**ADDIS ABABA UNIVERSITY**

**SCHOOL OF GRADUATE STUDIES**

**DEPARTMENT OF CHEMISTRY**

# Levels of trace Cadmium and essential Zinc in wheat flour commercially available in Addis Ababa, Ethiopia

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**JULY, 2006**

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## Graduate project (Chem.774)

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# ABSTRACT

**Levels of trace Cadmium and essential Zinc in wheat flour commercially available in Addis Ababa, Ethiopia**

By Zelalem Tadesse

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Samples of wheat flour were collected from five different wheat flour processing industries (DHGEDA, KOJJ, Akwan, Redfam, and Misrak.). Different digestion procedures were tested by varying the type of reagent, temperature and time of digestion to develop optimum digestion procedure. The optimal procedure required 4 hours and consumed 6mL of 70% $HNO_3$ and 2mL of 37% HCl to completely digest 10g of wheat flour sample. The accuracy of optimal procedure was checked by digesting a mixture of standard solutions and determining the percent recovery. The recoveries were 92% for Cd and 94% for Zn. the concentrations of Cd and Zn in wheat flour samples were measured by flame atomic absorption spectrophotometery employing a four point external calibration curve. The mean concentration of Cd and Zn in wheat flour in this study ranged (mg/kg DW) from 0.011 to 0.024 mg/kg and 5.93 to 9.88mg/kg respectively. There was no significant difference observed in the levels of Cd and Zn in wheat flour samples obtained from different industries. The wheat flour samples examined in this study are non compliant with the maximum permissible concentration (MPC) for Cd in wheat.

## 1. INTRODUCTION

Nutrition is an important factor that influences health and well being. Consumption of diets adequate both in quantity and quality is a prerequisite for the maintenance of good nutritional status. Agricultural production that determines food availability is, therefore, an important determinant of food consumption, though not a critical one if food imports can be assured. Self-sufficiency in food production is of particular importance for developing countries, not only because they tend to have high rates of population growth, but also because such countries have malnutrition as a public health problem. The quantitative aspects of food production are undoubtedly of primary concern, but it cannot be forgotten that the quality aspects are extremely important, if optimal nutrition is to be provided. Application of potentially toxic elements and other trace elements are of concern because they do not degrade and they remain in the soil indefinitely. Low levels of all of these elements occur naturally in soil and some are essential nutrients for plants or animals. Toxicity only becomes a problem if high levels are present in a form that can enter the food chain or leach into ground water. The amount of accumulation of trace elements in plants depends on a number of factors, including concentration of the elements in the biosolids, application rate, soil properties (especially pH), type of crop, and part of crop (e.g. leaves vs. grain) [1-4].

Toxic metals comprise a group of minerals that have no known function in the body and in fact are harmful. They affect everyone and are a major cause of illness, aging and even genetic defects. Minerals are classified into four groups: The macro minerals, or those needed in large quantities, include calcium, magnesium, sodium, potassium, phosphorus, sulfur, iron, copper and zinc. Required trace minerals include manganese, chromium, selenium, boron, bromine, silicon, iodine, vanadium, lithium, molybdenum, cobalt, germanium and others. Possibly required trace minerals include fluorine, arsenic, rubidium, tin, niobium, strontium, gold, and silver. Toxic metals include beryllium, mercury, lead, cadmium, aluminum, antimony, bismuth, barium, uranium and others [5].

## 1.1 Literature Review

Cadmium in human is derived primarily from vegetable foods, yet the extent to which the chemical form and dose of cadmium in such food influences the fate and toxicity of this metal poorly understood [6]. So attention should have to be given to improve our knowledge about the whole food chain [7] because a large number of elements occur in foodstuffs as environmental contaminants, sometimes at levels, which are considered toxic [7,8].

Cadmium (Cd) is a soft, ductile, silver-white metal that belongs together with zinc and mercury to group IIb in the Periodic Table. It has relatively low melting (320.9 °C) and boiling (765 °C) points and a relatively high vapor pressure. In the air cadmium is rapidly oxidized into cadmium oxide. However, when reactive gases or vapour such as carbon dioxide, water vapor, sulfur dioxide, sulfur trioxide or hydrogen chloride are present, cadmium vapor reacts to produce cadmium carbonate, hydroxide, sulfite, sulfate or chloride, respectively. These compounds may be formed in chimneystacks and emitted to the environment. Several inorganic cadmium compounds are quite soluble in water e.g. acetate, chloride and sulfate, whereas cadmium oxide, carbonate and sulfide are almost insoluble [9].

### 1.1.1 Sources of cadmium

Cadmium is a relatively rare element (0.2 mg/kg in the earth's crust) and is not found in the pure state in the nature. It occurs mainly in association with the sulfide ores of zinc, lead and copper. Cadmium has only been produced commercially in the twentieth century. It is a byproduct of the zinc industry; its production is thus determined essentially by that of zinc [10]. The average annual production of cadmium throughout the world increased from only 20 tonnes in the 1920s to about 12 000 tonnes in the period 1960–1969, 17000 tonnes in 1970–1984; since 1987 it has fluctuated around 20000 tonnes [11] The pattern of cadmium uses has changed in recent years. In the past cadmium was mainly used in the electroplating of metals and in pigments or as stabilizers for plastics. Nowadays, cadmium-nickel battery manufacture consumes 55% of the cadmium output and it is expected that this application will expand with the increasing use of rechargeable batteries and their potential use for electric vehicles. In many respects cadmium has become a vital component of modern technology, with countless applications in the electronics, communications, power generation and aerospace industries [11, 12].

### 1.1.2 Phosphate Rock as sources of Cadmium

Cadmium occurs naturally as a contaminant in all phosphate rock, but the concentrations vary considerably, depending on the origin of the material. Igneous rock or apatite has low concentrations of cadmium (often less than 1 mg per kg $P_2O_5$). Sedimentary rock, which accounts for some 85-90 percent of world production, contains cadmium in concentrations ranging from less than 20 to more than 200 mg per kg $P_2O_5$. The content of cadmium in raw phosphates vary significantly between phosphates mined in different countries [13]. Similarly, the cadmium content of fertilizers applied in different countries varies also. Global average of Cd levels in phosphates is about 21 mg Cd/kg of rock, but some Moroccan rocks have up to 40 mg and phosphates from Togo and Tunisia contain up to 50-55 mg Cd/kg. This may lead to restrictions or banning of some ores by countries trying to regulate the introduction of Cd into their environment [14].

### 1.1.3 Transport, Fate and Effects of Heavy Metals in Agricultural Soils

Physical processes are primary determinants of transport and fate of heavy metals applied to soil in fertilizers and related products. Erosion, leaching, export in harvested plants, and volatilization are major potential pathways for loss from soil at an application site. Since they are elements, heavy metals that are not subjected to chemical degradation are critically important in fate of organic compounds. Chemical conditions in soil are secondary determinants of heavy metal transport and fate. The importance of interactions between metals and solid phases of soils, soil water, and air within and above soil depends on a variety of chemical factors. Absorption of metals from soil water to soil particles is the most important chemical determinant that limits mobility in soils. There are four general classes of these interactions: specific adsorption, co-precipitation, cation exchange, and organic complexation. Specific adsorption involves partly covalent bonds of the heavy metal with lattice ions on soil particle surfaces. Co-precipitation involves formation of water insoluble precipitates from metal ions (cations) and anions such as carbonate, sulfide, or phosphate. Cation exchange is non-specific interaction of metals with negative surface charges on soils minerals, such as clay. Finally, soil organic matter (e.g., humus) adsorbs metals by forming chelate complexes, with carboxyl groups playing a predominant role. Given the chemical basis for each of the four general classes of metal absorption, it is clear that soil type is a fundamental determinant of heavy metal transport and fate

Soil pH is another chemical factor that influences heavy metal transport and fate, especially mobility in soil water. Firstly ionization of metals increase at low pH thereby increasing water solubility and mobility. Secondly, hydronium ions displace most other cations on negative surface charges. This reduces metal absorption by cation exchange and organic complexation.

Cadmium tends to be more mobile in soil systems and therefore more available to plants than many other heavy metals [15] $Cd^{2+}$ is the principal species in soil solution. Accumulation of cadmium in food crops at soil concentrations that are not phytotoxic is a significant concern. Plant species differ widely in their tendency to accumulate cadmium. Lettuce, spinach, celery and cabbage avidly accumulate cadmium while potato tubers, maize, French beans, and peas accumulate much less. Many studies show linear relationships between soil cadmium concentrations and wheat and barley grain, cabbage, and lettuce cadmium contents [16]. Soil chemistry also influences cadmium mobility and uptake by plants. As with other metals, low pH increases mobility. Absorption/desorption of cadmium is about 10-fold more rapid than for lead [17].

### 1.1.4 Routes of exposure

***Air:*** Assuming a daily inhalation of 20 $m^3$ of air and indoor concentrations similar to those outdoors, the average amount of cadmium inhaled daily by humans in rural, urban and industrialized areas should not exceed 0.01, 0.2 and 0.4 µg, respectively. Deposition of inhaled cadmium in the lungs varies between 10% and 50% depending on the size of airborne particles. Absorption of cadmium in the lung depends on the chemical nature of the particles deposited. It is around 50% for cadmium oxide but considerably less for insoluble salts such as cadmium sulfide. Cigarette smoking may represent an additional source of cadmium, which may equal or exceed that from food [18].

***Drinking water:*** Drinking water contains very low concentrations of cadmium, usually in the range 0.01–1µg/litre. In polluted areas, well-water may contain very high concentrations of cadmium (exceeding 25 µg/liter) [12] such unusual situations made the intake of cadmium via drinking- water, based on a water consumption of two liters per day is thus very low exceptionally.

***Food:*** For nonsmokers, food constitutes the principal environmental source of cadmium. The lowest concentrations are found in milk (around 1 µg/kg). The concentration of cadmium is in the range 1-50 µg/kg in meat, fish and fruit and 10-300 µg/kg in staple foods such as wheat, rice and potatoes. The highest cadmium levels (100-1000 µg/kg) are found in the internal organs (kidney and liver) of mammals and in certain species of mussels, scallops and oysters. When grown on a cadmium-polluted soil, some crops, such as wheat and rice, can accumulate considerable amounts of cadmium (more than 1000 µg/kg) (Figure 1). The average daily intake of cadmium via food in European countries and North America is 15-25 µg but there may be large variations depending on age and dietary habits. In Japan, the average intake is generally 40-50 µg but may be much higher in cadmium-polluted areas. The gastrointestinal absorption of cadmium in humans amounts to about 5% but may be increased by nutritional factors [19].

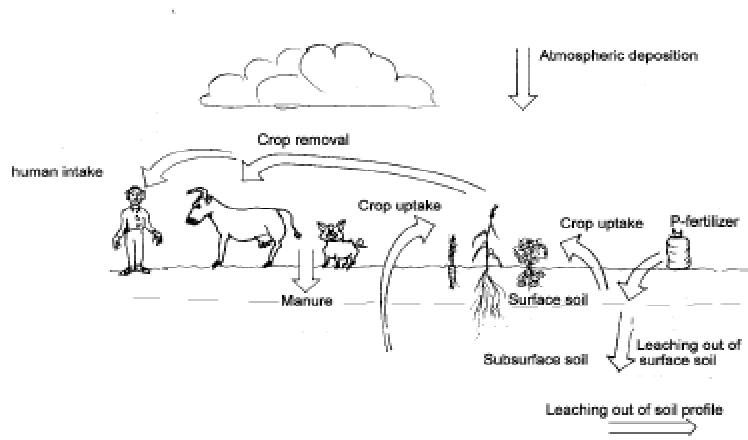


Fig.1 Routes of exposure of cadmium

### 1.1.5 Zinc in nutrition

Zinc (Zn) has been known to be an essential element for more than a hundred years, ever since it was discovered by Raulin in 1869 to be required for the growth of Aspergillus niger. However, it has not been until relatively modern times that the universal importance of this metal for both human and animal health became fully appreciated [20]. To date more than 200 zinc dependent enzymes have actually been identified in all the main biochemical pathways. It acts uniquely as a Lewis acid catalyst (an electron acceptor) in all life processes. The metal is known to be essential for the function and/or structure of several dehydrogenases, aldolases, peptidases, phosphatases, an isomerase, a transphosphorylase, aspartate transcarbamylase, pancreatic carboxypeptidase's, and tryptophan desmolase. Zinc-dependent metalloenzymes are also found among oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases. Zinc is also required for the action of both carbonic anhydrase and super oxide dismutase. The metal has also been found to be an essential component of both DNA and RNA polymerases. It is also vital for a variety of hormonal activities, including the thymic hormone, glucagons, insulin, growth hormone, as well as the sex hormones. Furthermore, zinc has been found to be essential for normal brain development, particularly concerning the hippocampal function. In addition, zinc is also known for its anti-viral, anti-bacterial, anti-fungal, and anti-cancer properties, and has been found to protect animals against otherwise lethal irradiation by neutrons [21].

Zinc is present in most foods, but meat and fish provide the best sources, as bioavailability of zinc from animal products is considered to be far greater than from plant foods. Even though plant foods do contain zinc, the bioavailability from them is relatively poor due to their high phytic acid and fibre content. In fact, zinc availability from vegetarian diets has been reported to be exceptionally low [22]. Wheat germ is very rich in zinc, but unfortunately it is invariably discarded during food processing, which further depletes the vegetarian diet of zinc.

### 1.1.6 Toxic elements and zinc

Zinc has a profound influence on the biochemistry and toxicology of cadmium. One reason for this is that cadmium can act as an antagonist to zinc in zinc- requiring metallo enzymes, such as carbonic anhydrase, alkaline phosphates, as well as with others. Thus inadequate zinc nutritional status can influence the absorption and uptake of tissue cadmium thereby increasing its toxic effect [23].

## 1.2 Cadmium in wheat

Wheat products are the major food items for the society. Thus the knowledge of mineral concentration in wheat and wheat products is of particular interest. In contrast to other toxic metals Cd in the soil is easily taken up by growing plants through the root systems, and Cd is thereby present in all food. In most foods it ranges between 0.01 and 0.05 mg/kg [24]. Wheat flour and potatoes are the main contributors to the average daily intake of Cd in Sweden. It was obtained that 43% of the total human Cd intake from food in Sweden is caused by wheat flour consumption [25].

Wheat (*Triticum* spp.) is important not only for its nutritional value, but also for its gluten content. Gluten is the protein of the wheat which, when properly developed by kneading, will trap and hold the yeast gas in the bread dough causing the bread to rise. Wheat is the only grain with the proper amount of gluten to facilitate the rising of bread dough to make light, soft loaves [24].

There are two basic categories of wheat, hard wheat and soft wheat. Hard wheat is grown in cool, dry climates, either in the winter or the spring. Dry winters and springs make the protein, or gluten, content high, and the moisture content low. High gluten content is necessary to make yeast breads. Hard wheat is named for the season it is grown (i.e. hard winter wheat or hard spring wheat). Soft wheat, known as pastry flour, cannot be used for making yeast breads. It is grown in wetter regions or is irrigated. The moisture content is high, making the gluten content too low for the proper rising of yeast breads. It is excellent for making cakes, cookies, or, pastries [25].

### 1.2.1 Wheat Kernel

Wheat kernels are the seeds of the wheat plant, and they are the part of the plant that is milled into flour. Wheat kernels have three main parts: the endosperm, the germ, and the bran as shown in Figure 2.

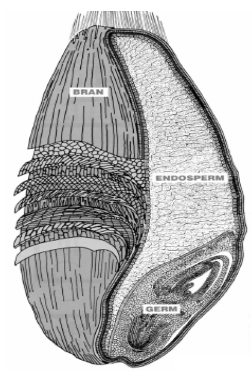


Fig. 2 The kernel of wheat

The *endosperm* makes up the bulk of the kernel. It is the whitest part, partly because it contains mostly starch typically 70–75 percent starch. The starch is embedded in chunks of protein. Two important proteins in the endosperm of wheat kernels are the gluten-forming proteins, glutenin and gliadin. When flour is mixed with water, glutenin and gliadin form strands of gluten, important in the structure of baked goods. In fact, wheat is the only common cereal grain that contains sufficient glutenin and gliadin for the formation of good-quality gluten for bread making.

The *germ* is the embryo of the wheat plant. Given the right conditions, the germ sprouts germinates and grows into a new plant. Wheat germ is high in protein, fat, B vitamins, vitamin E, and minerals. These nutrients are important to the germ as it sprouts. While germ protein does not form gluten, from nutritional standpoint it is of high quality.

The *bran* is the protective outer covering of the wheat kernel. It is usually darker in color than the endosperm, although white wheat, which has a light brown color, is also available. In either case, the bran is relatively high in dietary fiber. In fact, the bran is about 42 percent dietary fiber. It also contains a good amount of protein, fat, B vitamins, and minerals (Figure 3). As with wheat germ, the bran proteins do not form gluten.

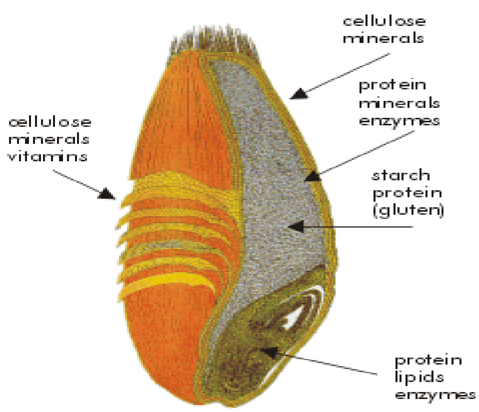


Fig.3 Chemical composition of soft wheat and durum wheat

Table1. Major components of wheat

| Component | Endosperm | Germ | Bran |
|---|---|---|---|
| Carbohydrates | 74.0 | 46.0 | 51.2 |
| Starch | 72.5 | 10-30 | 12.2 |
| Fiber (insoluble) | 3.3 | 8.1 | 45.0 |
| Protein | 10.6 | 26.6 | 16.0 |
| Lysine | 0.25 | 1.62 | 0.64 |
| Fat | 0.98 | 9.2 | 4.65 |
| Minerals | 0.35 | 4.2 | 4.15 |
| Phosphorus | 108 | 1100 | 1240 |
| Potassium | 108 | 837 | 1390 |
| Magnesium | 21 | 250 | 590 |
| Iron | 1.95 | 8.1 | 12.9 |
| Vitamins | | | |
| B1 (thiamin) | 0.06 | 2.01 | 0.65 |
| B2 (riboflavin) | 0.03 | 0.72 | 0.51 |
| Nicotinamide (or niacin) | 0.7 | 4.5 | 17.7 |
| Vitamin E | 2.3 | 27.6 | 9.1 |
| Water | 13.9 | 11.7 | 11.5 |
| Energy (KJ) | 1490 | 1450 | 789 |

*Values are in grams per 100 grams of the grain portion referred to, except for mineral quantities* which are expressed in milligrams and the energy units in kilojoules [26].*

### 1.3 Wheat flour

An ingredient used in many foods, flour is a fine powder made from cereals or other starchy food sources. It is most commonly made from wheat. Flour is the key ingredient of bread, which is the staple food in many countries, and therefore the availability of adequate supplies of flour has often been a major economic and political issue.

Flour is always based on the presence of starches, which are complex carbohydrates. usually, the word "flour" used alone refers to wheat flour, which is one of the most important items. Wheat flour is the main ingredient in most types of breads and pastries. Wheat is so widely used because of an important property: when wheat flour is mixed with water, a complex protein called gluten develops. The gluten development is what gives wheat dough an elastic structure that allows it to be worked in a variety of ways, and which allows the retention of gas bubbles in an intact structure, resulting in a sponge-like texture to the final product. This is highly desired for breads, cakes and other baked products.

### 1.3.1 Varieties of wheat flour

***Whole wheat flour:*** Since roller milling separates the bran and the germ from the endosperm, the three components actually have to be reconstituted to produce whole wheat flour. (The germ and bran are visible in the flour as minute brown flecks.) Whole wheat flour is higher in fiber, vitamin E, some B vitamins and trace minerals, and protein than enriched white flour. Because of the presence of bran, which reduces gluten development, baked goods made from whole wheat flour are naturally heavier and denser than those made with white flour.

***Refined flour (White flour):*** Refined, flour, or White flour consists of only the ground endosperm of the wheat kernel. White flour is popular because it produces lighter baked goods than whole wheat flour and has an unequalled ability to produce gluten [26].

**Types of white flours**

***All-purpose flour:*** Also known as family, plain, white, or general-purpose flour. This flour is made from a blend of hard and soft wheat. It has a "middle of the road" protein and starch content that makes it suitable for either breads or cakes and pastries. It can be either bleached or unbleached. All-purpose flour also is available presifted--that is, milled to a finer texture. This aerates the flour to make it lighter than standard all-purpose flour. However, all flour, whether labeled presifted or not, has a tendency to settle and become more compact on storage, so the benefit of presifting isn't always apparent.

***Bleached flour:*** When freshly milled, flour is slightly yellow. To whiten it, manufacturers either let the flour age naturally or speed up the process by adding chemicals (such as benzoyl peroxide or acetone peroxide) to bleach it. This process gives the flour more gluten-producing potential, but naturally aged flours develop more gluten as well.

***Bread flour:*** This is made entirely from hard wheat; high gluten content helps bread rise quickly. (It's also available in whole wheat form.)

***Bromated flour*** Some manufacturers add a maturing agent such as bromate to flour in order to further develop the gluten and to make the kneading of dough easier. Other maturing agents include phosphate, ascorbic acid, and malted barley.

***Cake flour:*** Finer than all-purpose flour, cake flour is made entirely from soft wheat. Because of its low gluten content, it is especially well suited for soft-textured cakes and cookies.

***Durum flour:*** Since it has the highest protein content of any flour, durum flour is the basis of nearly all noodles and pastas.

***Farina:*** This granular product, milled from the endosperm of any wheat but durum wheat, is primarily used in breakfast cereals and pastas.

***High-gluten flour:*** This has about twice the gluten strength of regular bread flour and is used as a strengthening agent with other flours that are low in gluten-producing potential.

***Instant flour:*** Also called instant blending, quick mixing, or granulated flour, this type of flour pours easily and mixes with liquids more quickly than other flours. It is used to thicken sauces and gravies, but is not appropriate for most baking because of its very fine, powdery texture and high starch content.

***Pastry flour (cookie or cracker flour):*** This flour has gluten content slightly higher than cake flour but lower than all-purpose flour. It is well suited for fine, light-textured pastries.

***Self-rising flour:*** Soft wheat is used to make this flour, which contains salt, a leavening agent such as baking soda or baking powder, and an acid-releasing substance. However, the strength of the leavener in some flours deteriorates within two months, so it's important to purchase only as much as you need during that period. Self-rising flour should never be used in yeast-leavened baked goods.

***Semolina:*** This yellow granular product is ground from durum wheat. Its high protein content makes it ideally suited for making pasta. It can also be used to make bread.

### 1.3.2 Advantages of fresh flour

Because grains contain only about 12% water (or about 0.6 water activity), they are not predisposed to spoilage. However, grinding removes the protective layers and endangers the grain's biological stability. Deterioration of sensory and nutritional qualities depends on storage conditions, such as temperature, humidity, oxygen concentration, and light exposure. The lower the water activity, the lower is the loss of vitamins. For example, vitamin E loss of only about 23% occurred after a 13 months of storage at a 0.6 water activity. In order to reduce oxidation of Essential compounds and the development of rancidity, many authors recommend storing ground flour for no more than two weeks Antioxidants present naturally in grains (vitamin E and lecithin) help prevent oxidation of the fatty acids and the associated rancidity only for a limited time, and under 'favorable' conditions.

Glutamic acid decarboxylase, the most sensitive enzyme in the grain, is used to indicate the health of the grain. When heated or exposed to increased humidity, even under favorable conditions, it losses activity very quickly in wheat. The B vitamins are liable to be destroyed by light and air, and it also seems that other substances, still unknown, are quickly destroyed. Other deteriorations include denaturation of lipoproteins, phospholipid hydrolysis, auto-oxidation of unsaturated fatty acids of phospholipids, polymerization within lipoproteins, browning, Maillard reaction of amino groups from phospholipids and aldehyde groups from sugars, and carotene and aroma losses.

Lipids in milled wheat are much more susceptible to enzymatic degradation, because enzymes are incorporated into the flour with fragments of bran and germ and with microorganisms from the surface of the grain. Associated with lipid deterioration are losses of carotenoids and vitamin E [26].

### 1.3.3 Enrichment of flour

The practice of adding back only those micronutrients that are lost during milling and for which there is good evidence that a deficiency exists within the general population for approximately 20 nutrients. There is an average loss of 70-80% in refined and enriched flour [27]. Its consumption clearly places the body at a disadvantage, casting a burden on the rest of the diet. The addition of more nutrients to refined flour has been considered, but it is limited by, for example, the effect of some nutrients on sensitive individuals. Since research is incomplete concerning nutrient requirements, interactions, optimal ratios, and toxicities, many believe that the safest option is to consume flour containing the nutrients in their natural proportions.

### 1.3.4 Adulteration of flour

This act is defined as the addition of any non-condimental substance to a food, such substance not constituting a portion of the food. Concerning grains, the separation of the milling and baking industries has led to the adulteration of flour with various chemicals, as flour manufacturers have sought to maximize profits and meet customer demands. For example, removing the germ not only prevents flour spoilage, it generates profits when sold to mill feed producers and pharmaceutical companies.

For centuries, bakers have known that 'good quality' baked goods could not be made with freshly milled flour, because the dough would lack strength and resilience to trap gas. Until the 20th century it was common practice of storing flour for months to allow oxygen to condition it. However, apart from storage costs, spoilage and insects caused losses. Chemical oxidizing agents or bleachers were developed to produce the same aging effects in 24-48 hours. They cause one of two effects: oxidation of the gluten (so less sulfhydryl groups are left to disturb disulfide bonds that need to form during dough fermentation for the bread to rise), and bleaching of the yellowish carotene pigments which could have been sources of vitamin A. Numerous chemicals are used to white, whole wheat flours. These include chlorine, chlorine dioxide, benzoyl peroxide, potassium bromate, ammonium per sulfate, ammonium chloride, acetone peroxide, azodicarbonamide, ascorbic acid, l-cysteine, mono-calcium phosphate. Nitrogen dichloride, also known as agene, was one of the earliest bleaching agents. After 40 years of use, it was finally found to cause canine hysteria, and was outlawed. The currently used most common bleaching agent is benzoyl peroxide. It must be neutralized by adding substances such as calcium carbonate, calcium sulphate, dicalcium phosphate, magnesium carbonate, potassium aluminum sulphate, sodium aluminum sulphate, starch, and tricalcium phosphate [24].

### 1.4 Developments in the milling of grain

The Egyptians were the first to use a selective milling system. With hand sieves, they separated the flour from large bran particles, dirt, and stone chips that had broken off their implements. The earliest version of today's iron roller mills were first used in Hungary in 1839. Between 1870 and 1890, they quickly replaced the stone mills throughout Europe and North America, and milling soon became completely automated.

Today a very sophisticated process is currently employed for the milling of grain. Cleaning is accomplished by means of separators, aspirators, scourers, magnets, and washer-stoners. The wheat is tempered or conditioned in water to toughen the bran to reduce fragmentation when it is removed, and to obtain a moisture content resulting in particles of the desired size. The processes of drying and conditioning with steam (25% humidity and 60°C), have been shown to cause minerals such as potassium and phosphorus migrated to the endosperm, whereas more strongly bound minerals like calcium and magnesium did not migrate. This may increase the content of certain minerals in refined flour. During the milling process, steel rollers crush the grain, and the flour released from the endosperm is separated by sifters into different grades or streams, according to fineness. Each of these has different mineral and protein contents, and may be recombined later to form a variety of flours to be sold for diverse baking purposes. The bran and germ, which make up about 28% of the wheat, are totally removed in this process. Whole wheat flour is produced by recombining ground bran with endosperm flour, but the germ is usually left out, because it would go rancid. The resulting flour may represent only 95% to of the total grain (by weight), or in other words a 95% extraction [24].

***Advantages of stone-ground wheat flour:*** There are several advantages of stone-ground wheat flour. The endosperm, bran, and germ remain in their natural, original proportions. Because the stones grind slowly, the wheat germ is not exposed to excessive temperatures. Heat causes the fat from the germ portion to oxidize and become rancid and much of the vitamins to be destroyed. Since only a small amount of grain is ground at once, the fat from the germ is well distributed which also minimizes spoilage. Nutritive losses due to oxygen exposure are also limited by the fact that stone-ground flour is usually coarser. Generally milling affects the nutritional value of grains in two ways as the physical separation of the different grain components has the greatest impact on the nutrient content of the grain. And Grinding reduces the particle size, which impacts on the glycaemic index and resistant starch content of grains.

In wheat milling, the bran, and germ components are separated from the endosperm, which is ground into flour. Since dietary fiber, vitamins, minerals and antinutrients (phytic acid and phenolic acid) are concentrated in the outer bran layer of the grain; the extent to which this layer is removed determines the nutrient content of the flour.

Flour milling have impact on the bioavailability of nutrients, although phytate and dietary fiber bind minerals, particularly calcium, iron, magnesium and zinc which reduces their absorption in the body, and white flour has a lower phytate content than whole meal flour therefore the absorption of minerals would not be affected as much as for whole meal flour. The whole meal flour is higher in minerals so overall they provide more minerals to the body than white flour. Extractions rate that is the number of parts by weight of flour that is produced from 100 parts of wheat. Has an impact on nutrient content the higher the extraction rate, the more bran is included in the wheat flour and hence the higher the amount of dietary fiber, vitamins and minerals in the flour [28].

### 1.5 Disadvantages of wheat in the diet

Wheat in the diet has many disadvantages. White flour that is used in many types of bread and confectionary is very popular in western societies it is 70% extraction from the original wheat grain, which results in it having only a quarter of the vitamins as whole meal flour. Wheat only contains 10%-12% essential amino acids and is not a good source of quality protein. Wheat is deficient in the essential amino acids methionine and lysine. To improve the quality of protein in wheat products these two amino acids are added in manufacturing. The body can only use 55% of the whole wheat protein. The better quality protein comes from the germ and bran, the poorer quality comes from the endosperm, which is used, in white flour. People who are protein deficient should not eat white bread, as it is deficient in protein. The endosperm which makes white flour contains less copper, manganese, zinc, vitamin B6, vitamin B3, vitamin B2 and iron. In fact there is no vitamin E in white bread.

Bleaching agents like bromate and chlorine dioxide damage the starch and protein in the flour by releasing active oxygen and altering the bulk material in the flour. Chlorine changes the protein chain that makes them toxic this is why some people are allergic to white bread and not whole meal. White bread also has less fibre in it this can cause problems with the intestines. Wheat can cause problems with the intestine and if the fibre is removed then the wheat remains in the intestine longer causing more problems. White bread can cause a rise in blood pressure. This is because zinc is lost in the manufacturing of white flour. White bread has high cadmium and low zinc this is the recipe for the body to produce high blood pressure. To lower blood pressure the exact opposite is needed high zinc low cadmium.

Gluten since it is hard to digest and is known to generate the bowel condition known as Diverticulitis. Some individuals are intolerant to gluten this is known as coeliac disease. This is when the gluten damages the lining of the small intestine which results in bloting, diarrhea and malabsorption of nutrients.

Increase in colon-related illnesses such as constipation, diverticulitis, irritable bowel syndrome, colon cancer is observed in those people consuming a refined Western type diet because of the lack of dietary fiber. A typical western diet consists of large amounts of refined foods, specially refined cereals and bread. Fiber binds water, minerals, salts, bile, toxins and drugs to increase the volume of stool, which speeds up the process of elimination. This deceases the time that the bowel is in contact with toxic elements. Chronic constipation is a big problem for those living in western countries.

Diverticulosis is a common disorder in western countries afflicting the large intestine. Diverticula are pockets found on the outside of the colon where pressure inserted on the colon has resulted in the colon being forced apart in weak areas. If an infection occurs in the diverticula then severe pain and fever can occur this may need surgery to correct. A diet high in fibre has shown to reduce the risk of colon cancer this is because the fibre speeds up the rate of elimination which results in potential cancer causing substances having less time in contact with the lining of the colon.

Besides the affliction already mentioned, there are many other problems associated with a low fibre diet. Appendicitis has been linked to the lack of fibre in the diet. The risk of becoming obese, suffering from coronary heart disease, diabetes and other cancers are reduced when consuming a high fibre diet. As illustrated to reduce the risk of disease and to maintain a healthy bowel it is recommended to include a good amount fibre in the diet. Modern wheat also causes blood sugar imbalances, a condition which is all too common in the typical Western individual [29].

### 1.6 Wheat flour production in Ethiopia

Ethiopia is the second largest producer of wheat in sub-Saharan Africa; following South Africa about 900,000 hectares of bread (*Triticum aestivum*) and durum (*T. turgidum* var. *durum*). Wheat is grown in Ethiopia, primarily as highland rain fed crops.

The development of the food processing industry in Ethiopia has to be viewed in the context of the low level of development of the industrial sector in general and the manufacturing component of the sector in particular. The food processing industry is the dominant group among the 15 groups of large and medium-scale manufacturing industries in Ethiopia in terms of product varieties, number of establishments, gross value of production and value-added at market prices. The food manufacturing enterprises are generally located in close proximity to major urban population centers, such as Addis Ababa, Dire Dawa, Nazareth, Bahirdar, Awassa, Gonder, Mekelle and Dessie. For instance: Flourmill and bakery products manufacturing plants are located in Addis (e.g. DH Geda, Kojj, Misrak), in Nazareth (Nazareth flour factory, Awassa, Debre-Zeit, Tigray (Tigray Flour Mill) and Bahirdar (Guder Maize Flour Mill).

The qualities of all products that are being produced by the formal food industry sector in Ethiopia are generally satisfactory that meet the quality standards of the Ethiopian Quality and Standards Authority. However, there seems to be a misperception among the general public that all products imported from aboard are of superior quality in comparison to some domestic food products, notably wheat flour. Informed sources on the other hand, testify to the non-organic character of may imported food products as opposed to the largely organic nature of Ethiopian food products. In this connection, the competitive and very good quality of the Dire Dawa Food Complex flour and flour products, including spaghetti and macaroni, is worth noting. Therefore, it is argued that the qualities of Ethiopian food items are not necessarily inferior.

It is difficult to make a sweeping generalization on the type and quality of technology being employed in the food industry in Ethiopia. This is because some factories are using state-of-the art modern technology while others are using old and sometimes obsolete technologies. Cereals, especially wheat and maize, provide the raw material inputs for grain mills, bakery products, baby food, animal feed and macaroni and spaghetti. Oilseeds serve as inputs for the edible oil industry. The peasant agricultural sector supplies more than 95% of the total agricultural crop production [30].

## 1.7 Objectives of the study

### General objective

The main objective of this project is to collect base line data on levels of trace cadmium and zinc in wheat flour commercially available in Addis Ababa.

### Specific objectives

1. To develop working procedure for digestion of wheat flour samples.
2. Determination of level of Cd and essential Zn in wheat flour by FAAS to be processed/ collected from DHGEDA, K.O.J.J, Misrak, Akwan and Redfam flour industries.
3. To compare level of Cd and Zn in wheat flour with other countries.

## 2. MATERIALS AND METHODS

### 2.1 Instrumentation

BUCK SCIENTIFIC MODEL 210VGP, USA atomic absorption spectrometer equipped with deuterium arc back ground corrector; Kejeltec Auto 1003, Tecator, Hoganas, Sweden; Tecator/Udy, Ra, Fa Tec Extraction unit, Hoganas, Sweden; Selecta model 2001241 drying oven, Spain were used.

### 2.2 Chemical and Reagents

All dissolution were prepared using pure analytical reagents: Nitric acid (65% Merch, Germany), and hydrochloric acid (37% Riedel-de Haen chem. Pure, Germany), 70% $HClO_4$ (ALDRICH, A.C.S. REAGENT, Germany). A stock standard solution of 1000 mg/L (Buck scientific PURO-Graphic$^{tm}$ calibration standards, prepared as nitrate in 2% $HNO_3$). The calibration solutions were made using distilled and deionized water immediately before use.

### 2.3 Sample Collection

Addis Ababa city is metropolitan of Ethiopia and has high intensive population. There are a number of flour industries that supply the flour needed by the people. Wheat flour samples were collected from products of DHGEDA, K.O.J.J, Misrak, Akwan and Red fam wheat flour industry commercially available and used by most people in Addis Ababa. About 200 gm. of sample was collected from each bag randomly totaling of 10 bags. The collected flour was pooled together and mixed well. The sample size was reduced to about 100 gm by coning and quartering process. And about 10 g. of the sample was used for analysis. The above sampling process was adopted for all the industries.

**Contamination Control**

The digestion vessels and other glassware were cleaned with metal ion free non-ionic detergent solution using tap water, then rinsed with deionized water and dried in oven. Blanks, consisting of deionized water and reagent were subjected to a similar sample preparation and analytical procedure.

## 2.4 Analytical procedures

### 2.4.1 Optimization of digestion methods

Trace metal determination in wheat flour or flour products like bread, pasta, and biscuit in some cases involves extraction technique before analysis by FAAS. Digestion with acids is most commonly employed. The digestion step depends on the nature of the sample, analytes and concentration but the very determinant factor is the technique of analysis to be used for the determination. In most cases wet digestion are commonly used than dry ashing for analysis by FAAS. Different combination of mineral acids has been employed in other studies for the decomposition of wheat flour. Various digestion procedures where tested to digest wheat flour samples starting from the procedure set by AQA 04-04. Trace metals and nutrient elements in wheat [31]. From the results obtained an appropriate digestion procedure was selected and optimized for analysis (Table 2).

Since acid digestion was used in analysis it is necessary to prepare acid/reagent blanks for each digestion employed. Reagent blanks prepared and digested with the same procedure as the sample can correct for impurities present in the acid and in the water. The method detection limit for Cd was calculated ($3\sigma$ blank n=5) as 0.01mg/kg.

Table 2. Attempted digestion procedure for wheat flour samples

| Sample | Method | Reagents | Condition of digestion | Time (Hour) | Remark |
|---|---|---|---|---|---|
| Wheat flour | I | 4mL $HNO_3$<br>2mLHCl,<br>50mL deionised water | Suspension | 2 | Deep yellow in Color |
| | II | 4 mL $HNO_3$<br>2mL$HClO_4$<br>50mL deionised water | Suspension | 2 | Pale red color |
| | III | 6mL $HNO_3$<br>2 mL HCl<br>50 mL deionised water | Suspension | 2 | Pale yellow |
| | IV | 6mL $HNO_3$<br>2 mL HCl<br>50 mL deionised water | Less suspension | 3 | Pale yellow |
| | V | 6mL $HNO_3$<br>2mLHCl<br>50 mL deionised water | Clear | 4 | Pale yellow<br>**Optimized Procedure** |

**2.4.2 Digestion of wheat flour samples**

Wheat flour samples were digested by optimization and modification of literature procedure, which was used to measure trace metals in wheat flour by FAAS [27]. 50ml of deionised water was added to about 10 g of the sample and the mixture was refluxed in 6mL 65% nitric acid and 2mL 37% hydrochloric acid for about 4h. The digest was then filtered through a whatman No.42 filter paper finally the filtrate was made up to 100ml with deionised water. Triplicate analysis of all wheat flour samples were made together with reagent blanks. Cd and Zn were determined in the digests by FAAS with deuterium arc background correction.

### 2.4.3 Determination of cadmium in wheat flour

BUCK SCIENTIFIC MODEL 210VGP atomic absorption spectrometer equipped with deuterium background corrector and standard air acetylene burner system was used. Hallow cathode lamp of cadmium and zinc operated at the manufacturers recommended conditions was used at its primary source line. Standard solutions containing 1000 mg element/L (Buck Scientific) were used for preparing intermediate standards (100 mg/L or 10 mg/L) and working standards (.01, .05, 0.15, 0.3 mg/L) for Cd and (0.125, 0.25, 0.5, 1 mg/L) for Zn were prepared freshly by appropriately diluting intermediate standards. The acetylene flow rate and airflow rate was managed to ensure suitable flame conditions. The burner height was adjusted for optimum sensitivity and the nebulizer uptake rate was optimized (6-7 mL/min) to provide optimum absorbance signal in conventional sample aspiration. The spectrometer was operated with the time constant of 0.2 s. The wavelength with the corresponding slit width was once selected and adjusted at the beginning of the experiment and analysis was performed in the same way through out the study. The flame condition for Cd and Zn is summarized in Table 3.

Table 3.Instrumental parameters

| | Cd | Zn |
|---|---|---|
| Wave length (nm) | 228.9 | 213.9 |
| Slit width (nm) | 0.7 | 0.7 |
| Lamp current (mA) | 2 | 2 |
| Detection limit mg/L | 0.005 | 0.005 |
| Energy (erg) | 3.235 | 3.218 |

### 2.4.4 Recovery of wheat flour sample

To validate the method for the metals Cd and Zn analysis, a 0.25 mL of a 10 mg/kg for Cd and a 0.25 mL 100 mg/kg for Zn known concentration of Buck Scientific standards of each element was added into a 10g sample and treated exactly in the same way as the other samples analyzed [32].

# 3. RESULTS AND DISCUSSION

## 3.1 Validation of Analytical procedures

### 3.1.1 Validation of Method

The analyses of spiked samples of wheat flour show recoveries for Cd 92% and for Zn 94% (Table 4). This value is within the acceptable range for the analysis of food samples and confirms the validity of optimized digestion.

Table 4. Concentration of trace metals determined in wheat flour samples spiked with standards.

| Metal | Concentrations (mg/kg) | | |
|---|---|---|---|
| | Added | Measured | % Recovery |
| Cd | 0.025 | 0.0230 ± 0.0001 | 92.0 ± 0.4 |
| Zn | 0.25 | 0.235± 0.016 | 94.0 ± 6.4 |

**N.B** measured results are the mean concentration (X ± SD n=3 dry weight) of wheat flour samples.

## 3.2. Concentration of Cadmium and Zinc in wheat flour

The suggested method was applied for the determination of concentrations of cadmium and zinc in wheat flour samples.

**Cadmium (Cd):**

The average cadmium in various wheat flour samples is summarized in Table 5. The cadmium concentration expressed in units of mg/kg on the normal dry condition in which they are available in the market. The cadmium content of wheat flour found in this study ranged from 0.011 to 0.024 mg/kg. The variation in the level of cadmium may be because wheat for flour production has various origins or the difference in processing of the industries like rate of extraction. It should be known that most of the industries are using wheat produced by some comparatively mechanized farms found in southeastern part of the country that employ phosphate fertilizers and manures which constitute or form the basic sources of cadmium, however the concentration of cadmium may be much lower in wheat produced by organic farming by most farmers in the countries. For general comparison of cadmium concentration in wheat flour with data from similar survey in the different regions is shown in Table 6.

Table 5. Average concentrations of cadmium and zinc in wheat flour samples

| Samples | Concentrations (mg/kg) | |
|---|---|---|
| | Cd | Zn |
| DHGEDA | 0.018±0.004 | 9.09±0.62 |
| Misrak | 0.021±0.003 | 9.02±0.14 |
| KOJJ | 0.015±0.001 | 7.82±0.53 |
| Akwan | 0.014±0.004 | 6.49±0.48 |
| Redfam | 0.020±0.005 | 9.39±0.51 |

**N.B** measured results are the mean concentration (X ± SD n=3 dry weight) of wheat flour samples.

Table 6. Average concentration of cadmium in wheat, by GEMS/Food region

| Country | Concentration of cadmium in regional diet[a], mg/kg (number of samples[b]) |
|---|---|
| Middle Eastern[c] | 0.034 (53) |
| Far Eastern | 0.030 (410) |
| African[d] | 0.153 (3) |
| European | 0.026 (752) |

a. Values for regional concentrations are the averages of aggregated data (means/medians).
b. Total number of samples represented by aggregated means/medians where available.
c. Averages for the Middle Eastern region are based on data from Greece only.
d. Averages for the African region are based on data from Nigeria only [34].

**Zinc (Zn):**

Micronutrients are gaining much importance in recent years and their deficiencies are recognized as major public health problems in many developing countries. The Zinc (Zn) content of foods varies up to 2000mg/kg fresh weight in oysters to below 5mg/kg in refined foods. The average concentration of zinc in various wheat flour samples obtained in this study ranges from 5.93 to 9.88mg/kg. The reason for this difference might be due to the use of raw material from different sources or difference in the rate of extraction. Even though wheat grain is known to be good source of zinc for vegetarians the result obtained in this study is low. It can be explained that minerals are always found in the grains especially in the germ and outer layer of the kernel and milling process is responsible to remove the germ and most of the outer layer of the kernel produces white flour which has a higher proportion of starch and higher caloric value than the wholewheat flour and much of the vitamin and mineral contents of the kernel are always lost in milling white flours. It is known that about 80% of zinc is removed from wheat flour during milling process. Studies by USDA results the mean concentration of zinc in wheat flour and white flour as 29mg/kg and 7mg/kg respectively [33]. For general comparison of zinc concentration in wheat flour with data from similar survey in the different countries is shown in Table 7 [35].

Table 7. Comparison of Zn levels (mg/kg) in wheat flours with other countries.

| | |
|---|---|
| Egypt | 8.2 |
| Iran | 7.32-12.17 |
| Romania | 13.97 |
| Nigeria | 2.93 |
| USA | 7.2 |

**Relations of cadmium and zinc in wheat flour**

As can be seen in Figure 4 there is a correlation in the concentration of cadmium and zinc in wheat flour samples that may explain the variation in concentration of Cd and Zn related to the rate of extraction.

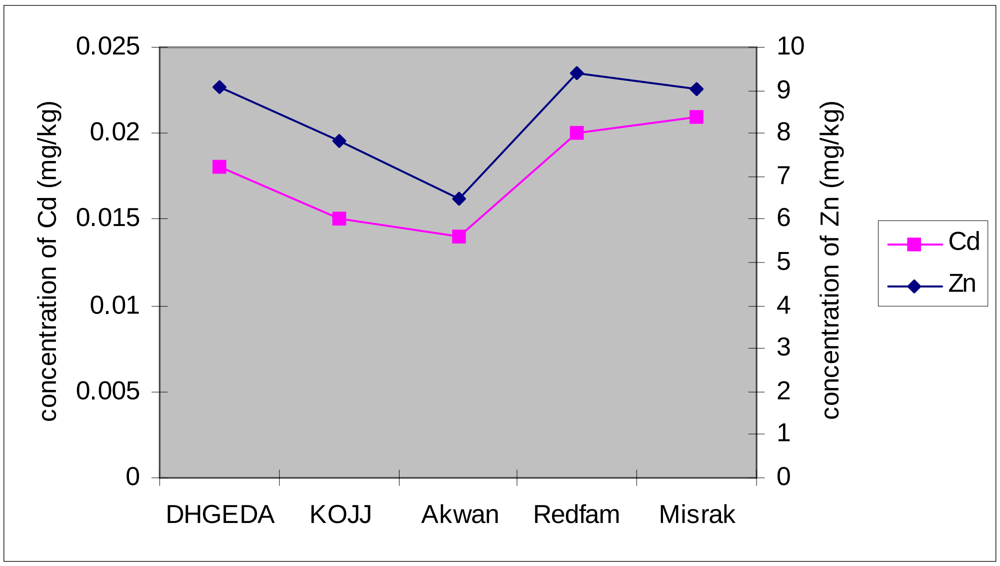


Fig.4 Cd and Zn relation in wheat flour samples

## 4. CONCLUSION AND RECOMMENDATIONS

Wheat being an important part of the diets of people in most of the countries, there has to be a knowledge of levels of toxic cadmium in it and essential zinc which has antagonistic effect on absorption of Cd. Cd and Zn in different of wheat flour products ranged from 0.011 to 0.024 mg/kg (mean 0.0175 mg/kg) and 5.93 to 9.88mg/kg (mean 7.905 mg/kg), respectively. The optimized acid digestion can be said as efficient from recovery values.

In this study the concentration of toxic cadmium in wheat flour was found to be much lower than the values in other countries and the values set by national food authority (NFA, 1997) and European Commission 1999 in which the MPL for cadmium concentration in wheat to be 0.1 mg/kg, 0.2 mg/kg respectively [36].

Refining may be the main cause for some decrease in the level of zinc in wheat flour, in addition to the mineral composition of soil. To minimize this problem some countries have set regulation on enrichment of flour with essential nutrients like Zn and Fe, however enriching, and addition of various chemicals to flour and baked breads cause many scientists and medical workers to question their nutritional quality as well as their safety [37].

The nutrient levels in processed foods can be greatly enhanced by changing milling and processing techniques. Instead of stripping away the nutritious bran and germ, higher-extraction and whole grain flours can be produced. Developing the technology is not a big problem. The real challenge is convincing consumers to accept and look for coarser products made with these ingredients.

It should be stressed at this point that a number of additional samples need to be analyzed before any general conclusion regarding the cadmium residue in wheat flour can be drawn. In addition further studies on toxic metals and even the essential one are required not only on wheat flour for quality assessment but also on wheat grain and on the soil where the wheat have been grown. Such studies should take in to consideration the various aspects like various characteristic properties of soil, like soil pH, total Cd total Zn, soil organic matter level, soil salinity, soil oxides, and cation exchange capacity (CEC) and identify bioaccumulation of heavy metals is relation to specific variety of wheat and geographical location.

In addition there has to be assessment on levels of cadmium on the imported fertilizer since a number of countries have established limits on the content of cadmium in phosphate fertilizers. The aim of these restrictions is generally to limit the supply of cadmium to agricultural soils. For example, in Austria commercial fertilizer must not contain more than 75mg Cd/kg of phosphorous. While in Denmark the maximum accepted cadmium concentration of fertilizers is 110 mg Cd/kg of phosphorous. In Australia, all states are aiming for a maximum permitted concentration of cadmium in phosphate fertilizers of 300 mg Cd/kg phosphorus [38].

Despite this inadequacy some conclusions may be drown from this review. Generally the concentration of cadmium in wheat flour is low but with the expected increases in mechanization, urbanization and socio economic activities there is a need to identify the sources and quantify the discharge of toxic cadmium via wheat.

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