from the zinc metal and alternatively if cadmium sulfate is precipitated from the electrolysis solution or zinc is smelted (Scoullos, 2001; Fthenakis, 2004). It also emitted in industrial processes, such as metal smelting and refining, dye making and so on. Its principal uses include: protective plating for steel, stabilizers for polyvinyl chloride, pigments in plastics and glasses, electrode material in nickel cadmium batteries and as a component of various alloys (Friberg *et al.,* 1992).

Food products account for most of the human exposure to cadmium due to its high mobility in soil and uptake by crops (Chunhabundit, 2016). Human cadmium toxicity caused by contaminated rice plants was first reported in Japan in the 1950s (Kaneta *et al,*. 1986). The author reiterated further that subsistence rice farmers had been sickened by ingested cadmium that passed from municipal wastes sludge's fertilizers through the rice crop.

Cadmium is today regarded as the most serious contaminant of the modern age (IOCC, 1996). It is absorbed by many plants and sea creatures and because of its toxicity, presents a major problem for food sources (Satarug *et al*., 2010). Contamination through fertilizers is also becoming an increasing problem due to its excessive use and negative effects on the environment (Mortvedt *et al.,* 1995). Cadmium is taken up through the roots of plants to edible leaves, fruits and seeds. It builds up in animal milk and fatty tissues (Kaneta *et al.,* 1986). Therefore, people are exposed to cadmium upon consumption of cadmium containing plants or animals. As pointed out earlier, the cadmium content of terrestrial foods varies significantly as a function of the type of food crop grown, the agricultural practices pursued and the atmospheric deposition of cadmium exposed plant parts and the soil surface (Smolders, 2001).

Cadmium in the Human Food Chain

Mortvedt *et al.* (1995), states that during the past years, increasing attention has been given to the fate of heavy metals contained in municipal wastes and in commercial fertilizers fertilizer applied to agricultural soils, with most of the attention paid to cadmium. The medical community has been trying to determine the relationships of various human maladies to heavy metal levels in the diet. Increasing interest has been given to various avenues of entry of cadmium and other heavy metals into the food chain, including the role of heavy metal contaminants in fertilizers (Chen and Lee, 1997). Among the food sources that present a problem are offal, crustaceans and shellfish but overall, vegetables are of greater importance for human cadmium contamination (IOCC, 1996).

When industrial effluents are disposed of onto farmland, metallic contents of the effluents are taken up by plants in some amounts (Ademoroti, 1996). The plants such as fruits and vegetables are readily consumed by grazing animals. The stimulation of Cd equally occurs owing to the use of sewage sludge, manure and limes (Nriagu 1988; Yanqun *et al*., 2005). The grazing animals as well as the plants (fruits and vegetables) serve as food for man. In effect, the heavy metals such as cadmium are passed unto man by the food chain. The cumulative effects of these metals, most of which are toxic are adverse generally.

The analysis below acknowledges that most human cadmium exposure comes from ingestion of food, and most of that arises from the uptake of cadmium by plants from fertilizers, industrial effluents, manure and atmospheric deposition. As tabulated in Table 1, Van Assche (1998) specifically came up with a model that estimated the relative importance of various cadmium sources to human exposure.

Table 1: Sources of cadmium exposure to humans

Sources	Percentage (%)
Phosphate Fertilizers	41.3
Fossil Fuel Combustion	22.0
Iron & Steel Production	16.7
Natural Sources	8.0
Non-ferrous Metals	6.3
Cement Production	2.5
Cadmium Products	2.5
Incineration	1.0

Source: *Van Assche (1998)*

Cadmium Toxic Effects and Health Implications to Humans

Oral exposure to cadmium may result in adverse effects on a number of tissues including kidney, liver, bone, testis, the immune system and the cardiovascular system (National Institute for Health, University of Illinois, 2001). Numerous studies have shown that chronic exposure leads to a selective accumulation of cadmium in the liver and kidneys (renal cortex) and in some studies, up to 75% of the total body burden was found in these organs (Friberg *et al.,* 1985). Seidel *et al.* (2001) stated that cadmium has a very long half-life in the body (10 to 30 years) and can build up over a long time. It has equally been established by WHO (1993) that cadmium has a long biological life of 20–30 years in the kidney. Hence, chronic exposure to cadmium may ultimately accrue to toxic levels due to its high level of bioavailability.

Cadmium like Lead is a cumulative poison and the danger lies primarily in the regular consumption of food sources with low contamination. Cheng (2006) and Chunhabundit (2016) stated that cadmium exposure can have symptoms that are chronic and subtle. Often the symptoms resemble those of other diseases. They further went on to state the various symptoms, which result from excessive cadmium exposure. These are tabulated in Table 2 below:

Table 2: Possible symptoms from excessive exposure cadmium

Serial number	Symptoms
1	Anaemia resistant to iron therapy (hypo chromic, microcytic anaemia with normal ferritin and iron indices, and normal haemoglobin electrophoresis)
2	Yellowing of teeth, excessive dental caries (tooth decay)
3	Kidney dysfunction, proteinuria, urinary tract problems
4	Emphysema (not due to smoking or other cause)
5	Osteomalacia (softening of the bones so that they become flexible or brittle)
6	Hypertension
7	Minor liver function changes
8	Possible prostate cancer
9	Lung cancer (from inhalation exposure)
10	Anosmia (loss of sense of smell)

Effects of Cadmium on Plants

It has been reported by Salt *et al*. (1995), that the regulatory limit of Cd in most agricultural soil is pegged at 100 mg kg^{-1}. Several authors (Sanita di Toppi and Gabbrielli, 1999; Wojcik and Tukiendorf, 2004; Mohanpuria *et al*., 2007; Guo *et al*., 2008) have reported that plants that are grown in soils having high levels of Cd exhibit noticeable symptoms of injury ranging from chlorosis, inhibition of growth, burning of root tips and eventual death.

According to Alcantara *et al*. (1994), Cd brings about the inhibition of root Fe (III) reductase to the deficiency of Fe (II) which in turn has severe effect on the rate of photosynthesis. Das *et al.* (1997) reported that Cd inhibits the uptake, transport and utilization of several elements ranging from Ca, Mg, P to K and water by plants. In a study conducted by Hernandez *et al.* (1996) it was observed and reported that Cd abridged the concentration of nitrate and its overall transport from roots to shoots, by obstructing the nitrate reductase activity in the shoots. Balestrasse *et al.* (2003) equally reported that Nitrogen fixation and primary ammonia assimilation diminished in the nodules of soybean plants employed in their experiment during treatments with Cd.

It has been reported that metal toxicity upsets the permeability of plasma membrane, leading to a reduction in the content of available water as Costa and Morel (1994), have reported that Cd has the ability to interact with the water balance in any system. According to Fodor *et al.* (1995), Cadmium treatments reduced ATPase activity of the plasma membrane portion of sunflower and wheat roots employed in their study. These authors further reiterated that Cadmium creates changes in the pattern by which membranes function through the induction of lipid peroxidation. Interestingly, De Filippis and Ziegler (1993) have reported earlier that the presence of Cd disturbs metabolism of chloroplast by preventing the biosynthesis of chlorophyll thereby incapacitating the activity of enzymes that are involved in the fixation of CO_2.

Factors Affecting the Uptake of Cadmium in Leafy Vegetables

According to Khan *et al.* (2017), the transfer of Cd to vegetables from Cd polluted soil has been documented in numerous studies. These authors went further to submit that less attention has been paid to the mechanisms involved in the bioaccumulation of Cd in many plant species and soil environments. This scientific assertion is seconded by Jan *et al*. (2010); Yang *et al.* (2011) who reported that most of the studies centered on soil to plant bioaccumulation of Cd with no shown mechanisms.

However, cadmium mobility and uptake by plant roots is enhanced in soil by the presence of dissolved organic matter. Cadmium is of particular worry in plants due to its ability to accumulate in leaves at a very high rate, which in turn can be invariably eaten up by animals or human beings (Nagajyoti *et al.*, 2010). When absorbed by the root, cadmium can be easily transferred to the other parts such as stem and leaves (Cheng and Huang, 2006). If excess quantity is accumulated in the plant body, cadmium will adversely affect the plant growth and metabolism (Barber and Brennan, 1974). Since cadmium has same similar chemical characteristics as zinc and manganese, it sometimes replaces the latter at the reactive site resulting in inhibited enzymatic activities thus leading to plant withering, yellowing and retarding growth (Taiz and Zeiger, 2002).

Results of some research indicate that vegetables have high absorption and accumulation of cadmium compared to grains (Kovacs *et al.,* 1993; Kim *et al.,* 2002; Chen *et al.,* 2004). Cadmium in the soil either form chelating substances, through ion exchange or are attached to other substances through the process of specific adsorption. When plants absorb water and nutrient from soil, cadmium is carried into the plant body via the root tissue (Evanko and Dzombak, 1997; Taiz and Zeiger, 2002). The plant root tissue may release low-molecular weight organic acids for example Acetic, Oxalic, Fumaric, Citric and Tartaric acid which facilitate metal absorption by forming more soluble compounds or chelates with cadmium (Mench and Martin, 1991; Taiz and Zeiger, 2002; Chen *et al.,* 2003; Rahman *et al.,* 2013).

Cadmium accumulation in plants according to the literature accelerates with growth time. Cheng *et al.* (2006) stated that reduction of cadmium accumulation in tissues of contaminated plants occurs when plants start to wither. Accordingly, the plant will no longer absorb large quantities of water and nutrients including cadmium at the later growth period. Research has also revealed that vegetables in an uncontaminated soil show increasing cadmium accumulation in leaves and roots with growing time (Cheng and Huang, 2006). When plants start to develop the edible parts, the absorption and accumulation of cadmium in the plant tissues will increase leading to rising cadmium concentrations in the various tissues. These authors submitted further that the accumulated cadmium will show obvious effect in retarding the plant growth. Therefore, when the crop yield of a farmland becomes lower than the expected under normal conditions, one must pay attention to a possible cadmium contamination of the farmland (Rolka, 2015).

Cadmium Bioavailability in Fertilizers

A major type of inorganic fertilizer with high levels of heavy metal content is the phosphate fertilizer. Phosphate fertilizers are produced from phosphate rocks that contain various metals and radionuclides as minor constituents in the ores (Mortvedt *et* *al.,* 1995). Most known phosphate rock deposits have been analyzed for their heavy metal contents (Kongshaug *et al.*, 1992). Attention is given mostly to phosphate fertilizers due to the fact they are mostly raw sources of other inorganic fertilizers. Van Kauwenbergh (2002) also found a close relationship between the concentrations of P and Cd in super phosphates and their respective phosphate rock deposits. According to Nagajyoti *et al.* (2010) inorganic and phosphate fertilizers have variable levels of Cd.

Wakefield (1980) and Modaihsh (2004) reported that Triple Super Phosphate (TSP) contains 60-70% of the cadmium phosphate rock and will likely affect the concentrations of Cd in the soil. The chemical form of cadmium in TSP and DAP (Diammonium Phosphate) was reported to be Cd $(H_2PO_4)_2$ or $CdHPO_4$, or a mixture of these salts in these two fertilizers (Mortvedt and Osborn, 1982). The needs for phosphate fertilizers are greatest on many infertile soils in those countries where crop production is severely limited. Bioavailability of heavy metals, especially cadmium, is greatest on acid soils (Mortvedt *et al.,* 1995). Therefore cadmium uptake may be increased in some crops fertilized by phosphate fertilizers containing appreciable levels of cadmium. Concentration of cadmium in organic fertilizers largely depends on the sources of raw materials. Such raw materials include farmyard manure, industrial effluents and crop residues. Industrial effluents as fertilizer are a major source of plant nutrients (especially Phosphorous and Nitrogen) and are beneficial as soil amendment (Petra *et al.,* 2005).

Bioavailability of Cadmium in Soils

According to Clemens (2006) while a trace amount is absorbed by the atmosphere via contaminated dust, plants uptake Cd from the soil depending on its concentration and bioavailability. The uptake of Cd happens through trans-membrane transferors that are involved in the uptake of Mg, Ca, Fe, Zn and Cu (Clemens, 2006; Roth *et al*., 2006).

In a typical polluted soil Cd can effortlessly be absorbed by plant roots and subsequently transported to where it will intermingle with biochemical and physiological processes that ultimately affect the morphology and growth rate of the plant (Sanita di Toppi and Gabbrielli, 1999; Sgherri *et al*., 2002; Uraguchi *et al.*, 2009). The release of Cd to the environment is done in variable amounts from natural (volcanic eruptions, forest fires, windblown dust, and sea spray) and anthropogenic activities (Khan *et al*., 2017). According to Khan *et al.* (2010); Liu *et al.* (2013), weathering of parent rocks equally adds to the discharge of Cd to the environment. Mafic and ultramafic rocks have been reported by Shah et al. (2010) to harbor abundant amounts of Cd, and therefore upon weathering, these rocks deposit significant amounts to soil.

Cadmium in soils is strongly controlled by soil pH (Christensen, 1984; McBride *et al.,* 1997), and is also influenced by a range of soil constituents, including clay minerals (Zachara *et al.*, 1992) and Mn, Al, and Fe oxides and hydroxides (Benjamin and Leckie, 1981; Fu *et al.,* 1991; Bolton and Evans, 1996). Cadmium solubility in soils is mainly controlled by the soil pH, the amount and the kind of sorption sites, and the total amount of cadmium in the soil (Brummer *et al.,* 1986; Hornburg and Brummer, 1993; Gray *et al.,* 1999). Cadmium is less available in soils containing high clay percentage and with pH > 7 making the solubility of cadmium to increase as pH decreases (Violante *et al*., 2010). Soil organic matter is usually identified as the soil constituent with the largest influence on cadmium sorption (Christensen, 1989; Yin *et al.,* 2002). As depicted in Figure 1, soil organic matter greatly increases soil physical features like colloidal

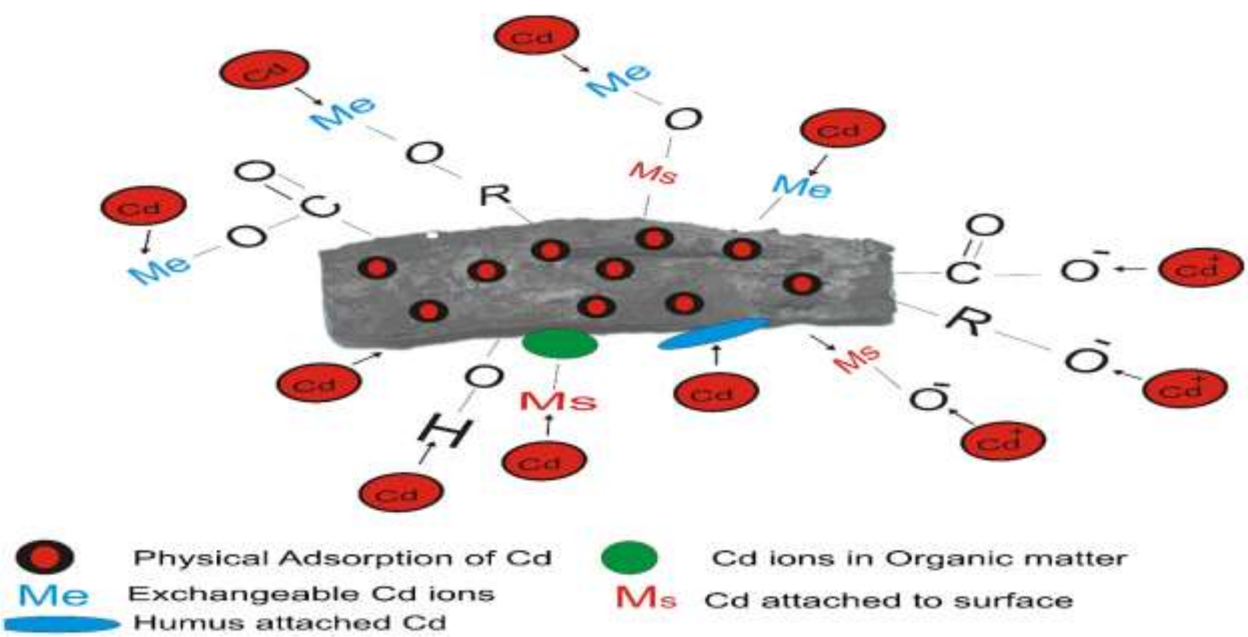

Fig. 1. The possible mechanisms of organic matter affecting Cd in soil as sourced from Khan *et al.* (2017)

Stability and cation exchange capacity and chemical features like plant available nutrients and chelating compounds that have a beneficial effect on soil biology (Rieuwerts *et al*., 1998). Organic matter may affect the transfer of heavy metals to plants by several mechanisms: enhancing metal adsorption as a result of increased surface charge and increasing the formation of organic complexes including changes of redox potential in soils towards negative values (Renate *et al.*, 2006). In addition, it may increase the solubility of some elements on one hand but also decrease the solubility of other elements. The oxidation of organic matter releases protons and lowers the pH of the soil, which increases the solution concentration of cadmium (Renate *et al.,* 2006). Soil storage capacity for cadmium is also increased with a higher cation exchange capacity and increased concentrations of chelating agents.

Limits of Cadmium in Fertilizers, Soils and Plants

Limitation of cadmium in food, soil, fertilizers and water vary worldwide. Most limits imposed by countries are usually based on the principle of prevention through risk assessment. These limits are often set considering the intense negative impact of cadmium on human health as well as legal and analytical data (which comprise of validated quantitative and qualitative data) (CODEX 2009). At present, owing to the precarious adverse effects of cadmium on the environment and human health, the stream and use of cadmium is regulated in Europe under the REACH Regulation (EUR-Lex, 2011). The European Food Safety Authority Panel on contaminants in the Food Chain has specified that 2.5 µg kg^{-1} body weights is the acceptable weekly intake for humans (EFSA, 2012). The Joint FAO/WHO Expert Committee on Food Additives has equally affirmed 7 µg kg^{-1} body weights to be the conditional allowable weekly intake level (JECFA, 2005).

For fertilizers, the fertilizer industry of the United States, the U.S. E.P.A, the California Department of Food and Agriculture (CDFA), the American Association of Plant Food Control Officials (AAPFCO) established a generalized risk model for establishing safe levels of metals (The Weinberg Group 2001). The risk model includes the following components:

Fertilizer product (NPK or micros)
↓
Application rates (vary by crop and soil)
↓
Metal level in soil at 50 to 100 years
↓
Metal uptake into plants
↓
Food ingestion rates for crops (FDA, USDA)
↓
Established acceptable metal level in diet (toxicity)

This risk assessment serves as a scientifically sound basis for setting health protective standards as part of the risk management strategy (The Weinberg Group, 2001).

CONCLUSION

As established in this current review, cadmium, due to its high level of bioavailability has the potential to get into human food chain, exert its toxicity and disrupt ecosystem balance thereby leading to public health issues. Its availability in soil is largely dependent on soil pH and other soil factors such as clay and organic matter content. Its occurrences in fertilizers especially phosphate fertilizers is strongly correlated with its presence as occlusions in rock phosphate. In view of this, there is a need to establish a national framework to monitor and assess its presence in soils and its uptake by crops. There is the need to evaluate potential fertilizer sources due to their eventual utilization in fertilizing agricultural land that produces crops that would be invariably consumed by humans so as to avert its imminent dangers that have been documented.

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