Determination of Gold Phytoavailability in Soil by Diffusive Gradients in Thin Films and *Brassica juncea* L Plant

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Abstract. Diffusive gradients in thin films (DGT) techniques, a recently developed approach for assessing gold (Au) phytoavailability is beginning to gain traction due to its advantages over conventional soil extractants. A greenhouse study was conducted to determine Au thresholds and the phytoavailability of Au to white mustard (brassica juncea L.), compared with DGT method. Treatments were Au 5 mg/kg levels in soil. In DGT method Au uptake were increase 0.1245 – 2.4697 µg/L To obtain various amounts of Au phytoavailability, the phytoaccumulative mechanism of gold metal (Au) in plants through variations in the length of planting time 2-8 weeks on the migration and accumulation of Au in plant root and shoot. The results of the research showed an increase in the concentration of gold metal with planting times of 2, 4, 6 and 8 weeks which was absorbed from 0.2662 – 2.1314 mg/kg with an average content of gold metal bound to the roots of 0.1398 – 1.1855 mg/kg is higher than gold metal which migrates to the shoot 0.1264 – 0.9459 mg/kg. The phytoaccumulative mechanism of plants regarding the concentration of bound metals is determined by calculating the bioconcentration factor (BCF) and translocation factor (TF) both of which are indicators that can differentiate the accumulation mechanism between phytostabilization and phytoextraction. The calculation results show the BCF value is 0.0532 – 0.4262 while the TF value is 0.3597 - 0.9041. so it can be said that the accumulation of gold metal in brassica juncea plants occurs through a phytoextraction mechanism. The performance of DGT and brassica juncea plant were similar for assessing Au phytoavailability.

Keywords: gold (Au), Diffusive Gradients in Thin Films, brassica juncea, bioconcentration factor, translocation factor.

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1. INTRODUCTION

Phytomining can produce high-value metals with an environmentally friendly method and economic feasibility[1-2]. All plants have the ability to absorb metals but in varying amounts. A number of plants from many families have been shown to have hypertolerant properties, namely being able to accumulate metals with high concentrations in their roots and shoots, so that they are hyperaccumulators. Several studies have reported several plant species as fast, cheap and effective tools for gold exploration in arid and semi-arid environments[3-11]. *Brassica juncea* plants have been

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studied by Suprabawati & Fudiesta, (2015)[12] to have the ability as a phytoremediator of heavy metals Cd (II) and Cr (VI) in the leaves, while Pb (II) metal is abundant in the roots. Furthermore, *Brassica juncea* L and *Stanleya pinnata* in absorbing Cr and Se metals in the soil were carried out by Vecchia *et al*., (2023)[13], the results obtained by B. juncea L were higher in accumulating Cr and Se metals in the roots of around 2000 mg Cr/kg and 400 mg Se/kg, compared to S. pinnata with accumulation of Cr metal in the roots <500 mg Cr/kg and <1000 mg Se/kg.

In addition to using plants and other conventional extraction techniques, currently the Diffusive Gradient in Thin Films (DGT) technique is being developed to measure the bioavailability of metals in soil (Wang et al., 2016)[14]. This diffusion technique can be applied in situ to measure labile metal types quantitatively. The working principle of DGT is based on Fick's first law of diffusion[15-17]. This technique is based on a simple tool where heavy metals diffuse through a diffusion layer to a binding phase in the form of cation exchange resin accumulating metal ions.

From various studies on the absorption of heavy metals in soil using both plants and DGT devices, this study aims to compare the ability of Au (III) ion accumulation in soil using the two techniques, namely the phytomining technique using mustard greens (Brassica juncea) and the DGT technique using Chelex-100.

2. MATERIALS AND METHOD

This research main stages were greenhouse for gold phytoaccumulation, plant digestion, preparation of the diffusive and binding gel DGT method, and gold (Au) analysis. Prepare polybags and fill them with 2.5 kg of Au(III) added in soil and leave for 1 day so that the soil is in a homogeneous condition. Plants are harvested at week 2 (two), week 4 (four), week 6 (six) until the plants are 8 weeks old after sowing, Plants are separated into roots and shoot. Each root and leaf sample was weighed by wet weight, then dried in an oven at 70ºC for 24 hours. Then put it in a desiccator for 20 - 30 minutes, then weigh the dry weight. The samples (roots and shoots of plants) were first ashed using a furnace at a temperature of 650°C, then destroyed by adding 10 mL of aqua regia and heated on a hotplate at a temperature of 105°C. This process took place in a fume hood for 3 hours, after which the sample solution was added with sufficient aquadest. In the DGT method test, the contact time was varied for 2, 4, 6, and 8 weeks. After that, the DGT device was planted in the soil. After the desired time, the resin was removed from the DGT device and then eluted with 10 mL of 1M HNO_3 for 24 hours. Furthermore, the sample was measured on the SSA.

3. RESULTS AND DISCUSSION

The research results show that *brassica juncea* plant and DGT can accumulate Au metal at various harvest times. A comparison between shoot and roots can be seen in **Fig 1**. It can be seen that the Au uptake was highest in the eighth week, with the highest uptake in the roots at 1.1855 mg/kg. The mechanism of gold uptake by plants is a complex phenomenon and involves several steps such as metal dissolution from the soil matrix, uptake into the roots, transport to the shoots, detoxification and sequestration.

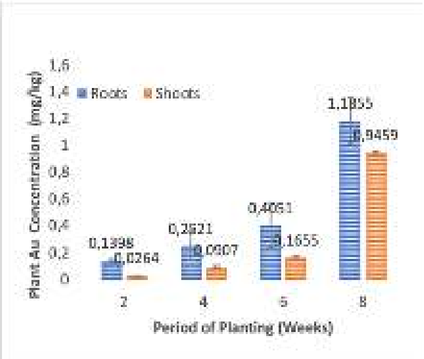


Fig 1. The effect of the period of planting in accumulating Au uptake

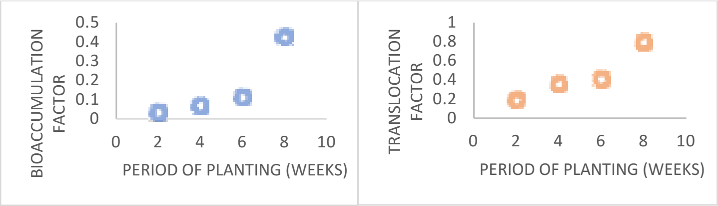
These findings align with Anderson et al. (1998)[1], Khan et al. (2003)[7], and Lamb et al. (2001)[8]. According to Wilson-Corral et al. (2011), the average concentration of gold in dried H. *annuus* for shoots, stems, and roots was 16 mg/kg, 21 mg/kg, and 15 mg/kg, respectively. Additionally, it was noted that the control plant's gold concentration was quite low. According to Anderson et al. (1998), the plant must accumulate 1 mg of gold per kilogram of dry weight biomass in order to be classified as a gold accumulator.

The Transfer Factor (TF) value is calculated based on the comparison of concentrations from shoot and roots. TF is used to see the translocation of metals from the roots to the shoots of plants, which is calculated by dividing the metal concentration in the shoots by the roots. The ability of a plant species to accumulate metals from the soil can be estimated from the BCF value, BCF > 1 is an indication that the species has potential as a heavy metal phytoremediator. Metals are transferred from the roots to the shoots through the plant transpiration pathway (xylem), the level of element transport is not the same for each element and each type of plant. The mechanism of gold absorption by plants is a complex phenomenon involving several stages such as dissolution of the metal from the soil matrix, uptake into the roots, and translocation of the metal to the shoots.

$$\text{BAF}=\frac{Au\ Concentration\ in\ Shoot}{Au\ Concentration\ in\ Ore} \quad \ldots\ldots.. (1)$$

$$\text{TF}=\frac{Au\ Concentration\ in\ Shoot}{Au\ Concentration\ in\ Root} \quad \ldots\ldots... (2)$$

By calculating the TF and BCF values as seen in **Fig** 2.**2**, we can find out whether the plant is a hyperaccumulator or not. It is not possible to classify mustard plants as hyperaccumulator plants based on the TF and BCF values as they are less than 1. Mustard plants can absorb up to 42.628% of the total amount of Au metal in the ground in the eighth week, despite not being hyperaccumulator plants. In order to increase the uptake of Au metal in plants, additional metal chelating compounds like sodium cyanide, thiocyanate, and thiosulfate were used in a number of studies on gold phytominning (Anderson et al., 1998). There were no extra metal chelating agents used in this study. Only fertilizer and compost are added for plant fertility, and environmental conditions are created to mimic those of the natural world. Water and soil can become contaminated by the addition of metal chelating chemicals.



(a) (b)

Fig 2. Biaccumulation Factors (BAF) (a) and Translocation Factors (TF) of *Brassica juncea* L plants (b)

For the aim of gold exploration, the diffusive gradients in thin films (DGT) approach may provide a new instrument for evaluating element speciation in soils. The method makes use of a device housed in a specially-designed plastic housing that contains a diffusive gel (polyacrylamide 0.8 mm thick), a binding resin gel (Chelex-100 in a cross-linked polyacrylamide gel), and a filter membrane (cellulose-nitrate, 0.45 µm porosity, 0.13 mm thick). The rate at which the flux of gold species is absorbed by the resin layer is constrained by the diffusive hydrogel (Zhang, et al 2001). The method in soils eliminates gold from soil solutions and thus causes desorption, or dissolution, of the elements from solid phases. When measuring element concentrations in soils, the DGT technique has a number of benefits. These include: pre-concentrating metals through diffusive transport through the soil solution (Zhang, et al., 2001); inducing resupply from elements bound to the solid phase; having very good sensitivity, particularly when deployment times are extended; not significantly altering the soil's chemical or physical properties; and possessing behavior similar to plant roots and shoots for a variety of trace elements (Zhang et al., 2001).

$$C_{DGT} = \frac{M\Delta g}{D\,t\,A} \quad \text{.........} \ (3)$$

where A is the area of the DGT device window, *t* is the deployment time, D is the element's diffusion coefficient, M is the mass of the element accumulated onto the resin gel, Δg is the thickness of the diffusion layer, and C_{DGT} is the concentration of the target element in the soil solution.

The characterization results for diffusive gel and binding gel can be seen in **3,** in the resin spectrum there is an absorption in the 1606 cm^{-1} area which indicates the presence of the –COO- group which comes from the iminodiacetate group in Chelex resin. In the FTIR spectrum of the diffusive gel, it can be seen that there is absorption at a wave number of 3200 cm^{-1}, which indicates the presence of a primary amide derived from acrylamide. Apart from that, there is also an absorption at the wave number 2962 cm^{-1} indicating the presence of –CH2- which comes from the polymer chain and there is also an absorption at the wave number 1673 cm^{-1} indicating the presence of C=O stretching which comes from the amide.

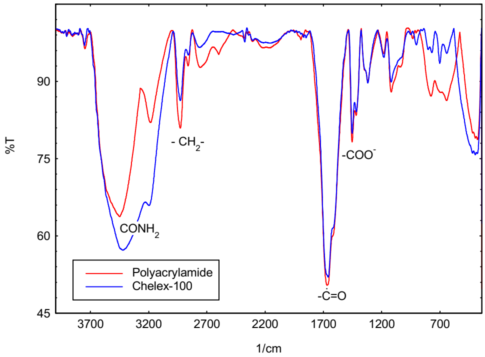


Fig 3. FTIR Spectrum of polyacrylamide diffusive gel and chelex binding gel

The Chelex resin capability test aims to determine the bioavailable binding ability of Au metal to the resin in tests of variations in contact time in soil. From **Figure 4**, it can be seen that as the DGT contact time in the soil increases, the mass of Au metal bound in the resin increases. This proves that the gel resin has the ability to bind Au metal. Based on these data, it can be concluded that Chelex gel resin was able to provide linear absorption until the eighth week of the study. The results of this study are similar to the results of research by Lucas et al., 2012, which showed the ability of the Barssica juncea plant to absorb Zn metal in the grass type *Sorghum vulgare var. Sudanese*.

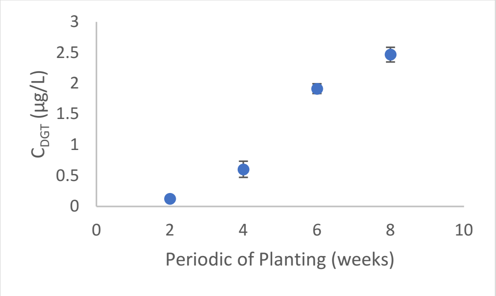


Fig 4 . Au concentration in DGT relation to soil deployment time

4. CONCLUSIONS

Gold (Au) concentrations in brassica juncea plant and DGT were increased by increasing deployment time in soils. The results of the research showed an increase in the concentration of gold metal with planting times of 2, 4, 6 and 8 weeks which was absorbed from 0.2662 – 2.1314 mg/kg. In DGT method Au uptake were 0.1245 – 2.4697 µg/L. The phytoaccumulative mechanism of plants regarding the concentration of bound metals is determined by calculating the bioconcentration factor (BCF), which is the ratio of the metal concentration in the roots to the concentration of gold metal added to the soil, and the translocation factor (TF), which is the ratio of the metal concentration in the shoot to the metal concentration in the shoot. Au at the root. The calculation results show the BCF value is 0.0532 – 0.4262 while the TF value is 0.3597 - 0.9041 for variations in planting time of 2 -8 weeks. BAF value < 1 and TF < 1 so it can be said that the accumulation of gold metal in brassica juncea plants occurs through a phytoextraction mechanism.

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