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Analysis of metals (Pb, Mn, Cd, Zn, Cu) in Purple Rice and Purple Rice Stems Cultivated Organically using Biogas Slug in Padang Pariaman, West Sumatra Province

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Abstract. The presence of heavy metals in rice plants can be a problem if the content exceeds the specified threshold. The aim of the study was to determine the content of heavy metals in purple rice stems and purple rice broken rice in Kelonpok Tani Indah Sakato I Kanagarian Kasang, Batang Anai District, Padang Pariaman Regency. Purple rice stem and 'milled purple rice' were analysed using AAS (Atomic Absorption Spectrophotometer). . Analysis of heavy metals includes lead (Pb), manganese (Mn), copper (Cu), zinc (Zn) and cadmium (Cd). The results of laboratory analysis showed that lead (Pb) in purple rice straw and milled purple rice was detected at 0.0256 mg / kg and 0.0196 mg / kg. Manganese (Mn) metal was detected at 0.1046 mg / kg and 0.3675 mg / kg, the copper (Cu) metal detected was 0.01165 mg / kg and 0.010815 mg / kg. Furthermore, Cadmium (Cd) metal was detected at 0.01465 mg / kg and 0.0141 mg / kg and zinc (Zn) metal detected at 0.083125 mg / kg and 0.2659 mg / kg. All observations of metal content do not exceed the quality standards set by ANZECC. It can be concluded that Purple rice stem and 'milled rice' are safe for consumption.

1.Introduction

Rice is a staple food in many Asian countries and other parts of the world. Morning is the most important staple food for about half of the human race [1]. Rice is classified as the most important food that is relied upon by more than 50 percent of the world's population for around 80 percent of their food needs. Rice is relatively easy to produce and grow for sale and for home consumption. Heavy metals form naturally in ecosystems, but rarely at toxic levels. Heavy metals are persistent environmental contaminants because they are not easily degraded or destroyed; this is because they are stable [2]. Heavy metals are absorbed by plants through the atmosphere, fertilizers, pesticides and urban and industrial sewage deposits in the soil and water used to irrigate plants [3]. Mechanical farming and also the use of fertilizers and chemicals are agricultural practices that exist today. These practices are implemented in Indonesian territory in an effort to ensure food security. The consequence of this practice is that the environment is contaminated with heavy metals from fertilizers, chemicals and smoke from machinery. Plants grown in soil that is contaminated with heavy metals have a greater accumulation of heavy metals compared to those planted in land that is not contaminated. So, when humans consume one of these food sources, they tend to absorb some of these heavy metals into their bodies [4]. Excessive accumulation of heavy metals in the environment has toxicological implications in humans, plants and other animals [5].

Human health can be at risk due to consumption of contaminated food. Many contaminated foods are produced from plant products that grow in contaminated soil. Food is often polluted by inorganic components, including various dangerous heavy metals. Heavy metals are metal elements with high molecular weight, in low levels heavy metals are generally already toxic to plants, animals

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and humans. Dangerous heavy metals often pollute the environment from motor vehicle fumes, soil dust and fish raw materials such as lead (Pb), mercury (Hg), copper (Cu) and arsenic (As), so research on analysis is needed heavy metal content in this purple rice. These metals, such as lead, cadmium, nickel and mercury are toxic to humans even in small amounts and cause various health problems, such as kidney damage, lung problems, cancer and bone injuries [6].

The heavy metal content of agricultural soils can affect human health directly through the consumption of plants grown in contaminated soil. There is clear evidence linking human renal tubular dysfunction with contamination of rice with Cd in subsistence agriculture in Asia [7]. Indeed, in Asia rice has been identified as one of the main sources of Cd and Pb intake for humans [8]. In Japan, Ref. [9] specifically reported that rice is the main source of Cd contamination in humans, but there are efforts to minimize heavy metal pollutants in food. One recent approach to reduce food crop pollution that grows in contaminated soils is to plant safe cultivars, varieties that are heavy metal accumulators less efficient [10]. It has also been reported that plants have different abilities to absorb and accumulate metals in different parts and that there are wide variations in metal absorption and translocation between plant species and even between cultivars of the same species [10]. Plants absorb heavy metals from the soil, the surface zone of the depth of 25 cm of soil is the most affected by such pollutants resulting from anthropogenic activity. Heavy metals accumulate in this soil layer due to the relatively high content of organic matter. This depth zone is also where the roots of most cereal plants are located [11]. Interesting plant parts for direct transfer of metal pollutants to humans are edible parts such as grains. In the case of cadmium which is one of the most mobile geochemical toxic metals, it is easily taken by plants and transferred to the parts of the air plant where it is accumulated [12]. There are a number of reports on the concentration of toxic metals such as Cd in rice and rice soils in Japan, China and Indonesia [13]

Contamination of arsenic in groundwater has resulted in a gradual increase in the element in wheat rice. Carcinogenic properties of arsenic have been proven; therefore, several strategies must be employed to effectively reduce arsenic in rice consumption [14]. There is some evidence that if rice has been washed and cooked with a lot of water, arsenic levels will be reduced [15]. According to guidelines from the National Standards Institute, the maximum permissible level of heavy metal rice to lead is 0/15 mg, cadmium 0/06 mg and arsenic 0/15 mg for per kilogram of rice [16].

Until now there has been no research that shows the amount of Lead needs (Pb) in the body, but the excess can cause anemia, brain damage, miscarriage, and fetal death at birth [17]. The minimum amount of Lead (Pb) in the blood that can cause poisoning ranges from 60-100 micro grams per 100 ml of blood.

The need for copper (Cu) for adults is approximately 2 mg per day and 0.005-0.1 mg per day for infants and children [18]. If the intake of copper (Cu) exceeds the need, it can cause cell membrane lesions or lipid oxidation which causes hemolysis and necrosis of liver cells (Darmono, 1995: Sunardi, 2006). The threshold for Copper (Cu) in the blood according to WHO provisions is 800 - 1200 ppb.

Based on existing data, household chemicals rank first in causing poisoning. Household chemicals (ZKRT) include cleaning fluids, detergents, insecticides, kerosene, cosmetics, herbicides, insect repellent / rodents, shampoos, soaps, and deodorizing agents. These substances are chemicals that we generally do not know exactly what they are, how to use the right and its toxicity if we use it in the long run [19]. Some pollution in rivers certainly results from the life around them both in the river itself and human behavior as users. Due to discharge from household activities and even waste coming from industrial areas causes disruption of river ecosystems [20] especially in rice plants.

Heavy metals are metals that usually have a specific gravity above 5.0 and are toxic. Quite a lot of heavy metals include lead or lead (Pb), mercury (Hg), Arsenic (As), cobalt (Co), nickel (Ni), Chromium (Cr), cadmium (Cd), and phosphorus (P). These metals are widely used in various industries, but for the body these metals are toxic substances. Heavy metals are very dangerous because they can not experience metabolism in the body, and remain in the body and cause toxic effects by joining one or several reactive groups that are essential for normal physiological function. Lead and its compounds are widely used in the battery industry as active ingredients in the flowing of electron currents, and also used in the paint industry, where Pb metal (Lead) and its compounds are toxic if in high doses because the Pb metal will accumulate in the body (nervous system center).

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Besides this Pb can come from cans which are soldered in the process of joining between the two sides of the body of the can or part of the tin and the lid being sealed [21].

As a result of Pb poisoning, it can cause neurological disorders (encephalopathy, ataxia, stupor, and coma), impaired kidney function, reproductive disorders, and blood disorders [21]. Excessive absorption of Zn can cause symptoms of nausea, vomiting, dizziness, heartburn / abdominal pain, fever, diarrhea and most occur after intake of 4 - 8 g of Zn. intake of 2g ZnS can cause acute poisoning which affects stomach pain and vomiting. What is more important is that Zn is a class one element with cadmium (Cd) and mercury (Hg) which are both toxic. Zn in relation to health can cause infection of the mucous membranes with lethal doses (LD) 3 - 5 g ZnCl2 and ZnS are toxic at lethal doses (LD) 5 g. This amount is very dangerous because oral doses in the long run cause digestive problems, reduce HDL and cause damage to the immune system (Mawardi, 2007). This study aims to determine the presence of heavy metals content of Pb, Mn, Cd, Zn, Cu in broken purple rice and purple rice stem from NagariKasang, BatangAnai District, PadangPariaman Regency.

2. Materials and Method

2.1. Sample Destruction Process [22]

Samples of rice stems continue to be put into the Teflon beaker evenly, as well as purple rice, in order to experience a perfect drying process in the oven at a temperature of 105 ° C for 4 hours. Samples that have been dried until finely ground and sifted with a 150 μ m sieve, then the sample is weighed with an analytical balance of 0.4 grams and then put into a Vessel add 9 ml HNO3 and 3 ml HF heated in a microwave syrup at 180 ° C with pressure 30 bars for 25 minutes until all sediment dissolves, then the sample was cooled at room temperature and filtered with Whatman paper into a 50 ml measuring flask, adding 3 ml saturated boric acid and aquabides to the mark limit of 50 ml. then measured with AAS using acetylene air flames

2.2. Calibration Curve [22]

Analysis of heavy metals is carried out using Atomic Absorption Spectrophotometrics (AAS) based on the Lambert-Beer law, namely the amount of light absorbed is directly proportional to the content of the substance. Because the atom absorbs light, the ion or heavy metal compound must be converted into an atomic form. A standard sample solution is inserted into the test tube available on the AAS device, made adjustments on the user's AAS device computer, turned on the fire and AAS cathode lamp, the position of the lamp is also set to obtain maximum absorption. Then aspirated the standard solution into the air of acrylene, the designation of the reading results must be zero. Consequently the standard solution is analysed using AAS, the results of the measurement of atomic absorption will be recorded and then calculated to get the metal concentration in the sample solution.

2.3. Sample Analysis with Atomic Absorption Spectrophotometer (AAS) [22]

Analysis of heavy metals is carried out using Atomic Absorption Spectrophotometrics (AAS) based on the Lambert-Beer law, namely the amount of light absorbed is directly proportional to the content of the substance. Because the atom absorbs light, the ion or heavy metal compound must be converted into an atomic form. A standard sample solution is inserted into the test tube available on the AAS device, made adjustments on the user's AAS device computer, turned on the fire and AAS cathode lamp, the position of the lamp is also set to obtain maximum absorption. Then aspirated the standard solution into the air of acrylene, the designation of the reading results must be zero. Consequently the standard solution is analysed using AAS, the results of the measurement of atomic absorption will be recorded and then calculated to get the metal concentration in the sample solution.

2.4.Data analysis

Heavy metal content will be calculated based on the value of the regression concentration displayed on the AAS. Regression concentration is obtained based on the calibration curve regression value. The formula used to determine lead (Pb), manganese (Mn), copper (Cu) and cadmium (Cd) metals is as follows [23].

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 $\begin{array}{ll} \mbox{Metal content} & \mbox{mg/kg} = \ \underline{Creg \ x \ P \ x \ V} \\ \hline G \end{array}$

Information :

Creg = Unreadable concentration(mg/L)

P = Dilution factor

G = Sample Weight (Kg)

V = Volume of sample Solution (L)

3.Result and Discussion

The levels of Pb, Mn, Cd, Zn and Cu in the purple rice broken skin and purple rice stems occur in Tables 1 and 2.

Table 1. Data from the analysis of the metal content of Pb, Mn, Cd, Zn and Cu in purple rice broken

SKIN			
	Metal	Test Result	Quality Standard
		(mg/kg)	ANZECC (mg/kg)
	Pb	0.0256	50
	Mn	0.1046	5
	Cd	0.0147	1.5
	Zn	0.0832	200
	Cu	0.0116	65

Table 2. Data from the analysis of the metal content of Pb, Mn, Cd, Zn and Cu on purple rice stems

Μ	letal	Test Result	Quality Standard
		(mg/kg)	ANZECC (mg/kg)
	Pb	0.0196	50
I	Mn	0.3675	5
(Cd	0.0141	1.5
	Zn	0.2659	200
	Cu	0.0108	65

The results of the analysis of Pb, Mn, Cd, Zn and Cu metals in purple rice broken skin and in purple rice stems can be seen in Table 1 and Table 2. Measured metal lead (Pb) levels from purple rice samples is 0.0256 mg / kg for purple rice broken skin and 0.0196 mg / kg for purple rice stems. This value is still far below the quality standard set by the Australian and New Zealand Environment and Conservation (ANZECC), which is 50 mg / kg. Lead metal is a heavy metal whose existence is not expected in purple rice. The minimum amount of lead metal in the blood that can cause poisoning ranges from 60-100 micro grams per 100 ml of blood. Lead poisoning can cause inhibition of the activity of enzymes involved in the formation of haemoglobin, causing anemia, causing brain damage with symptoms of epilepsy, hallucinations, damage, cerebrum, and delirium, causing increased vascular permeability, in pregnant women can cause miscarriages, brain cells do not develop embryo, fetal death at birth, and gametotoxicity, whereas in men it can cause loss of libido and infertility [17] ... The levels of manganese metal (Mn) contained in the purple broken rice sample were 0.1046 mg / kgand in the purple rice stem sample was 0.3675 mg / kg. Both of these values are still below the ANZECC quality standard, which is 5 mg / kg. Manganese is an important metal ion for humans. Manganese is present as a coenzyme in several biological processes, which include macronutrient metabolism, bone formation, and free radical defense systems. Manganese is an important component in dozens of proteins and enzymes. The human body contains about 12 mg of manganese, mostly in bones. The remaining soft tissue is concentrated in the liver and kidneys [24]. In the human brain, manganese is bound in the form of metallo protein manganese [25].

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The cadmium metal content (Cd) contained in the sample of broken brown rice was 0.0147 mg / kg and in the sample of purple rice stem was 0.0141 mg / kg. Both of these values are still below the ANZECC quality standard, which is 1.5 mg / kg. Cadmium is one of the heavy metals that can pollute the environment. Cadmium is toxic to living things. Cadmium poisoning can be acute and chronic. Poisoning effects that can be caused in the form of lung disease, cancer, liver, high blood pressure, disorders of the kidney system and digestive glands and cause fragility of the bones [26].

The level of zinc metal (Zn) contained in the purple broken rice sample was 0.1046 mg / kg while in the purple rice stem sample was 0.2659 mg / kg. These values are still below the ANZECC quality standard, which is 200 mg / kg. Zinc (Zn) is an essential metal that humans need in small amounts <100 mg / day, which is very important for the body's metabolism. In proteins, zinc ions are often coordinated with amino acid side chains of aspartic acid, glutamic acid, cysteine and histidine. About 2-4 grams of zinc are distributed throughout the human body [27]. Most of the zinc is in the brain, muscles, bones, kidneys, and liver, with the highest concentration in the prostate and eye area [28].

Copper metal content (Cu) contained in the sample of broken rice purple skin is 0.0116 mg / kg and in the sample of purple rice stems is 0.0108 mg / kg. Both of these values are still below the ANZECC quality standard, which is 65 mg / kg. Human needs for copper are quite high, in adults need Cu 30 μ g / kg body weight, in children the amount of Cu needed 40 μ g / kg body weight, whereas in infants it takes 80 μ g / kg body weight. In humans, Cu metals are needed for oxidative enzyme systems such as the ascorbate oxidase enzyme, cystic C oxidase, polyphenol oxidase, amino oxidase and others. Cu metal is also needed by humans as a Cu-protein complex that has a function in the formation of haemoglobin, collagen, blood vessels and brain myelin The copper threshold in the blood according to WHO provisions is 800-1200 ppb in the body can cause cell membrane lesions or lipid oxidation which causes haemolysis and necrosis of liver cells [26].

The results of the analysis of Pb, Mn, Cd, Zn and Cu metals in purple rice broken skin and purple rice stem using AAS showed that the metal content of Pb, Mn, Cd and Cu was below the quality standard limits set by the Australian and New Zealand Environment and Conservation Council (ANZECC, 2000). Comparison of the metal content of Pb, Mn, Cd, Zn and Cu between the purple rice broken skin and purple rice stems can be observed in Figure 1. Purple rice broken skin and purple rice stem are agricultural products that are cultivated organically using biogas slug fertilizer. The process of fertilizing rice is carried out by administering 600 liters of biogas / ha slug. The sample taken from this study is a place that is not polluted with heavy metals. This location is safe from heavy metal pollution because water sources come directly from the mountains so there is little chance of being contaminated with heavy metal elements contained in water.



Fig 1. The metal content of Pb, Mn, Cd, Zn and Cu in purple rice broken skin and purple rice stalks

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The increase in heavy metal content in water that occurs is generally caused by the influx of industrial, mining, agricultural and domestic wastes that contain heavy metals. Industrial activities in general can trigger sources of heavy metal pollutants. Based on quality standards set by the Australian and New Zealand Environment and Conservation Council (ANZECC, 2000) the metal content of Pb, Mn, Cu and Cd in broken purple rice and purple rice straw is still far below the threshold or does not exceed the quality standard. If there is heavy metal found in the sample, the rice is broken skin and purple rice straw can become pollutants if the concentration exceeds the specified threshold.

Heavy metals usually enter the body of water and settle to the sediment due to three stages, namely the presence of rainfall, adsorption and absorption by aquatic organisms. Heavy metals in the aquatic environment will be absorbed by particles and then accumulated in the sediment. Heavy metals have the property of binding to other particles and organic matter and then settle to the bottom of the waters and unite with other sediments. This causes heavy metal concentrations in sediments to be usually higher than in waters. [29]

According to [30] surface water currents affect metal accumulation, the higher the current velocity the smaller the accumulation of metals in the sediment. Lead (Pb) is widely used in industry for example as a fuel additive, lead pigment in paint which is a major cause of increased levels of Pb in the environment [31]. The low content of lead (Pb) in purple rice broken skin and purple rice straw allegedly because this area is free of pollutants so the results of the metal content analysed are very low. According to [32] that if pollution occurs it is suspected that the main source of lead (Pb) comes from the residual combustion of motor vehicle exhaust gases and paint. So that metals in the waters will accumulate in the sediment.

The metal content of copper (Cu) which is low in purple rice broken skin and purple rice stem is still far from the quality standard threshold of 65 mg / kg. This is due to the fact that there is no community waste disposal activity. Copper that enters the environment can be derived from natural events and as a side effect of activities carried out by humans [33].

The same thing was also seen in the cadmium metal content (Cd) which showed that the observation of almost no accumulation of cadmium metal (Cd) in the purple rice samples broke the skin and purple rice stems. It is suspected that the presence of Cd is very low in purple rice samples that break the skin and purple rice stems. This is because it is influenced by the minimum content of the cadmium (Cd) element present in the field so that the accumulation of cadmium (Cd) in the sample becomes very small.

4. Conclusion

Based on the analysis of the metal content of Pb, Mn, Cd, Zn and Cu in milled rice and purple rice stem indicate that the metal content is still below the quality standards set by the Australian and New Zealand Environment and Conservation Council (ANZECC, 2000). Then it can be concluded that the purple rice sample is milled rice and the purple rice stem sample is free from metal contamination that can interfere with health.

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