

# STUDY OF THE “*Impatiens walleriana*” FOR PHYTOREMEDIATION OF CHROMIUM, THORIUM, URANIUM AND ZINC SOIL CONTAMINATION

Jefferson K. Torrecilha, Gabriela P. Mariano, Paulo S. C. da Silva

Instituto de Pesquisas Energéticas e Nucleares IPEN - CNEN/SP  
Av. Prof. Lineu Prestes 2242  
CEP 05508 000, São Paulo, Brasil  
jeffkoy@usp.br

## ABSTRACT

The objective of this study was to determine the Cr, Th, U and Zn transfer from soil to *Impatiens walleriana* and verify if this plant species is suitable for soil decontamination. Samples of small, medium and large size of the plant were collected in three different locations, University of São Paulo, IPEN and Cotia, as well as soil samples from the surroundings. Instrumental neutron activation analysis was applied to determine the element concentrations. Roots, stems and leaves of the plant samples were analyzed in separate in order to verify the preferential site of concentration of these elements in the plant. For the analyses, samples of the soil and the plants were dried and pulverized into a fine powder, accurately weighed and sealed in polyethylene bags, irradiated together with reference standard materials in the IEA-R1 IPEN reactor and counted in a Ge-hiperpure detector. Cr, Th, and U did not present a significant potential to be accumulated in none of the plant parts. Zinc, on the other hand, showed great capacity to be accumulated in in all parts of *Impatiens walleriana* and, therefore, this species is a good candidate to be used for phytoremediation purpose, in case of soil contamination with zinc.

## 1. INTRODUCTION

In the last century, it was observed that soil pollution with heavy metals was a growing problem due to industrial activities, agriculture and urbanization, causing serious impacts to the environment. The eventual destination of heavy metals is its deposition and burial in soil and sediment. Among the biological processes developed to solve problems of soil contamination, phytoremediation is an emerging technology that can be defined as the selection and use of plant species to extract, assimilate, transform and also decompose certain contaminants [1].

The principle of operation is the capacity that plants have in absorbing elements from the soil, by the roots, together with water and nutrients. Some species are able to absorb organic or inorganic pollutants, acting as biological filters. The plants can remediate contaminated soils through some mechanisms, such as: phytoextraction, phytostabilization, rhizofiltration, phytodegradation, phytostimulation, artificial reservoirs and hydraulic barriers [2-3]. Some requirements to perform phytoremediation should be taken into consideration, especially the physical and chemical characteristics of the soil, type of contaminant and its distribution. Any factor that may adversely affect plant performance should be minimized to promote its decontaminating action. It is desirable that plants with phytoremediation potential show some characteristics that can be used as markers for their selection: the plant needs to have good

absorption capacity and a deep root system, being perennial and with the ability to grow in different environments. It is, generally, accepted that the *Impatiens walleriana* presents several of these characteristics and, therefore, the study of its potential for phytoremediation in soil contaminated with uranium, thorium, chromium and zinc is of great importance.

Uranium and thorium are radioactive elements, present naturally in the soil, and they form the natural decay series. The presence of these elements and their daughters in soils is responsible for the major part of the external dose exposition. As these elements are alpha emitters, their ingestion also represents a source of internal radiological contamination. Furthermore, they also represent a pronounced toxicological threat [4-5].

Chromium is found naturally in rocks, soils, plants and animals. It is found in combination with other elements like chromium salts, some of which are soluble in water. Chromium does not evaporate, but it can be present in air as dust particles. Once in the bloodstream, after ingestion or inhalation, chromium moves to all parts of the body. The trivalent form is not metabolized, but hexavalent chromium is reduced by enzymatic reactions to trivalent chromium in the body. Ingestion of food is the major source of exposure for this element. The trivalent form of chromium is an essential nutrient in our diet and is needed for many important functions, including lipid, protein, and fat metabolism. Even at levels above those required to health maintenance, chromium exhibits very low toxicity and it is not known to cause cancer. In contrast, hexavalent chromium can be toxic and even cause cancer, from its inhalation; the lethal dose is estimated at about 7 mg of hexavalent chromium per kilogram of body weight [6].

Zinc is one of the most common elements in the earth's crust. It is, also, an essential element for all living beings. Zinc is found throughout the environment and, besides, it is present in all foods. It can be released by natural processes, but mostly as a result from human activities. In soil, zinc, generally, remains in the upper layers, bound to soil particles, but it can be leached to groundwater depending on the soil characteristics, moving more readily in sandy soil. Zinc is one of the most abundant trace elements in the human body. It is, typically, taken in by ingestion of food and water, although, it can also enter the lungs by inhaling zinc dust contaminated air. Harmful effects from high zinc amounts, generally, begin at levels from 10 to 15 times higher than the recommended dietary allowances of 5, 12, and 15 mg per day for infants, women, and men, respectively. Ingestion of high amounts of zinc can cause stomach cramps, nausea, and vomiting. The intake of large amounts of zinc over an extended period can cause anemia, damage the pancreas and lower the levels of high-density lipoprotein cholesterol (the good form of cholesterol) [7].

The objectives of this study was to determine the ratio of Cr, Th, U and Zn concentrations, by neutron activation analysis in *Impatiens walleriana* and in soil, to verify whether this species is suitable for soil decontamination of these elements.

## 2. METHODS

Plant samples were collected in three different points: in the University of São Paulo (USP) campus, in IPEN, inside Cidade Universitária, São Paulo city, and in the city of Cotia. The plant height was considered as an indicative of its age. Plant samples of three different heights (10, 20 and 30 cm), named small, medium and large, respectively, were collected. In

each place, three to four plants were collected to compose a sample of each height. Soil samples, surrounding the plants, were also collected. In the laboratory, the plant samples were washed to completely remove soil particles and dust. The plant of each height group was separated in root (R), stem (S) and leaf (L) and each part was analyzed in separate. Each part of the plant was washed to remove dust and soil particles and, then, they were dried at room temperature. After that, the samples were weighed, transferred to a crucible, calcinated at 400°C, for four hours, and macerated after cooling.

For neutron activation analysis, approximately 200 mg of the dry plant samples and 120 mg of soil samples were packed in polyethylene bags. Standard reference materials (SRM) Estuarine Sediment, SRM 1646a, from the National Institute of Standards and Technology (NIST) and Syenite, Table Mountain, from the United States Geological Survey (USGS) were prepared in the same way of the samples. In the IEA-R1 nuclear reactor, at IPEN, the samples and reference materials were irradiated for 8 h, under a thermal neutron flux of 1 to 5  $10^{12}$  n  $\text{cm}^{-2}$   $\text{s}^{-1}$  and the induced activity was counted after 7 days for uranium determination and, after 15 days, for thorium, chromium and zinc determination. Gamma spectrometry was performed using a Ge-Hyperpure EG & G Ortec detector and an associated electronics system, with a resolution of 0.88 keV and 1.90 keV for  $^{57}\text{Co}$  (122 keV) and  $^{60}\text{Co}$  (1332 keV), respectively. The analysis of the data was done by using in-house gamma ray software, VISPECT program, to obtain gamma ray energies for radioisotope identification and peak areas. The concentration calculations were performed in a spreadsheet. The dry weight was corrected to the fresh weight and all the results were determined on fresh weight basis.

The concentrations were obtained by comparing the photopeak area of the target element in the spectrum of the sample with that of the standard reference material, using the following expression:

$$C_{ai} = \frac{(A_{ai} w_p C_{pi}) e^{-\lambda(t_a - t_p)}}{A_{pi} w_a} \quad (1)$$

Where,  $C_{ai}$  is the sample element concentration (in  $\text{mg kg}^{-1}$ );  $C_{pi}$  is the SRM element concentration (in  $\text{mg kg}^{-1}$ );  $A_{ai}$  is the activity of the element in the sample (in counts per second);  $A_{pi}$  is the activity of the element in the SRM (in counts per second);  $w_a$  e  $w_p$  are the weights of the sample and SRM (in g), respectively;  $\lambda$  is the decay constant isotope and  $t_a - t_p$  is the difference between the decay times of the sample and the standard.

### 3. RESULTS AND DISCUSSION

For the methodology precision and accuracy verification, the certified reference materials Estuarine Sediment 1646a (ES), and Syenite, Table Mountain (STM), were analyzed. The results are shown in Table 1 where it can be observed that good precision and accuracy were obtained for chromium, thorium and zinc, with relative standard deviation (RSD) and relative error (RE), generally, lower than 10%. In the case of uranium, the relative error is slightly higher than the other elements, possibly due to the fact that this value is reported as information value in the certificate.

**Table 1: Values obtained in the certified analysis of the reference materials, for quality control of the results, in mg kg<sup>-1</sup>**

Elements	SRM 1646a				STM			
	Certified Value	Measured Value	RSD	RE	Certified Value	Measured Value	RSD	RE
Cr	40.9 ± 1.9	44 ± 1	3.4	8.1				
Th	5.8	5.5 ± 0.5	9.9	4.3	27 ± 5	28 ± 3	9.5	5.1
U	2	1.6 ± 0.2	10.6	14.9	7.6	9.4 ± 0.6	6.52	15.2
Zn	48.9 ± 1.6	48 ± 5	11.5	0.9	223 ± 19	235 ± 20	8.56	5.7

The concentrations obtained for the USP, IPEN and Cotia soil and plant samples are presented in Tables 2, 3 and 4, respectively. Considering the elements addressed in this study, the uranium concentration in soil is slightly above than the mean values for the Upper Continental Crust (UCC) that varies from 1.5 to 2.8 mg kg<sup>-1</sup> [8] and the average background concentration of uranium in soil, according to Rudnick and Gao [9], of about 2 mg kg<sup>-1</sup>. Nevertheless, the U concentration obtained in the present soil samples is in agreement with the worldwide uranium concentrations for non-contaminated soil, reported by the UNSCEAR [10], ranging from 0.3 to 11.7 mg kg<sup>-1</sup>. In the case of Th, according to ATSDR [11], the average concentration in soil is around 6 mg kg<sup>-1</sup> and varies from 8.6 to 10.5 mg kg<sup>-1</sup> in the UCC [8]. The values found for the present soil samples varied from two to three times these reference values. Unpolluted soil presents levels of Cr varying from 1 to 1000 mg kg<sup>-1</sup> and for Zn, from 3 to 264 mg kg<sup>-1</sup> [12]. The values observed in the UCC, for these two elements, vary from 35 to 112 mg kg<sup>-1</sup> for Cr and from 52 to 71 mg kg<sup>-1</sup>, for Zn. The values obtained for chromium in this work were in the range established by the UCC, while the zinc concentration observed is slightly above.

**Table 2. Concentration in mg kg<sup>-1</sup> on fresh weight basis, in soil and small root (RS), medium root (RM) and large root (RL), small stem (SS), medium stem (SM) and large stem (SL) and small leaf (LS), medium leaf (LM) and large leaf (LL) of *Impatiens walleriana* samples from USP.**

Samples	Cr	1σ	Th	1σ	U	1σ	Zn	1σ
USP Soil	59	± 2	21.5	± 0.2	4.3	± 0.2	93	± 3
USP RS	2.43	± 0.09	0.58	± 0.01	0.16	± 0.02	178	± 4
USP RM	5.3	± 0.2	0.61	± 0.01	0.19	± 0.04	163	± 4
USP RL	15.1	± 0.5	2.15	± 0.03	0.58	± 0.06	140	± 4
USP SS	1.4	± 0.1	0.041	± 0.003	ND		146	± 4
USP SM	0.81	± 0.05	0.038	± 0.003	ND		111	± 3
USP SL			0.04	± 0.01	ND		137	± 4
USP LS	1.33	± 0.08	0.122	± 0.005	ND		111	± 8
USP LM	2.2	± 0.1	0.11	± 0.01	ND		148	± 5
USP LL	2.0	± 0.1	0.13	± 0.01	ND		136	± 4

ND = not determined. 1σ = uncertainty

**Table 3. Concentration in mg kg<sup>-1</sup> on fresh weight basis, in the soil and small root (RS), medium root (RM) and large root (RL), small stem (SS), medium stem (SM) and large stem (SL) and small leaf (LS), medium leaf (LM) and large leaf (LL) of *Impatiens walleriana* samples from IPEN.**

<b>Samples</b>	<b>Cr</b>	<b>1σ</b>	<b>Th</b>	<b>1σ</b>	<b>U</b>	<b>1σ</b>	<b>Zn</b>	<b>1σ</b>
<b>IPEN Soil</b>	73	± 2	31	± 3	7.7	± 0.6	134	± 4
<b>IPEN RS</b>	8.6	± 0.2	2.3	± 0.2	0.48	± 0.04	24.0	± 0.8
<b>IPEN RM</b>	6.2	± 0.2	1.9	± 0.2	0.74	± 0.06	44	± 1
<b>IPEN RL</b>	0.60	± 0.02	0.23	± 0.02	0.046	± 0.003	4.8	± 0.4
<b>IPEN SS</b>	11.2	± 0.3	0.58	± 0.05	0.31	± 0.04	150	± 5
<b>IPEN SM</b>	0.91	± 0.05	0.17	± 0.02	0.02	± 0.01	60	± 4
<b>IPEN SL</b>	0.16	± 0.01	0.06	± 0.01	0.0091	± 0.0009	11	± 1
<b>IPEN LS</b>	ND		1.02	± 0.09	0.25	± 0.02	75	± 2
<b>IPEN LM</b>	28.9	± 0.8	0.13	± 0.01	0.016	± 0.001	14.21	± 1.03
<b>IPEN LL</b>	2.79	± 0.08	0.019	± 0.002	0.0034	± 0.0004	2.9	± 0.2

ND = not determined. 1σ = uncertainty

**Table 4. Concentration in mg kg<sup>-1</sup> on fresh weight basis, in the soil and small root (RS), medium root (RM) and large root (RL), small stem (SS), medium stem (SM) and large stem (SL) and small leaf (LS), medium leaf (LM) and large leaf (LL) of *Impatiens walleriana* samples from Cotia.**

<b>Samples</b>	<b>Cr</b>	<b>1σ</b>	<b>Th</b>	<b>1σ</b>	<b>U</b>	<b>1σ</b>	<b>Zn</b>	<b>1σ</b>
<b>COTIA Soil</b>	78	± 2	27	± 2	6.7	± 0.5	70	± 8
<b>COTIA RS</b>	6.4	± 0.2	2.0	± 0.2	0.48	± 0.03	86	± 3
<b>COTIA RM</b>	6.9	± 0.2	1.7	± 0.1	0.45	± 0.04	189	± 15
<b>COTIA RL</b>	18.3	± 0.5	5.3	± 0.5	1.4	± 0.1	16	± 1
<b>COTIA SS</b>	0.53	± 0.07	0.10	± 0.01	ND		70	± 3
<b>COTIA SM</b>	0.30	± 0.05	0.10	± 0.01	ND		197	± 16
<b>COTIA SL</b>	0.25	± 0.05	0.07	± 0.01	ND		55	± 2
<b>COTIA LS</b>	0.97	± 0.04	0.17	± 0.02	0.05	± 0.01	91	± 3
<b>COTIA LM</b>	4.1	± 0.1	0.36	± 0.03	0.10	± 0.02	154	± 12
<b>COTIA LL</b>	1.28	± 0.09	0.28	± 0.03	0.11	± 0.02	112	± 4

ND = not determined. 1σ = uncertainty

In Figure 1, the percentage of elements in the root, stem and leaf, relatively to the soil and for the different heights of plants, is shown. Although uranium can bio-concentrate in certain food crops [13], this is not the case for the *Impatiens walleriana*, as this element was only determined as a small fraction of the soil concentration.

The concentration of thorium in plants is usually about 0.42% of that in the soil [15]. In the case of *Impatiens walleriana*, Th present in the root varies from 2.7 to 2.83%, 6.5 to 7.5 and 6.4 to 7.5 of the soil concentration in the small and medium USP, IPEN and Cotia plants,

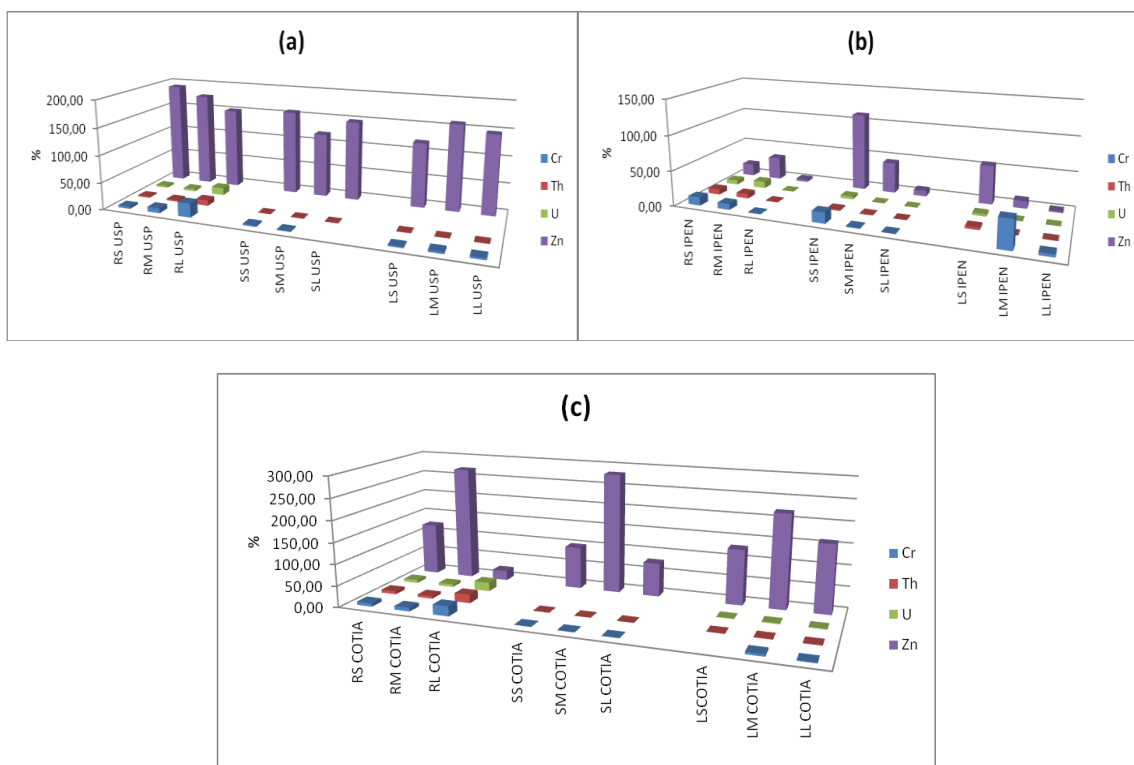
respectively and 0.75, 10 and 20.1% in the roots of large plants. The stem accumulates from 0.18 to 1.9% of the Th present in soil and the leaves, 0.5 to 3.3, whatever the size considered.

The typical ratio of chromium in plants, to chromium in soil, is estimated at 0.45%. In these samples, it was observed that the chromium amount was higher in the roots, with 0.8, 24 and 25.8% of the soil concentration in IPEN, Cotia and USP samples, respectively, but the same was not observed in the stems or leaves. In the stems, the percentage varied from 1.4 to 2.4%, 1.24 to 15.4% and 0.4 to 0.7% for medium and small USP, IPEN and Cotia samples. In the large stem, the percentage was 0.22 and 0.32% to IPEN and Cotia plants (in the USP large stem samples this value was not measured); in the leaves, this quantity varied from 2.3 to 3.8%, 3.3 to 39.7 and 1.6 to 5.19% for USP, IPEN and Cotia samples, respectively.

When compared to the other elements, it is possible to note that zinc was accumulated at the highest amounts in all parts of the plants. At high concentrations, this metal is potentially toxic. The toxicity of Zn in plants leads to a decrease in the dry matter production of shoots and root biomass; radicle necrosis in contact with the ground; seedling death and inhibition of plant growth [14].

The typical ratio of the concentration in plants to that in soil is estimated around 90% for zinc [13]. In the small, medium and large roots from USP, IPEN and Cotia samples, the percentage varied from 3.61 to 271.01%; in stem, it varied from 8.09 to 222.7% and in the leaves, it varied from 2.19 to 220.19% of the soil concentration.

Although Zn is an important micronutrient to plants, depending on the dose, it may become toxic and cause contamination to the environment. It is also known that the concentrations of this element in steel industry residues can vary, depending on the type of waste and the process adopted by the industry [15]. Heavy metals can express their potential pollutant directly in soil organisms, plants and there is, also, the possibility of both surface water contamination, via soil erosion, and subsurface waters, when these metals move vertically downwards the soil [16]. Zinc is mobile in the soil, representing a high risk of groundwater contamination [13]. In a study with Eucalyptus, it was shown that the plants may have been affected by zinc excess in the soil [17].



**Figure 1: Cr, Th, U and Zn plant/soil ratio, in %, in the samples of roots, stems and leaves of *Impatiens walleriana* from USP (a), IPEN (b) and COTIA (c)**

As a conclusion, it can be drawn that *Impatiens walleriana* is a good candidate for being employed with phytoremediation purpose in the case of zinc contamination in soil.

#### 4. CONCLUSIONS

The concentrations of uranium, thorium, chromium and zinc were determined in samples of uncontaminated soil, in different parts of the species *Impatiens walleriana*, of different sizes. It was observed that the elements U, Th and Cr do not present a significant potential to be accumulated in none of the plant parts. Zinc, on the other hand, has great capacity to be accumulated in the root, stem and leaves of this vegetable; therefore, the species *Impatiens walleriana* is a good candidate to be used for phytoremediation purpose, in case of soil contamination with this element, since this plant presents several of the requirements for this task. However, further studies still should be done to verify if this behavior remains in case the plant has grown in contaminated soil.

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