STUDY OF HEAVY METALS IN CASHEW AND SOURSOP LEAVES ON BANGKA ISLAND

Ratna Sari Hasibuan[1*], Asmanur Jannah [2], Adhy Pradana[3],Muhammad Waliuddin Zuhdi[4]

1Faculty of Forestry, University of Nusa Bangsa Bogor, Tanah Sereal, Bogor Indonesia
2Faculty of Agriculture, University of Nusa Bangsa Bogor, Tanah Sereal, Bogor Indonesia
3PT. IMDEX Ltd. Jl.Raya Cirendeu No 38 Ciputat Tangerang, Indonesia
4Faculty of Environmental Engineering Sepuluh November Institute of Technology, Indonesia

**Corresponding author: ratnasylva@gmail.com*

Abstract. *The largest tin source in Indonesia is located in Bangka Island which is managed by PT. Timah Tbk and also by the community. One of the problems in the ex-mining area on Bangka Island is the large amount of tailings waste which still contains heavy metals. The purpose of this study is to analyze the heavy metals Sn, Cu, Cd, Pb, and Hg in Cashew and Soursop leaves in the reclamation area of the former tin mining site in Belilik Village, Namang District, Bangka Tengah Regency. The research included taking samples of Cashew and Soursop leaves, then digesting them for further analysis of their heavy metal content using Atomic Absorption Spectroscopy (AAS). The level of heavy metal as much as Pb (20,7598 mg/kg), Hg (2,3712 mg/kg), Sn (615,1274 mg/kg) are contained in Cashew leaf samples, and the level of heavy metal Hg (0,2507 mg/kg), Sn (443.1026 mg/kg) in the Soursop leaf sample on the level above the Maximum Limit of Heavy Metal Contamination in Vegetables and Fruits according to SNI 7387: 2009, BPOM Regulation No. 5 of 2018, hence it is not suitable for consumption due to it is a danger to health.*

Keywords: *heavy metals, reclamations, Cashew, Soursop*

1. INTRODUCTION

Indonesia is a country that has the fourth-largest tin deposit in the world after China, the United States, and Peru, amounting to 900,000 tones (Irawan et al. 2015). Among other tin-producing area, Bangka Island is the largest tin-producing island in Indonesia. Bangka Island, which covers an area of 1,294,050 ha, as much as 27.56 percent of the island's land is a tin mining concession area. The largest mining area on the island is controlled by PT Timah Tbk. Also, there are some other private smelters and traditional miners who are often referred to as Unconventional Mining whose mining locations are spread across the land and sea of Bangka Belitung (Inonu 2008). The main mineral that forms tin is cassiterite (SnO_2), with the carrier rock is granite (Noer, 1998).

One of the problems in ex-mining land on the islands of Bangka and Belitung is a large amount of tailings waste from the tin mining that covers the landscape both inside and outside the mining site. According to Dariah et al. (2010), this tailings waste has a very low carrying capacity for flora and fauna, because it has a soil texture dominated by quartz sand (> 90%), with organic C <1%, so the ability to hold nutrients and water is very low. The technical reclamation planning effort, the utilization of tin mining materials, is linked to the re-vegetation plan so that the reclamation results are as expected and can be used for agricultural cultivation (Iskandar et al. 2012). However, according to Sukarman and Gani (2017) research, ex-tin mining tailings on Bangka and Belitung Islands are characterized by coarse texture and very low nutrient content, the upper soil is relatively better characterized by medium to slightly coarse texture, and organic C content and nutrients higher than other parts, and heavy metals were found, namely Cu, Pb, Cd, and Hg.

In 2017, reclamation was carried out at the ex-mining site of Belilik Village, Namang District, Central Bangka Regency. The ex-mining land is planted with agricultural crops such as Cashew (*Anacardium occidentale*) and Soursop (*Annona muricata L.*) which the community will consume, especially fruit and leaves. The presence of heavy metals in the soil has implications for the transport of these heavy metals in plant tissues, especially if heavy metals are present in dissolved form, if the plants that bind them are food plants, heavy metal pollution will be more dangerous for humans. Plants need metal minerals for their growth, which are used for respiration, the formation of pigment or leaf green matter, as cofactors, and many more. But there are some heavy metals whose presence in the body has no function. So that even a small amount of it can harm our bodies, for example, Pb and Cd metals. Heavy metals are easily dissolved by water and heating. Bearing that in mind, heavy metal tracing must be carried out for the sake of safety for consumption (Gama, 2017). Based on the description above, research was carried out on the analysis of heavy metals in agricultural crops in reclaimed land for the former tin mining of Bangka Belitung, in this case on Cashew (*Anacardium occidentale*) and Soursop (*Annona muricata L.*). Cashew Tree produces Cashew Nuts at a quite expensive price of around Rp. 35,000 / kg. While soursop produces soursop fruit and soursop leaves which can prevent cancer (Pertiwi w et al, 2020).

The purpose of this study is to analyze the heavy metals Sn, Cu, Cd, Pb, and Hg in Cashew (*Anacardium occidentale*) and Soursop (*Annona muricata L.*) leaves planted in the reclamation area of former tin mining in Belilik Village, Namang District, Central Bangka Regency Bangka Belitung.

2. LITERATURE REVIEW

2.1. Heavy Metals

After the tin mining activity is declared complete, the company is obliged to carry out reclamation activities as stated in the Mining Business License it owns. This reclamation aims to improve habitat and biodiversity so that it resembles the land conditions before mining. The reclamation stages are carried out in the form of: (1) surveying the location of the reclamation plan, (2) disseminating reclamation activities, (3) land arrangement, (4) planting, and (5) maintenance (PT Timah, 2012). Unlike in the case of mining companies, In conventional miners (people's mines) do not carry out reclamation of their former mining areas. The In conventional Miners left the former tin mining area with an irregular landscape and then the in conventional miners looked for other land to be mined. Ex-mining land sometimes still contains heavy metals, especially abandoned tailings. Heavy metals can enter the environment in various ways, such as weathering of rocks containing heavy metals, volcanic activity, and disposal of waste originating from mining, industry and transportation. The main source of heavy metal contaminants comes from air and water that pollutes the soil. Furthermore, all plants that grow on contaminated soil will accumulate these metals. After that, livestock will harvest the heavy metals in the plants they eat. In the end, humans will be contaminated with these metals from four main sources, namely the air that is inhaled while breathing, drinking water, plants, and livestock that are consumed (Notohadiprawiro, 2006)

Some examples of heavy metals that are toxic to humans include arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn). Metal toxicities in humans which can cause mainly detoxification and excretion tissue damage (liver and kidney). Some metals have carcinogenic (cancer-forming) and teratogenic properties (Darmono, 2002).

2.2. Leaf analysis

Leaf analysis has been used as a reference in diagnosing nutrient problems and as a basis for fertilization recommendations for fruit crops in various countries. Leaves have the best correlation between nutrient concentration in leaves and yield and growth. The difference in leaf age will affect the nutrient content in it. The concentration of N, P, and K leaves decreased with increasing age. It is more practical to analyze plant tissue to determine nutrient status in plants than other methods. The plant tissue that is generally used for nutrient analysis is leaves, because leaves are a very active site for photosynthesis and other metabolic processes. Leaves are also a storage place for carbohydrates and minerals. (Liferdi, 2009).

Food products that are produced, imported and circulated in the territory of Indonesia must meet the requirements for food safety, quality and nutrition, including the requirements for the maximum limit of heavy metal contamination. Based on the provisions of the Food and Drug Supervisory Agency (BPOM) and the National Standardization Agency for Indonesia (BSN) in 2009, the limit of cadmium (Cd) and lead (Pb) metal contamination in food, especially fruit and vegetable products, is 0.2 mg / kg and 0 , 5 mg / kg. Meanwhile, the maximum limit for tin (Sn) contamination in food products processed by heat processing and packaged in cans is 250 mg / kg (BPOM, 2009; BSN, 2009).

Atomic Absorption Spectrophotometer (AAS) is a technique often used for heavy metal analysis. The working principle of SSA is the evaporation of the sample solution, then the metal contained therein is converted into free atoms. The atom absorbs radiation from the light source emitted from a hollow cathode lamp containing the element to be determined. Much radiation absorption is then measured at a specific wavelength depending on the type of metal (Darmono, 2002).

3. RESEARCH METHODS/METHODOLOGY

3.1. Time and Place

This research was conducted from April to July 2019, located in Belilik Village, Namang District, Central Bangka Regency (Figure 1 and 2), with coordinates 10020'- 30015 'LS and 100 40 50' - 100 80 18 'East Longitude, Chemistry Laboratory, University of Nusa Bangsa. and the Joint Laboratory of the Bogor Agricultural Institute.

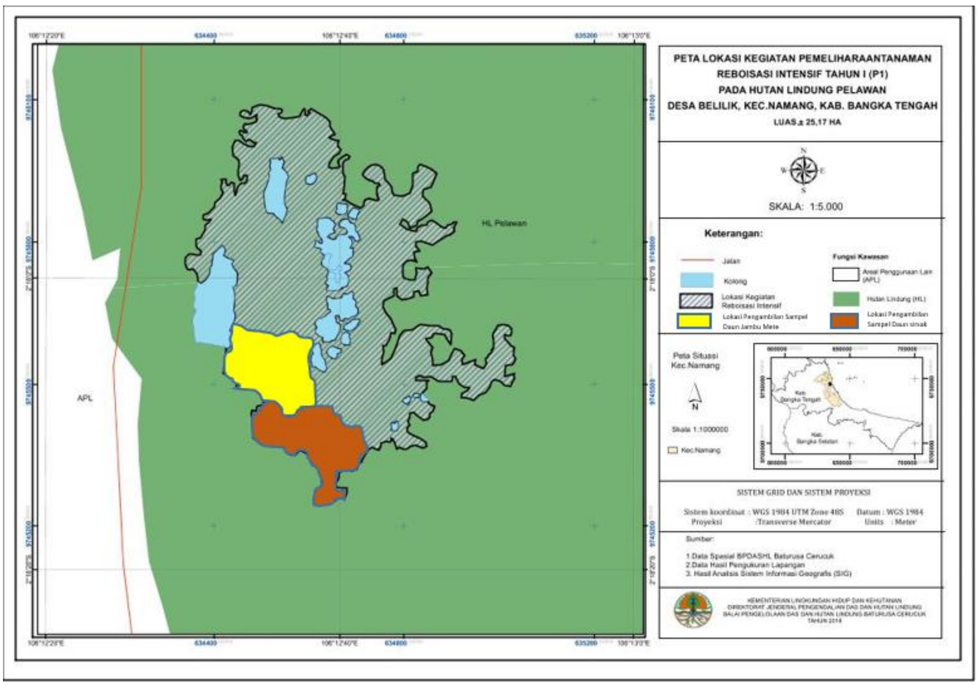

Figure 1. Map of Sampling Location

Figure 2. Location of the land reclamation

3.2. Materials and Tools

The materials and tools used in the study consisted of Cashew leaves, Soursop leaves, aquadest, concentrated $HCLO_4$, concentrated HNO_3, scissors, paper envelopes, trays, ovens, blenders, hotplates, analytical scales, desiccators, glassware, Atomic Absorption Spectroscopy Instruments (SSA) brand Shimadzu AA-7000 and Atomizer Mercury Vaporizer Unit (MVU) from Shimadzu brand.

3.3. Research Procedures

a. Sampling

The leaves used as samples were cashew leaves and soursop leaves which were about 6 months old. Each individual sampled was selected 2% of the total population (6050 trees), namely 121 trees and 1 leaf was taken with the location for the shoot, middle, and bottom (figure 3) using scissors cut on the petiole and put into a large envelope and given a code based on individual samples and the location of the leaf collection (Lamanda, 2018).

(A)

(B)

Figure 3. Sampling-based on the location of Cashew (A) and Soursop (B) leaves

b. Sample Preparation

Samples were cleaned and dried at 80 ° C for 12 hours, then weighed and after that stored in a desiccator. Drying was repeated until a constant weight was obtained and then weighed. Then the sample is crushed in a blender and stored in a clean, dry, and tightly closed container (Setiawan, 2013).

c. Digestion

The sample powder was weighed as much as 2 grams then put into the Erlenmeyer glass pyrex and added 5 ml of concentrated HNO_3 and 0.5 ml of concentrated $HClO_4$, then the Erlenmeyer was heated on a hotplate for 30 minutes in an acid chamber until the acid solution evaporated and dried, after which the Erlenmeyer was cooled. The sample solution was transferred to a 50 ml volumetric flask using a glass funnel covered with filter paper and dropped with distilled water until the volume of the solution was exactly 50 ml. The sample solution is then poured into a plastic bottle and ready to be analyzed for its heavy metal content (Setiawan, 2013).

d. Analysis by Atomic Absorption Spectrophotometry (AAS)

SSA Tool Shimadzu AA-7000 set with different wavelength and lamp cathode for Sn 235.5; Cu 324.8 nm; Cd 228.8; Pb 283.3 nm; and Hg 253.7 nm. The adjustable acetylene flow rate is 1.8-3 L / minute; 0.2 nm gap width, 10 µm cathode lamp current (Lestari, 2015).

4. RESULTS AND DISCUSSION

The results of the analysis of heavy metal levels using Atomic Absorption Spectrophotometry (AAS) for Cu, Cd, Pb, Hg, and Sn levels in samples of Cashew and Soursop Leaves with AAS can be seen in Figures 3 to 6. Besides that, there are also heavy metal hazard levels Cu, Cd, Pb, Hg, and Sn in fruit by the Maximum Limit for Heavy Metal Contamination, namely the maximum concentration of heavy metals that are legally permitted or known as acceptable concentrations in agricultural products expressed in milligrams of heavy metal per kilogram of agricultural products according to SNI 7387: 2009 (National Standardization Agency for Indonesia. 2009), BPOM Regulation No. 5/2018, and Regulation and Recommendation for Heavy Metals by the Food and Drugs (Indonesian Food and Drug Administration Agency. 2009).

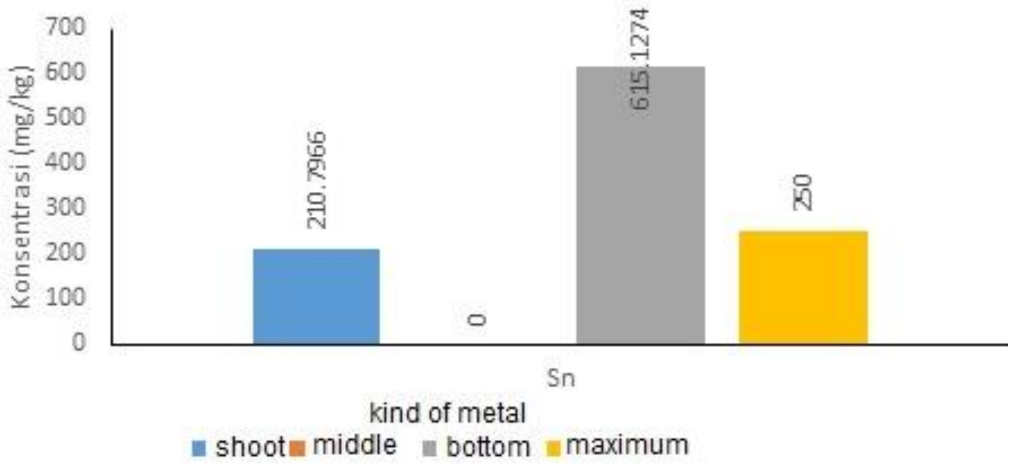

Figure 3. Heavy Metal Sn Content on Cashew Leaves

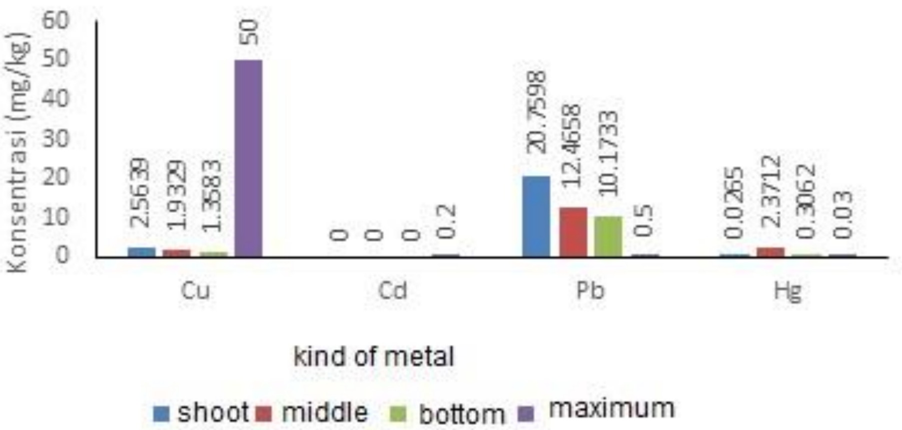

Figure 4. Heavy Metal Content of Cu, Cd, Pb, and Hg on Cashew Leaves

In Figures 3 and 4, the sample of cashew leaves is positive for heavy metals Cu, Pb, Hg, and Sn. In heavy metal Cu, levels were still below the specified quality standard limit, namely 50 mg/kg, and experienced a tendency, namely a decrease in heavy metal content from the top leaves of the trees to the lower leaves of the trees. Heavy metal levels of Pb shoot (20.7598 mg / kg), middle (12.4658 mg / kg) and lower (10.1733mg / kg). Heavy metal Pb tends to decrease in heavy metal content from the top of the tree leaves to the lower leaves of the tree, but its levels exceed the predetermined quality standard, namely 0.5 mg/kg. Heavy metal levels of Hg shoot (0.0265 mg / kg), middle (2.3712 mg / kg) and lower (0.3062 mg / kg). Heavy metal levels of Sn shoot (201.7966 mg / kg), and lower (615.1274 mg / kg). Heavy metals Hg and Sn, their levels exceed the predetermined quality standard, namely 0.03 mg/kg for Hg and 250 mg/kg for Sn, and do not show a tendency to decrease in heavy metal levels from the leaves of the tree shoots (top) to the leaves the bottom tree. Heavy metal Cd was not found in cashew leaf samples which were suspected because of the high AAS limit of detection (LOD) used (0.06 mg/kg).

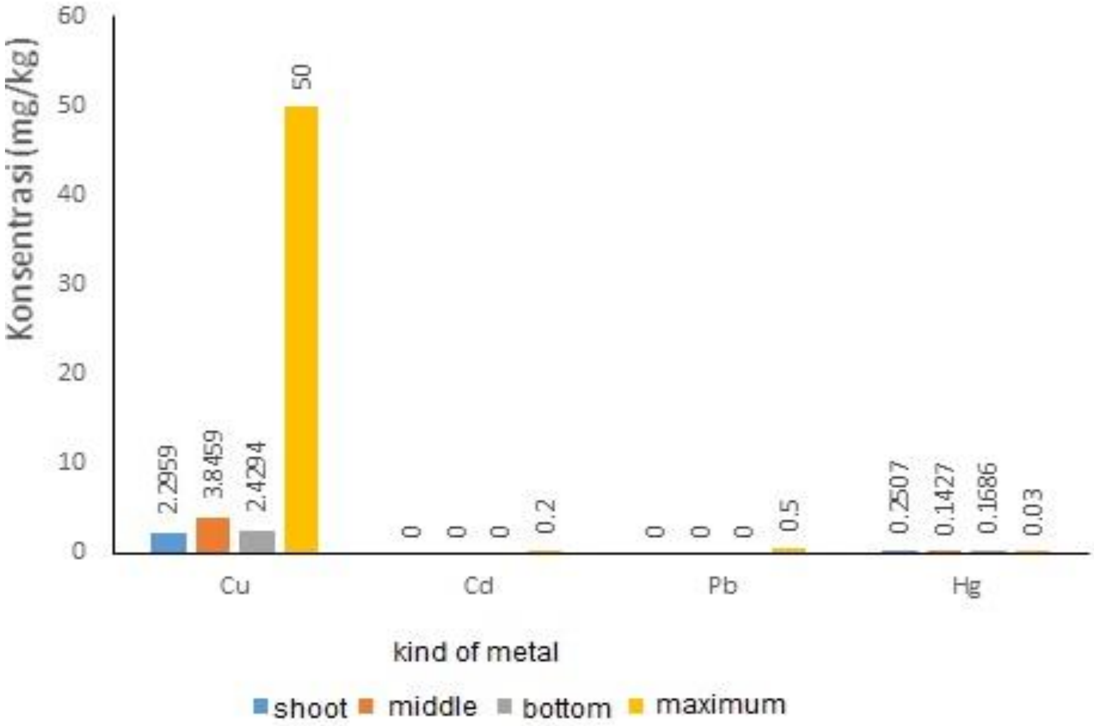

Figure 5. Heavy Metal Content of Cu, Cd, Pb, and Hg in Soursop Leaves

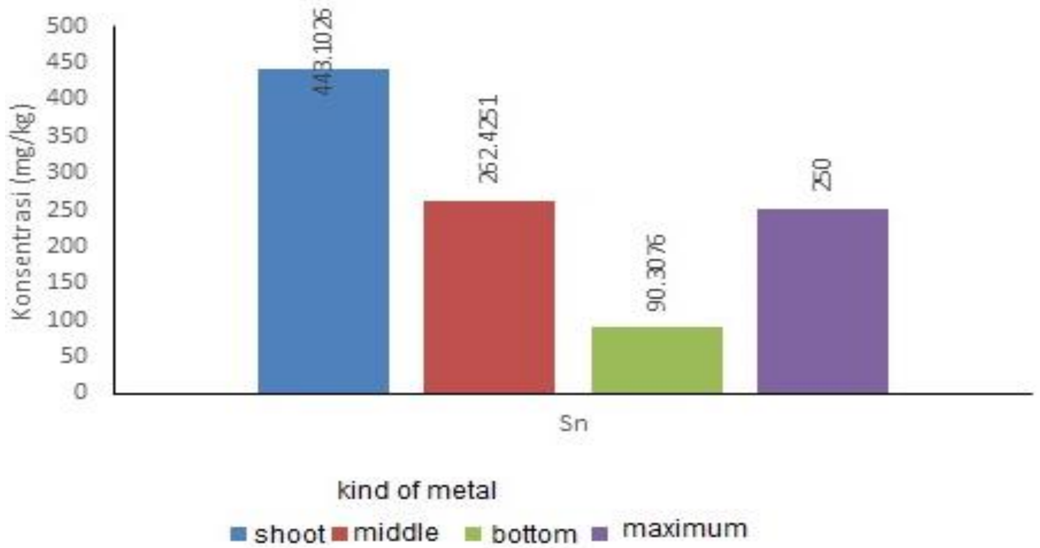

Figure 6. Heavy Metal Sn Content in Soursop Leaves

Soursop leaf samples, positive for heavy metals Cu, Hg, and Sn. Heavy metal Cu, levels are still below the specified quality standard limit, while heavy metal Hg levels have exceeded the predetermined quality standard limit, but neither of them has a tendency to decrease in levels from the top of the tree leaves (shoots) to the lower leaves of the tree. Heavy metal Sn tends to decrease in content from the upper leaves (shoots) to the lower leaves of the trees, and samples that exceed the predetermined quality standard are the upper and middle leaves.

The tendency of decreasing heavy metal content from the upper leaves to the lower leaves is by following what was stated by Liferdi (2009), namely, the difference in leaf age will affect the nutrient content in it, the leaf mineral concentration has decreased with age. This is related to changes in the function of the leaf as a sink and source. Young leaves function as sinks, so they have to import mineral nutrients and photosynthetic from other organs, which serve as a source for growth and development in large quantities. On the other hand, mature leaves function as a source, so that they can fulfill their own needs and export mineral nutrients and photosynthetic to other organs that require sinks (Liferdi, 2009).

D. High levels of Sn in Cashew Leaves and Soursop Leaves and beyond the predetermined limit (250 mg/kg) occur because of the high levels of Sn in ex-mining soil (227 mg/kg) (Sukarman 2016). The Sn content in cashew leaves was 210.7966 mg/kg in the upper leaves of the trees and 615.1274 mg/kg in the lower cashew leaves of the trees, and in the Soursop leaves, 443.1026 mg/kg in the leaves of the upper trees; 262,4251 mg/kg in the middle leaves of the tree; and 90.3076 mg/kg of lower leaves. High levels of Pb metal because Pb metal is a complex mineral between copper-iron-tin-sulfur and cylindrite ($PbSn_4FeSb_2S_{14}$) (Satya, 2011). High levels of Hg metal occur due to a series of chemical reactions and complex physical transformations in the cycle in the atmosphere, soil, and water. Hg metal undergoes physical transformations such as leaching, erosion, and evaporation and undergoes biochemical transformations such as methylation and photochemical reduction. Mobilization of Hg can occur through exchange reactions with ligands containing sulfur and chloride ions, resulting in an increase in the solubility of Hg in soil solution (Putranto, 2011). Therefore, Cashew and Soursop Leave planted in the former tin mining area of Belilik Village, Namang District, Central Bangka Regency are not suitable for consumption because they can cause health problems in the body such as triggering the growth of cancer cells, local irritation of the digestive tract, obstructive pulmonary disease, emphysema, renal tubular damage, and bone deformation (Godt et al, 2006). This occurs because of the indestructible nature of heavy metals (Darmono, 2002).

CONCLUSION

Heavy metals found in the cashew leaf samples were Cu, Pb, Hg, and Sn, while those in the soursop leaf samples were Cu, Hg, and Sn. Heavy metal levels of Pb, Hg, Sn in cashew leaf samples and levels of heavy metal Hg, Sn in soursop leaf samples have the levels above the threshold limit value according to SNI 7387: 2009, BPOM Regulation No. 5 of 2018, making it inconsumable due to it endangers health.

REFERENCES

[BSN] Badan Standardisasi Nasional. 2009. *SNI 7387:2009: Batas maksimum cemaran logam berat dalam pangan.* Jakarta: Badan Standardisasi Nasional.

[BPOM] Badan Pengawas Obat dan Makanan Republik Indonesia. 2009. *Peraturan Kepala Badan Pengawas Obat dan Makanan Republik Indonesia Nomor HK.00.06.1.52.4011 tentang penetapan batas maksimum cemaran mikroba dan kimia dalam makanan*. Jakarta: Badan Pengawas Obat dan Makanan Republik Indonesia.

Dariah A, Abdurachman A, Subardja D. 2010. *Reklamasi lahan eks-penambangan untuk perluasan areal pertanian.* Jurnal Sumberdaya Lahan Vol. 4 No. 1 Juli 2010: 1-12..

Darmono. 2002. *Logam dalam sistem biologi makhluk hidup*. Jakarta: UI Press

Gama, S. I. 2017. *Analisis Logam Berat dalam Daun Sirsak dan Daun Beluntas.* Samarinda: Universitas Mulawarman.

Godt, J., Scheidig, F., Grosse-Siestrup, C., Esche, V., Brandenburg, P., Reich, A., dan Groneberg D. A. 2006. *The toxicity of cadmium and resulting hazards for human health*.

Inonu I. 2008. *Pengelolaan lahan tailing timah di pulau Bangka: penelitian yang telah dilakukan dan prospek ke depan*. Program Studi Agroteknologi FPPB, Universitas Bangka Belitung.

Irawan RR, Sumarwan U, Suhardjo B, Djohar S. 2014. *Strategic model of tin mining industry in indonesia (Case study of Bangka Belitung Province).* International Journal of Business and Management Review Vol.2, No.3, pp.48-58, July 2014

Iskandar dan Soebagyo. 1993. *Pedoman Reklamasi Lahan Bakas Tambang*. Jakarta : Departemen Pertambangan dan Energi, Ditjen Pertambangan Umum.

Iskandar, Suwardi, Suryaningtyas DT. 2012. *Reklamasi lahanlahan bekas tambang: beberapa permasalahan terkait sifatsifat tanah dan solusinya*. Kementerian Pertanian: Badan Penelitian dan Pengembangan Pertanian,.

Lamanda, S. A. 2018. *Analisis Morfofisiologis Jati* (*Tectona grandis* Linn. F.). Makassar: Universitas Hasanuddin

Lestari, W. F. 2015. *Analisis Kadar Logam Merkuri (Hg) dan Timbal (Pb) pada Teripang Terung (Phylloporus sp) Asal Pantai Kenjeran Surabaya Secara Spektroskopi Serapan Atom (SSA).* Malang : UIN Maulana Malik Ibrahim.

Liferdi, L. 2009. *Analisis Jaringan Daun sebagai Alat untuk Menentukan Status Hara Fosfor pada Tanaman Manggis.* Solok: Balai Penelitian Tanaman Buah Tropika

Noer A. 1998. Potensi dan prospek investasi di sektor pertambangan dan energi 1998-1999 Dalam Nazaruddin *et al.* (eds). Departemen Pertambangan dan Energi. Yayasan Krida Caraka Bhumi. Jakarta.

Notohadiprawiro.2006. *Pengelolaan Kesuburan Tanah dan Peningkatan Efisiensi Pemupukan*. http://soil.faperta.ugm.ac.id/tj/1981/1984%20penge .pdf. Diakses tanggal 16 Desember 2020

Pertiwi W, Dessy Arisanty , Linosefa. 2020. Pengaruh Ekstrak Daun Sirsak (Annona muricata lin) Terhadap Viabilitas Cell Line Kanker Payudara T47D Secara In Vitro. Jurnal Kesehatan Andalas. http://jurnal.fk.unand.ac.id/index.php/jka/article/download/1173/1059

Putranto. 2011. *Pencemaran Logam Berat Merkuri (Hg) Pada Airtanah*.

PT Timah. 2012. Laporan Tahunan. PT Timah. Pangkalpinang

Satya, Awalina. 2011 . *Biokumulasi Ion Logam Timbal (Pb) dan Cadmium (Cd) Dalam Fitoplankton Pada Perairan Situ Di Sekitar Kabupaten Bogor*

Setiawan, H. 2013. *Akumulasi dan Distribusi Logam Berat pada Vegetasi Mangrove di Perairan Pesisir Sulawesi Selatan.* Makassar : Balai Penelitian Kehutanan Makassar

Sukarman, Ritung S, Suryani E, Anda M. 2016. *Pedoman Pengamatan Tanah di Lapangan.* Bogor: Badan Penelitian dan Pengembangan Pertanian, Kementerian Pertanian.

Sukarman dan Gani. 2017. Lahan Bekas Tambang Timah di Pulau Bangka dan Belitung, Indonesia dan Kesesuaiannya untuk Komoditas Pertanian. Jurnal Tanah dan Iklim Vol. 41 No. 2, Desember 2017: 101-112