

Eucalyptus Leaves as Potential Indicators of Gold Mine in Indonesia

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Abstract: Eucalyptus is a plant that is able to absorb gold (Au) particles from the soil and store them in the leaves. Eucalyptus roots have the ability to penetrate the soil of the calcrete zone, which is rich in the mineral calcium (Ca). Calcium is a chemical element with the symbol Ca and atomic number 20. As an alkaline earth metal, calcium is a reactive metal that forms a dark oxide-nitride layer when exposed to air, and contains Au particles as impurities, making this plant a potential natural indicator (biogeochemical) of potential Au metal mining. The Au content in eucalyptus leaves can be determined by using the XRF (X-Ray Fluorescence) instrumentation material analysis method for qualitative analysis and AAS (Atomic Absorption Spectroscopy) for quantitative results. The form of XRF characterization of the intensity versus energy spectrum of certain elements from the XRF analysis results obtained is a spectrum with a peak power of 9.731 keV which indicates the presence of Au metal in the sample. The results obtained qualitatively are the Au metal content in the eucalyptus leaf sample of $(9.0 \pm 0.5) 10^{-1}$ ppm. However, the Au metal content in each leaf sample was different. This provides information that Eucalyptus from different plants has the potential to be a biogeochemical indicator of potential Au metal mining in Indonesia.

Keywords: Eucalyptus; calcrete; X-Ray Fluorescence; Atomic Absorption Spectroscopy.

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Introduction

Indonesia is a country with a large area and has abundant natural resources. Geologically, Indonesia is located at the confluence of three plates which causes the emergence of a series of volcanoes and will automatically support plant growth and is rich in metal mineral resources. These metal mineral resources have a fairly important role for human life and have various types, ranging from gold, diamond, tin, sulfur and others (Alamsyah, 2006). Gold is one of the most desirable metallic minerals because it has special characteristics that other metals do not have. Some types of plants such as *Pinus radiata*, *Cassinia aculeata* and Eucalyptus are good indicators of biogeochemistry used to identify gold. However Eucalyptus shows the highest concentration of Au compared to other types of

plants (Arne, et al., 1999). The results of research by Lintern et al., (2013) identified the presence of gold particles in Eucalyptus plants that grow in Australia so that this plant has the potential to be a biogeochemical indicator in gold metal exploration. Eucalyptus requires more calcium nutrition to meet the needs of its life. Plants do not have the ability to choose certain elements in the absorption so that gold particles as impurities are also absorbed. The results obtained are gold metal nanoparticles that are mostly found in leaves compared to twigs, branches and wood.

Minerals are solids of homogeneous, non-organic, chemical compounds that are regular in shape (crystal system) and occur naturally. While gold is a precious metal with atomic number 79 (in the periodic table) with the symbol Au. Gold (Au) has an FCC-shaped crystal structure with a unit cell consisting of one lattice point at

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each corner and one lattice point on each side of the cube (Gardea-Torresdey, et al., 2002). Au metal is found in every metallic mineral rock in various sizes, ranging from atomic size (picometers), nanometers, namely colloidal gold, and even large ones that are visible to the naked eye. According to Lintern (2013) gold particles are commonly found in calcrete (calcium rich) soils, which are soils that are rich in metallic minerals. The area is dominated by carbonate minerals such as calcite ($CaCO_3$) and there is an Au impurity mineral. There is one plant that requires high calcium as a nutrient so that the root system of the plant is able to reach the area, namely the Eucalyptus plant.

Eucalyptus is a plant native to the Australian continent. Indonesia is one of the countries in the Asia Pacific that has a wide Eucalyptus distribution. Indonesia's tropical climate makes Eucalyptus to grow faster because the tree can adapt to a humid tropical environment with a dry season of no more than 6 months (Morris, 2003). Species belonging to the Eucalyptus genus have the shape of a tree with a high main trunk, however, some species in this genus are in the form of woody shrubs (Wills, et al., 2004). The genus Eucalyptus is one of the genera that is widely cultivated in the form of plantation forests in various parts of the world. The trees can be used as ornaments, as shade trees, soil conservation, carpentry wood and pulp or pulp (Old, et al., 2003). Eucalyptus has a variety of species that are able to adapt to different environments. The adaptability of Eucalyptus can be seen from the anatomy of the leaves in each species. The larger the vascular tissue of the leaves, the more adaptable it is to diverse environmental conditions (Ali, et al., 2009). Two types of Eucalyptus species that grow in Indonesia are *Eucalyptus pellita* as a pure species, and *Eucalyptus* hybrid as the result of inter-specific crossing between two Eucalyptus species.

Eucalyptus plants need calcium as a nutrient. These plants have the ability to accelerate the dissolution of metals in the rhizosphere. Metal uptake by roots is determined, among other things, by permeability, transpiration and root pressure as well as the presence of an enhanced metal uptake system (Ida and Purwiyanto, 2013). The results of research conducted in Freddo, Australia from samples of Eucalyptus trees with a height of more than 10 meters have proven that gold metal content dominates in several plant parts such as leaves, twigs, bark, and surrounding soil. Figure 1 provides information on the results of the study with a land area of about 1.3 km, indicating that the area with the highest content of Au metal is in the living area of the Eucalyptus plant and it is known that the highest content is in the leaf sample, which is up to 90 ppb (Koswandy and Ramadhania, 2016).

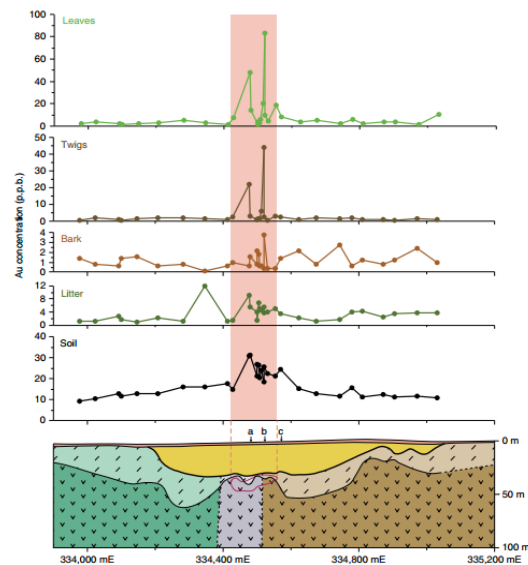


Figure 1. Graph of gold mineral content in Eucalyptus body parts (Lintern et al., 2013).

AS is a tool used in analytical methods for the determination of metallic elements and metalloids based on the absorption of radiation absorption by free atoms. AAS is a quantitative analysis technique of elements that is widely used in various fields because of the procedure is selective, specific, relatively cheap, high sensitivity (ppm), which can easily create a matrix that conforms to standards, and the analysis time is very fast and easy to do (Boss and Fredeen, 1997). The AAS method is based on the absorption of light by atoms. The atoms absorb the light at certain wavelengths, depending on the properties of the elements. The absorption process occurs because a beam of light with a certain wavelength passes through an absorbing medium consisting of atoms.

In this study, various types of eucalyptus plants will be investigated. The part of the eucalyptus plant that will be studied is the leaf part. The age of different plants will also be investigated and characterized using XRF and AAS spectroscopy.

Method

Tools and materials used in this study includes: Eucalyptus leaves, Gold Standard Solution 1000 ppm, Hot Plate, Aquademineral, HCL Solution, Filter Paper 42, Volumetric flask, Erlenmayer, Stirrer, plastic bags, ghoni Sack, A set of XRF devices (RIGAKU NEX QC+QuanTEZ), and A set of AAS devices (Perkin-Elmer 3110). The details of characterization showed in Table 1.

The first research stage is the preparation of samples (leaves) taken from several regions in Indonesia, namely Wonogiri, and Riau. Wonogiri is an area where Eucalyptus is preserved by the government and managed as a part of tree breeding program so that

each tree has complete genetic information and the annual tree growth, such as trunk diameter. The steps in sampling are as follows: the types of leaves taken were *E. pellita* and *Eucalyptus* hybrid. The age of the trees sampled are < 15 years for the second-generation breeding (F2) and > 20 years for the first-generation (F1), with the detail number of trees sampled as shown in Table 1.

Leaves are taken from several different points of position (3 - 5 points) throughout the trees. The leaves are taken along with the branches. The leaves are separated from the twigs, and then placed in gunny sacks to avoid the leaves-decay.

Table 1. Sampling

Age (Years)	Type	Number of trees	Leaf weight (gr)	Origin
<15	<i>E.pellita</i>	3	600	Wonogiri
<15	<i>E.hybrid</i>	1	200	Wonogiri
>20	<i>E.pellita</i>	3	600	Wonogiri
>20	<i>E.hybrid</i>	1	200	Wonogiri

After the leaves were collected, the samples were grouped according to plant type species and cleaned with deionized water to sterilize them from dirt. Furthermore, the leaves were dried in an oven for 48 hours at a temperature of 450 °C to remove the water content in the sample. Then the leaves were mashed using a disk mill / blender to a powder with a size of ~10 m to ~250 m. After the sample becomes powder, the next preparation can be done, namely preparation for XRF and AAS.

Sample preparation for XRF analysis is divided into two, namely "cup method" and "press method" (Figure 1). The difference between the two methods is in the form of the results to be tested. For the cup method, the sample is placed in a small 2.5 cm diameter cup with a POLYPROPYLENE X-Ray Film Roll base, then pressurized so that the bottom surface of the sample is very tight. As for the press method, the sample output is in the form of pellets weighing 4 grams. Samples ready for analysis with XRF instruments.

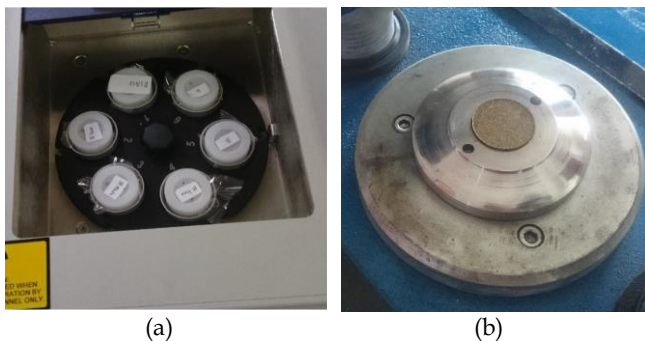
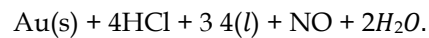


Figure 2. (a) Sample preparation by cup method and (b) Press sample preparation for XRF.

Sample preparation for AAS analysis was carried out using the wet digestion method (Figure 2), which is the process of destroying organic matter by chemical means. Powder sample weighting 2 grams was dissolved with 10 ml 3 in Erlenmeyer and left overnight at room temperature to destroy organic matter in the sample. Then it was added Aqua Regia (*HNO3* + *HCl* in a ratio of 1: 4) and heated using a hotplate at a temperature of 80 °C for 2 hours. Chemically it can be written:



The dissolved sample was then diluted with an ion-free solution, namely aquademineral and filtered with Filter Paper 42 in a 25 ml volumetric flask. The solution in a 25 ml volumetric flask was ready to be analyzed with the AAS instrument.

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Figure 3. Sample preparation by wet digestion method or chemical method

Results and Discussion

Qualitative Analysis

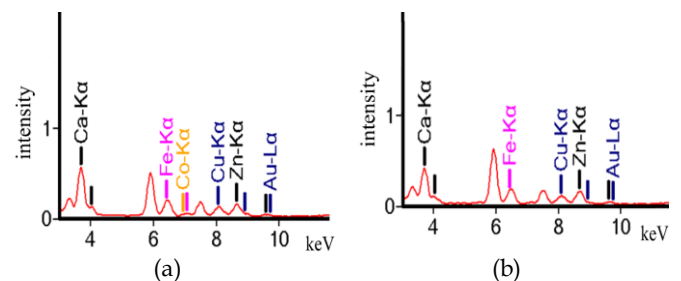


Figure 4. Spectrum of the results of the XRF analysis of Eucalyptus leaves. (a) Eucalyptus Hybrid F1 and (b) Eucalyptus Pellita F2

Figure 4 is a spectrum of intensity versus energy characteristic of certain elements from the results of XRF analysis. The presence of a peak indicates a certain

element is detected. Energy is obtained from the de-excitation of electrons (the transition of electrons from a higher energy level to a lower energy level) due to the vacancy of electrons in certain shells and the X-rays that are fired. The de-excitation process produces characteristic X-rays whose values are different for each metal element, then these characteristic X-rays are used as a reference to determine certain elements by XRF instrumentation.

In XRF instrumentation, there is available a data base on the energy of a certain element, so there is no need to make a standard. For example, Au metal has an energy of 9.731 keV, so that if there is a peak with that energy, the XRF instrument detects the presence of Au metal.

In Figure 4 there is no significant difference between the Au peaks in *Eucalyptus* hybrid F1 and *E.pellita* F2. The difference is seen only in the peak height of the Ca element of the two samples.

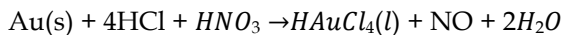
Table 2. Experimental results of the XRF method of *Eucalyptus pellita* leaves

Component	Result	Unit	Statistical Error	Detection limit	Quantitation limit
Au	2.36	Mass%	0.0009	0.0123	0.0368
Ag	ND	Mass%	-	-	-
Cu	2.96	Mass%	0.0014	0.0029	0.0088
Ca	82.8	Mass%	0.0669	0.0433	0.130
Zn	1.91	Mass%	0.0012	0.0061	0.0184
Fe	10.0	Mass%	0.0048	0.0056	0.0168
Co	ND	Mass%	-	-	-

Table 2 shows that the eucalyptus leaf sample contained several metal elements, including Au, Cu, Ca, Zn, and Fe. The element Ca dominates in the sample because it is the main food for Eucalyptus plants, and the highest peak is in the element Ca. Some noble metals such as Ag are not found in the leaves because Ag is a metal that is difficult to dissolve in hydrochloric acid so that the roots of Eucalyptus are unable to absorb it. While Au can be a solution, namely Au³⁺, due to several factors including its interaction with hydrochloric acid.

Quantitative analysis

Quantitative analysis was carried out to determine the elemental content of Au in the sample. The instrumentation used is AAS, so the sample must be in the form of a solution. The leaf sample that has been in powder form is added with Aqua Regia, namely HCl + HNO₃ with a ratio of 4: 1. Chemically, the process can be written as:



In contrast to XRF, the AAS Analysis method requires a standard solution to determine the elemental content in the sample. Then a standard solution of Au was made with a concentration of (0, 5, 10, 15, 20, 25) ppm and tested for calibration to obtain a graph of absorbance versus concentration as shown in Figure 4. This calibration data, which distinguishes it from XRF analysis, is that it can be used to quantitatively determine the elemental Au content in the sample. However, this analysis is only for one metal element.

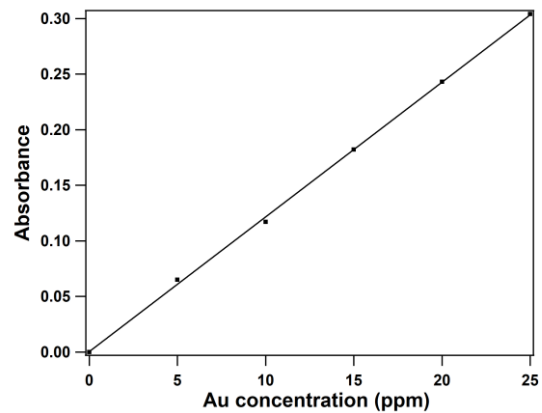


Figure 5. Graph of Au standard solution for AAS calibration Calibration graph Figure 5 to determine the elemental Au content in the sample after being tested and the absorbance value obtained using the linear line method. The test results of the AAS instrumentation are presented in Table 4.

Table 4. Data from AAS analysis test results

Nama Sampel	Parameter	Au Concentration (ppm)		
		I	II	III
<i>E. pellita</i> (Riau)	Au	0.336	0.330	0.450
<i>E. pellita</i> (F1)	Au	0.184	0.263	0.184
<i>E. pellita</i> (F2)	Au	0.657	0.736	0.578
<i>Eucalyptus</i> hybrid (F1)	Au	0.342	0.263	0.263
<i>Eucalyptus</i> hybrid (F2)	Au	0.905	0.905	0.792

Table 4 shows that all types of Eucalyptus leaf samples detected that the presence of Au element was less than 1 ppm with a not too large difference among the types.

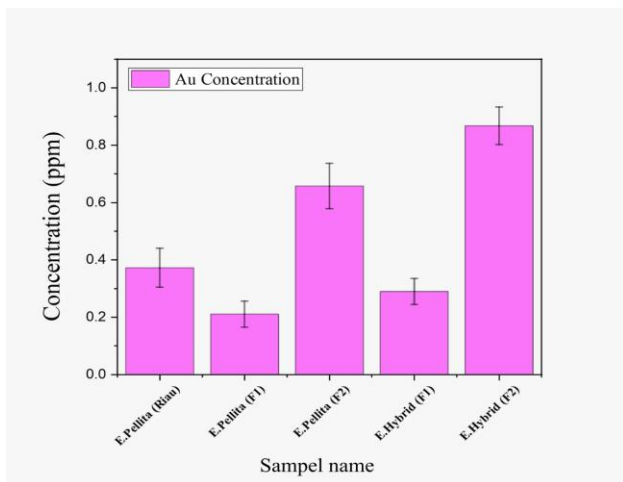


Figure 6. Comparison diagram of the elemental Au in various samples of Eucalyptus leaves

The concentration obtained from the absorbance value is then entered in the calibration graph equation using the linear line method.

Figure 6 shows that the highest Au concentration is found in *Eucalyptus* hybrid (F2) and *E. pellita* (F2). In lineage, *Eucalyptus* hybrid (F2) and *E. pellita* (F2) are descendants of *E. pellita* (F1). *E. pellita* (F2) is the best offspring of *E. pellita* (F1) representing the pure species. While for the *Eucalyptus* hybrid, it is a descendant of *E. pellita* (F1) as female parent which inter-crossed with other *Eucalyptus* species. Phenotypically, *Eucalyptus* hybrid has better growth than the pure species of *E. pellita*, as can be observed from the stem diameter growth of the plant. This shows that the Au concentration in plants depends on the Sability of plants to absorb minerals from the soil. Figure 7 is a lineage chart of *Eucalyptus* in Wonogiri.

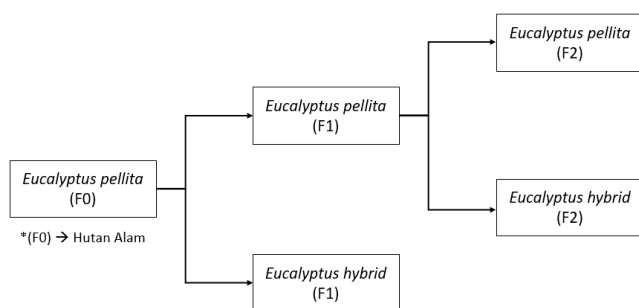


Figure 7. Chart of Eucalyptus Descendants in Wonogiri

The results of the analysis showed that the Au content in *Eucalyptus* leaves was quite high, which was almost 1 ppm. This indicates that the *Eucalyptus* plant in Indonesia has the potential as an indicator of biogeochemical exploration of Au metal mines in Indonesia. Au particles in *Eucalyptus* leaves are nanometer in size. In the application of exploitation, it is

necessary to know the form of metal in the soil so that it gets maximum results, so it is necessary to study more regarding on the form of Au in the soil that can be mined. In addition, it suggests that breeding work to obtain superior *Eucalyptus* trees would provide a good challenges to find the potential as biogeochemical indicator in gold metal exploration.

Conclusion

Based on the results of research, observations, and measurements that have been made, it can be concluded that: (1) *Eucalyptus* plants in Indonesia, both *E. pellita* and *Eucalyptus* hybrid can be used as natural indicators of potential Au metal mining in Indonesia; (2) The two methods used, namely the qualitative method with XRF analysis and quantitative with AAS analysis, need to be carried out and used as a reference in determining the potential for Au metal mining in the territory of Indonesia.

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