

Could ^{137}Cs remediation be accomplished with stable cesium (CsCl) on tropical soils?

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Abstract

Stable cesium can be considered as the best element for desorption of soil radio-cesium. It is considered an element that slightly absorbed by plants, so that the application of high doses to the soil could increase the absorption of ^{137}Cs , which is desired for the remediation of contaminated soils. There is shortage of knowledge on remediation of tropical and subtropical soils contaminated with ^{137}Cs . The aim of this work was to evaluate the use of ^{133}Cs for the remediation of Brazilian tropical and subtropical soils contaminated with ^{137}Cs . In addition, we investigated the Cs uptake by bean plants (*Phaseolus vulgaris* L.) grown in Cs contaminated soil. The experiment was carried out in pots under greenhouse conditions. Seven soil types were used in the experiment (Oxisol, Udox, Psamment, Ochrept; Aquoll; Udox and Udult), which received the application of four doses of ^{133}Cs (0, 5, 10 and 20 mg/pot) in a completely randomized design arranged in a factorial scheme (7 soil types x 4 doses of ^{133}Cs) with three replicates. An increase in transfer factor values of ^{137}Cs was observed for both shoot growth and grains, as well as in percentage of total activity of ^{137}Cs removed from the soil regarding to addition of stable cesium levels in all soils. The results showed that psamment soil presented higher specific activity of ^{137}Cs in the soil and grains, as well as for the transfer coefficient from soil to shoot growth and grains. The application of stable cesium chloride to soil did not cause any effects on dry matter production of shoot growth and grains. The addition of ^{133}Cs increased the transfer from soil ^{137}Cs to the plant regardless of soil type, proving the efficiency of this practice for the remediation of soils contaminated with radioactive Cs. In addition, the plants of common bean were efficient for use in phytoremediation.

Keywords: Environmental pollution, phytoremediation, heavy metals, transfer factor, *Phaseolus vulgaris*.

Abbreviations: Cs_ cesium; K_ potassium; NH_4 _ ammonium; Na_ sodium; Bq.kg^{-1} _ becquerel per kilogram of dry material; VH_ vermiculite; PIR_ potential of Cs interception of soils; $\mu\text{eq g}^{-1}$ _ soil_ microequivalent/gram of soil; SOM_ Soil organic matter; Soil EC_ Soil Cation Exchange Capacity.

Introduction

All soils may contain radionuclides with natural or anthropogenic origin. Cesium (Cs) is one of the rarest alkaline metals in the nature. It has a high chemical similarity with other metals, such as potassium (Bowen, 1979). It is predominantly found as a monovalent cation in the soil solution (Avery, 1995). The Cs mean concentration of $13.4 \mu\text{g g}^{-1}$ in coal, $10 \mu\text{g g}^{-1}$ in seawater, $4 \mu\text{g g}^{-1}$ in sedimentary rocks and $1 \mu\text{g g}^{-1}$ in granites have been reported (Davis, 1963; Bowen, 1979; Coughtrey and Thorne, 1983). There are at least 21 isotopes of Cs, mostly in the range of atomic masses 123-144 (Davis, 1963). The ^{133}Cs is the only natural stable isotope of Cs, whose main source is pollucite, an aluminosilicate mineral (White and Broadley, 2000). The most important radioactive isotopes of Cs are ^{134}Cs and ^{137}Cs , which has been received attention because of their potential impacts on health and environment due to the relatively long half-lives (2.07 and 30.07 years, respectively) (Takehi et al., 2015).

Radiological accidents in Goiania – Brazil and Chernobyl –

Ukraine, as well as that due to an earthquake and subsequent tsunami in Fukushima Daiichi nuclear power plant in Japan, have caused soil contamination with ^{137}Cs in small or possibly larger scales. Radioactive isotopes that contaminate soils may become available for plants and soil organisms, and subsequently entering the food chain (Sreenivasa et al., 2012). It has been noted that the availability of ^{137}Cs for plants is influenced by soil chemical, physical and biological properties. In addition, the plant species affect the transfer of soil Cs to the plant tissues (Massas et al., 2010). Therefore, removal of ^{137}Cs from contaminated soils is an urgent issue (Yasunari et al., 2011). However, few results are available on ^{137}Cs absorption by plants in tropical and subtropical ecosystems and its formation from the soil (Monira et al., 2005; Sandeep et al., 2009). Thus, understanding the dynamics of ^{133}Cs in soils is crucial for assessing the remediation of contaminated soils with ^{137}Cs (Murota et al., 2016). Some studies were performed in regions with a temperate climate using ^{133}Cs to study the sorption and mobility of ^{137}Cs in the environment

(Hilton et al., 1997; Gossuin et al., 2002; Yoshida et al., 2004, De Koning and Comans, 2004; Williams et al., 2004; Rowan, 2013). The ^{133}Cs is considered as an useful isotope for long-term assessment of ^{137}Cs in agricultural environments because the behavior of radionuclides in the environment is similar to that of their stable isotopes (Tsukada et al., 2002; Uchida; Tagami, 2007). A review on this topic showed that ^{133}Cs does not perform any activity in biological systems, both at the level of essentiality and toxicity. The high adsorption of radioisotopes of Cs in clay and organic fractions of the soil increases the dwell time of this element in the environment (White and Broadley, 2000). The Cs desorption in tropical soils is increased with stable Cs application (Moreira et al., 1995) These results demonstrate that stable Cs, even when applied to soils at low concentrations, has a great ability to desorb the solid phase radicals to the liquid phase of the soil. However, in the literature, there are no studies on the use of Cs for the remediation of the soils contaminated with radioactivity. The ^{133}Cs has the ability to desorb ^{137}Cs from the solid phases of soil even when applied to soils at low levels. In this way, studies that evaluate the possibility of removing ^{137}Cs by ^{133}Cs are very important, considering that only few studies are available in to use ^{133}Cs for the remediation of soils contaminated with ^{137}Cs in tropical and subtropical conditions. Plants grown in contaminated areas with Cs can uptake this element and when they are consumed by human. They can cause numerous health problems, such as gastric, emphysema, dysfunction and cancer (Koptsik, 2014). Studies on Cs uptake by plants have found no evidence that plants could discriminate between ^{133}Cs and Cs radioactive isotopes (Cook et al., 2007; Soudek et al., 2004; 2006). In contaminated areas, Saito et al. (2014) observed that the ^{133}Cs can be found naturally in soils at steady state, which strongly retained in the soil, with a greater interaction with the minerals of clay. On the other hand, the ^{137}Cs was introduced into the soils because the accident could only be present in the labile parts as the ion exchange fraction in the slow fixation mechanism in the soil. However, in the long period the ^{137}Cs could be strongly captured by soil minerals over time, which will affect the behaviors of ^{137}Cs and ^{133}Cs in the ecosystems.

In this work, a different approach was used from those that reported contamination of ^{137}Cs and the application of ^{133}Cs , instead we observed the behavior of $^{133}\text{Cs}/^{137}\text{Cs}$ in the soil and the potential of remediation of ^{133}Cs . So, the aim of this work was to evaluate the effect of doses of ^{133}Cs on desorption and absorption of ^{137}Cs and ^{133}Cs by common bean plants cultivated in Brazilian tropical and subtropical soils contaminated with ^{137}Cs . Our hypothesis is that ^{133}Cs can desorb ^{137}Cs from the solid phase of the soil and the common bean plants are able to absorb the available Cs.

Results and Discussion

Transfer factor of ^{137}Cs to plants

A significant increase in transfer factor values was observed for shoot growth and grains, as well as for the increase in total activity removed from the soil in relation to the addition rates of stable Cs (Table 4). In six soil types (Aquoll, Ocherept, Oxisol, Psamment, Udox-1, Udult), the transfer factor was increased from 1 to 3 in magnitude, comparing

with control (0.030 and/or 0.060 mmol L⁻¹ ^{133}Cs). The increase in soil transfer factor for shoot and grain was associated with desorption of ^{137}Cs in soils caused by the addition of ^{133}Cs .

Common bean grown in Udox-2 and Udoll soils presented a different behavior in relation to the transfer of ^{137}Cs from soil to plant (Table 1). In relation to these soils, greater values of intercepting potential of ^{137}Cs were observed as consequence of the adsorption capacity of clay minerals. It can be observed that the PIR values of soils with significant occurrence of vermiculite or smectite as primary or secondary minerals are higher than those of soils with predominance of kaolinite and gibbsite.

Also for Udoll, which has characteristics of soils from temperate climate, the percentage of total activity that was removed from the soil, increased from 0.25 to 1.94%. This indicates the possibility of remediation with ^{133}Cs in temperate climate soils in the case of use of a crop that can absorb and accumulate ^{137}Cs , such as common bean.

Smolders et al. (1997) observed that PIR values in tropical soils are much lower than those normally observed for soils for temperate regions. In the studied soils, as the plants uptake the ions present in the soil solution, the PIR values that evaluate the Cs retention in the soils point to the tendency of ^{137}Cs transfer factor values of plants. For Psamment, a significant transfer factor from 33% of the total activity was observed (Table 4), while Udox-1, Udult and Oxisol presented an increase in the ^{137}Cs transfer factor from 6–8%. The differences observed in the soils was mainly due to the clay concentration (Table 1). The ^{133}Cs affected the equilibrium between Cs concentration in the colloid and in the soil solution, increasing the ^{137}Cs desorption from colloid, make it available in the soil solution.

Cs has a high affinity for sorption on clay minerals and this process can affect its uptake by plants (Cornell, 1993; Ishikawa et al., 2007; Carver et al., 2007). However, Cs adsorption by clay minerals depends on the concentration of ^{133}Cs in the soil solution and/or the ratio between the concentration of clay minerals and ^{133}Cs ions in soil solution (Ohnuki and Kozai, 2013). The ^{133}Cs is probably adsorbed in the interlayer of expanded clay mineals, becoming stable in soil, with the available fraction decreasing over time (Morota et al., 2016). ^{133}Cs affects the partition of ^{137}Cs in soil, increasing its shift from the exchange complex to the soil solution, where it could be more readily uptaken by the plants (Burger and Lichtscheidl, 2018).

The transfer factor increased with the increasing in the doses of ^{133}Cs , where there was no inflection point. The maximal dose of ^{133}Cs was probably insufficient to cause both inhibitions of cesium (stable and radioactive) absorption and toxic effects on common bean. It can be concluded that application of higher doses of cesium chloride can increase uptake of ^{137}Cs .

Studies of the transfer of ^{137}Cs from soil to plants and/or animals are carried out in countries of the Northern Hemisphere (temperate climate), where the ^{136}Cs contamination has been occurred due to nuclear tests and nuclear incidents. In those studies, legume species uptake more ^{137}Cs than plants of the Poaceae family (Uchida and Tagami, 2018).

Studies of soil contamination and transfer of ^{137}Cs in the Southern Hemisphere are incipient. According to Roque

Table 1. Semi-quantitative mineralogical composition of the clay fraction, x-ray diffraction, soil granulometry radiocesium interception potential (PIR) of the seven selected soil (adapted from Roque, 2003).

Soil	Soil Mineralogy		Sand	Silt	Clay	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Si:Al Ki	PIR* eq g ⁻¹ solo*
	Principal	Secondary									
Aquoll	Kaolinite	Gibbsite, V-H*	550	130	320	16.4	16.6	0.5	1.00	1.68	169
Ochrept	Kaolinite	Gibbsite; V-H*, Mica	290	220	490	26.1	20.9	4.6	1.00	2.12	645
Oxisol	Kaolinite	Gibbsite, V-H*	300	380	320	18.1	17.9	24.5	5.80	1.72	1026
Psamment	Kaolinite	Gibbsite, V-H*	950	20	30	2.0	1.1	1.1	0.30	3.09	20
Udoll	Esmectita	V-H*	200	450	350	18.5	7.7	23.6	6.60	4.08	207
Udox-1	Kaolinite	Gibbsite	480	100	420	14.3	12.9	3.7	0.80	1.88	1138
Udox-2	Kaolinite	Gibbsite; V-H*	80	310	610	14.1	14.6	22.8	7.40	1.64	129
Udult	Kaolinite	Gibbsite; Esmectite	490	140	370	11.8	10.9	7.0	2.50	1.84	392

V-H*: vermiculite. PIR*: potential of Cs interception of soils, calculated in this soils for Roque (2000) $\mu\text{eq g}^{-1}$ soil*: microequivalent/gram of the soil.

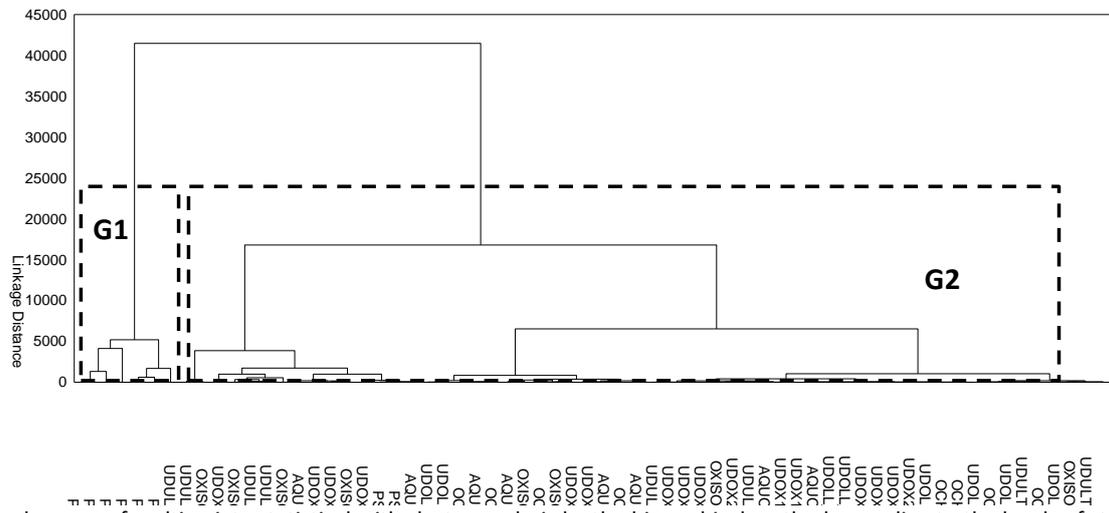


Fig 1. Dendrogram of multivariate statistical with cluster analysis by the hierarchical method according to the levels of stable Cs (0, 15, 30 and 60) and seven soil types (Aquoll, Ochrept, Oxisol, Psamment, Udox-1, Udox-2, Udult) contaminated with ¹³⁷Cs. The captions in the figure are: AQUOLL_0, 15, 30, 60: Aquoll soil treated with 0, 0.015, 0.030 and 0.060 mmol L⁻¹ ¹³³Cs; OCHREPT_0, 15, 30, 60: Ochrept soil treated with 0, 0.015, 0.030 and 0.060 mmol L⁻¹ ¹³³Cs; OXISOL_0, 15, 30, 60: Oxisol soil treated with 0, 0.015, 0.030 and 0.060 mmol L⁻¹ ¹³³Cs; PSAMMENT_0, 15, 30, 60: Psamment soil treated with 0, 0.015, 0.030 and 0.060 mmol L⁻¹ ¹³³Cs; UDOX1_0, 15, 30, 60: soil Udox-1 treated with 0, 0.015, 0.030 and 0.060 mmol L⁻¹ ¹³³Cs; UDOX2_0, 15, 30, 60: soil Udox-2 treated with 0, 0.015, 0.030 and 0.060 mmol L⁻¹ ¹³³Cs; UDULT_0, 15, 30, 60: soil Udox-1 treated with 0, 0.015, 0.030 and 0.060 mmol L⁻¹ ¹³³Cs.

Table 2. Chemical analyses for soil types.

Soil	pH	SOM*	P	K	Ca	Mg	Al ³⁺ + H ⁺	S	CEC*
	CaCl ₂	g kg ⁻¹	mg kg ⁻¹				-----cmol _c kg ⁻¹ -----		
Aquoll	4.6	181	42	0.5	3.3	1.5	17.6	5.3	22.8
Ochrept	5.4	23	58	0.5	7.7	4.3	2.8	12.5	15.2
Oxisol	4.3	40	14	0.3	2.8	1.0	9.3	4.1	13.3
Psamment	4.6	19	23	0.1	1.0	0.4	2.7	1.5	4.1
Udoll	4.9	48	57	0.3	11.4	3.1	5.5	14.8	20.3
Udox-1	4.5	34	120	0.7	2.6	0.8	8.8	4.0	12.8
Udox-2	5.4	33	30	0.7	6.5	2.1	1.9	9.3	11.1
Udult	6.5	24	90	0.3	10.1	5.0	1.1	15.4	16.4

SOM* Soil organic matter CEC* Soil Cation Exchange Capacity.

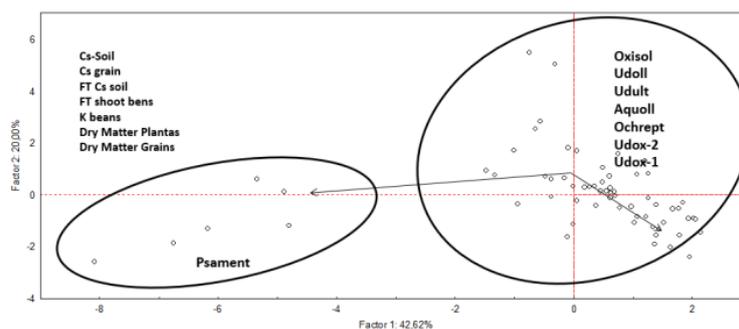


Fig 2. Principal component analysis of tropical and subtropical soils contaminated with ¹³⁷Cs and treated with rates of ¹³³Cs, evaluating the seven soil types with the application of different doses of cesium stable, observing that the soil Psamment has different behavior to the other soils evaluating the characteristics: Cs_{soil}: ¹³⁷Cs activity in soil; Cs_{grain}: ¹³⁷Cs activity in grains of beans; FT_{Cs soil}: ¹³⁷Cs transfer factor of tropical soils for bean; FT_{shoot beans}: ¹³⁷Cs transfer factor of tropical for shoot beans; Dry_{matter plants}; Dry_{matter grains}; K_{beans}: potassium concentrations in bean grains.

Table 3. Nutrients added to the soil before sowing.

Source	Element	Rates	Solution	Volume/Mass per pot (mL/g)
		mg kg ⁻¹	g L ⁻¹	
NaNO ₃	N	10	6.08	20
H ₃ BO ₃	B	0.5	0.28	20
CoCl ₂ .2H ₂ O	Co	0.05	0.01	20
CuSO ₄ .5H ₂ O	Cu	1	0.39	20
H ₂ MoO ₄	Mo	0.1	0.01	20
MnSO ₄ .H ₂ O	Mn	15	4.60	20
ZnSO ₄ .7H ₂ O	Zn	3	1.32	20
SINGLE SUPERPHOSPHATE	P	200		
	S	133		2.22 g commercial product

Table 4. Transfer factor of ¹³⁷Cs from soil to common bean plants for the four doses of stable Cs (0, 0,015 mmol L⁻¹ ¹³³Cs; 0,030 mmol L⁻¹ ¹³³Cs; 0,060 mmol L⁻¹ ¹³³Cs) ¹³⁷Cs applied in the seven soil types (Aquoll, Ochrept, Oxisol, Psamment, Udoll, Udox-1, Udox-2, Udull).

Soils	¹³³ Cs rates (mmol L ⁻¹)	¹³⁷ Cs transfer factor in bean				¹³⁷ Cs activity in soil
		SHOOT	SD*	GRAIN	SD*	
Aquoll	0.000	0.36 b	0.04	0.05 c	0.01	0.19 b
	0.015	3.06 ab	0.16	1.01 bc	0.10	2.52 ab
	0.030	3.13 ab	0.79	1.27 ab	0.16	2.19 ab
	0.060	4.98 a	0.86	2.10 a	0.32	5.71 a
Ochrept	0.000	0.17 b	0.03	0.08 b	0.01	0.19 b
	0.015	1.63 a	0.17	0.55 ab	0.11	1.22 ab
	0.030	1.94 a	0.47	0.72 ab	0.16	1.73 ab
	0.060	2.97 a	0.03	1.42 a	0.08	3.20 a
Oxisol	0.000	0.41 c	0.06	0.36 c	0.03	0.62 c
	0.015	2.96 b	0.19	2.07 bc	0.15	3.75 b
	0.030	4.20 b	0.20	3.44 ab	0.06	6.18 a
	0.060	6.39 a	0.20	4.38 a	0.80	6.41 a
Psamment	0.000	6.41 c	0.24	15.87 d	0.71	6.34 b
	0.015	26.88 b	1.58	50.50 c	1.03	25.27 a
	0.030	41.26 a	2.04	59.12 b	1.06	28.14 a
	0.060	44.68 a	0.59	73.62 a	1.01	31.06 a
Udoll	0.000	0.13 c	0.02	0.12b	0.01	0.25 c
	0.015	6.06 b	0.03	0.25 b	0.08	0.46 bc
	0.030	6.74 b	0.17	0.49 ab	0.12	1.27 ab
	0.060	9.53 a	0.28	0.98 a	0.09	1.94 a
Udox-1	0.000	0.05 b	0.02	0.02 a	0.01	0.06 c
	0.015	0.11 ab	0.02	0.04 a	0.01	0.17 b
	0.030	0.11 ab	0.01	0.05 a	0.01	0.20 b
	0.060	0.41 a	0.10	0.09 a	0.02	0.49 a
Udox-2	0.000	0.16 b	0.02	0.21 c	0.06	0.26 b
	0.015	2.12 ab	0.05	0.98 bc	0.01	2.96 ab
	0.030	4.02 ab	0.11	1.75 ab	0.15	5.47 a
	0.060	4.86 a	0.68	2.56 a	0.40	6.44 a
Udult	0.000	0.62 b	0.02	0.70 d	0.01	1.09 a
	0.015	6.06 ab	0.07	5.22 c	0.17	8.08 a
	0.030	7.74 ab	0.23	7.27 b	0.29	7.98 a
	0.060	11.53 a	0.49	8.87 a	0.45	7.55 a

SD* Standard deviation, Medium preceded by the same letter in the same column do not differ at 5% probability.

Table 5. Total dry matter and grain dry matter production, and potassium concentration in grain of common bean.

Soils	¹³³ Cs rates (mmol L ⁻¹)	Dry Matter				Concentration K in GRAIN	
		GRAIN	SD	TOTAL	SD		SD
Aquoll	0.000	6.23 b	0.81	5.97 b	0.66	8.55 b	0.50
	0.015	9.71 a	0.48	10.83 a	0.64	14.20 a	0.20
	0.030	5.31 b	0.92	4.08 b	0.53	13.50 a	0.70
	0.060	6.65 b	0.09	6.53 b	0.43	14.80 a	0.80
Ochrept	0.000	9.95 a	0.49	5.87 b	0.53	13.45 ab	0.20
	0.015	8.35 ab	0.60	9.86 a	0.97	12.34 b	0.70
	0.030	7.43 b	0.28	7.37 ab	0.36	14.20 ab	0.20
	0.060	7.83 ab	0.04	7.31 ab	0.35	15.00 a	0.20
Oxisol	0.000	8.99 a	0.28	6.73 ab	0.33	11.65 a	0.80
	0.015	8.44 a	0.02	6.71 ab	0.54	14.20 a	0.20
	0.030	10.19 a	0.94	8.35 a	0.57	13.55 a	0.90
	0.060	9.85 a	0.16	4.57 b	0.40	14.20 a	0.90
Psamment	0.000	7.64 a	0.69	2.16 a	0.49	11.30 a	0.80
	0.015	5.91 a	0.50	3.90 a	0.95	11.65 a	0.80
	0.030	9.15 a	0.37	2.65 a	0.57	10.95 a	0.40
	0.060	5.91 a	0.78	3.78 a	0.77	12.85 a	0.40
Udoll	0.000	11.24 a	0.26	10.01 ab	0.13	13.00 a	0.20
	0.015	10.88 a	0.68	9.81 ab	0.71	14.30 a	0.10
	0.030	11.41 a	0.20	12.30 a	0.63	13.20 a	0.40
	0.060	10.39 a	1.24	6.81 b	0.62	14.50 a	0.30
Udox-1	0.000	11.05 a	0.26	10.47 a	0.71	13.00 a	0.20
	0.015	9.58 a	0.48	11.35 a	0.20	14.40 a	0.40
	0.030	9.73 a	0.37	11.38 a	0.37	13.45 a	0.60
	0.060	9.17 a	0.71	12.79 a	0.92	14.00 a	0.40
Udox-2	0.000	6.74 b	0.15	9.11 a	0.08	12.50 a	0.70
	0.015	9.41 a	0.01	10.72 a	0.93	14.10 a	0.10
	0.030	9.73 a	0.85	11.49 a	0.03	14.60 a	0.20
	0.060	8.17 ab	0.23	9.63 a	0.92	14.50 a	0.10
Udult	0.000	10.70 a	0.64	7.51 a	0.62	12.45 b	0.20
	0.015	7.29 b	0.15	8.62 a	0.66	13.80 ab	0.20
	0.030	9.83 a	0.33	9.81 a	0.86	17.10 a	1.0
	0.060	7.12 b	0.24	8.32 a	0.52	15.40 ab	0.60

SD* Standard deviation. Medium preceded by the same letter in the same column do not differ at 5% probability

(1998) and Wässermann (2002), the transfer factor values obtained for carrot, radish, bean, corn, soybeans and tropical grasses were about 3 to 4 orders of magnitude higher than those found in temperate climate conditions. These values denote the existence of a great difference between temperate and tropical climate soils with regard to the bioavailability of ¹³⁷Cs to crops and point to the need for more studies concerning the behavior of ¹³⁷Cs in tropical soils. Availability and the transfer factor of ¹³⁷Cs depend on plant species and its development stage, soil type and its ionic composition, and climatic conditions. The main cations that interfere in ¹³⁷Cs sorption are potassium (K⁺), ammonium (NH₄⁺) and sodium (Na⁺), which competes with ¹³⁷Cs by specific adsorption sites with a ratio of 1:1000, 1:200 and 1:50000, respectively. This is due to the decrease in the degree of hydration of the alkali metal cation with the increase of atomic number, which makes Cs very competitive by specific exchange sites. Competition between ¹³⁷Cs and stable Cs for soil exchange sites occurs at a 1:1 ratio. Therefore, considering only a physicochemical characteristic, Cs can be considered the best element for desorption of ¹³⁷Cs from soil colloids. The application of higher levels of ¹³³Cs can increase the absorption of ¹³⁷Cs even more by plants. This could be an important factor for phytoremediation of soils.

Production factors

Dry matter production by common bean was affected by the dose of ¹³³Cs (Table 5). The application of ¹³³Cs did not affect the production factors evaluated in Psamment and Udox-1

soils. Considering total dry mass production, the Psamment, Udult, Udox-1, and Udox-2 soils did not present significant difference between doses of Cs compared to control. Aquol and Ochrept soils presented higher dry matter production at the 0.015 mmol L⁻¹ doses of ¹³³Cs. For the soils Oxisol and Udoll, the higher dry matter production was observed at 0.030 mmol L⁻¹ ¹³³Cs. The dose of ¹³³Cs and the control showed difference grain production in Oxisol, Psamment, Udoll and Udox-1. In three soil types such as Udult (dose 0.030 mmol L⁻¹), Aquol (dose 0.015 mmol L⁻¹) and Udox-2 (no difference among doses), the presence of ¹³³Cs increased the legume grain production. In Ochrept, the highest grain production was observed in the control treatment.

The doses of ¹³³Cs did not negatively affect the absorption of potassium and its concentration in the bean grains. There was no significant difference between control and the rates of ¹³³Cs in five soil types: Oxisol, Psamment, Udoll, Udox-1 and Udox-2. In the soils Ochrept, Aquoll and Udult, there was a higher K concentration in the grain with the application of ¹³³Cs, compared to the control treatment (Table 5). The ¹³⁷Cs is not an essential nutrient-element for plants and its excess can significantly induce cytotoxicity and inhibit plant growth (Ivshina et al., 2002). However, Cs natural concentrations in soil is too low to affect plant growth inhibition at high (White and Broadley 2000).

Multivariate analysis

Figure 1 shows the dendrogram resulting from cluster analysis by the hierarchical method, where two distinct groups were formed. G1 consists of the three doses (0.015,

0.030 and 0.060 mmol L⁻¹ of ¹³⁷Cs applied to the Psamment soil, representing the condition of this type of soil an isolated characterization with the application of the treatments. G2 was divided into two subgroups including the seven other soil types (Figure 2) it is only possible to state that the Udox-1 and Udol soils remained in all treatments in one of the subgroups of G2 (B); thus, they present greater similarities with each other in the 2 subgroups of G2. The first two eigenvalues were higher than 1, sufficient to describe the results obtained in the multivariate statistical analysis. The biplot (Figure 2) generated by the first two principal components (PC1 and PC2) retained 92.2% (63.3% by PC1 and 28.9% by PC2) of original variance and presented an excellent agreement with the results of the structure of groups in the dendrogram (Fig 1). The common bean cultivation in Psamment soil showed a higher specific activity of ¹³⁷Cs in grains and in transfer coefficient from soil to shoot growth and grains. In this soil, a reduced shoot growth, dry matter and grains production was observed. This soil is extremely young and sandy with low content of clay (6%) and soil organic matter (1.9%). It presented lower ¹³⁷Cs adsorption capacity, higher desorption of radiocesium with the addition of ¹³⁷Cs and a higher degree of remediation and transfer of ¹³⁷Cs to the plants.

Sandy particles are generally chemically inert because of their large size (Burger and Lichtscheidl, 2018). It is important to consider the role of clay fraction in adsorption of Cs due to its higher surface area per unit mass (Golmakani et al., 2008). The ¹³⁷Cs tends to be strongly retained according to the increase of soil clay content (Smolders and Tsukada, 2011).

The transference of ¹³⁷Cs to food chain mainly depends to the soil properties and the mobility of ¹³⁷Cs in the soil. Soils used in this study differed in degree of weathering, content and type of clay minerals. Iron and aluminum oxide components of tropical and subtropical soils complexed with organic compounds play important roles in the dynamics of Cs in soil (Chiang et al., 2010). The tropical soils generally show variable charges or pH-dependent charges being caused by clay fraction, which mainly consist of iron and aluminum oxides and 1:1 clay minerals. The influence of important soil properties on Cs transfer capacity is mainly due to the type of clay mineral and its quantity, organic matter content, pH, ammonium and potassium content (Livens and Loveland, 1988). Soils of which clay fraction has a low CEC enables the transference of Cs from the soil to the crops (Wässerman et al., 2002).

Materials and Methods

Plant material

The common bean variety was Carioca cultivar Pitoco, developed by the Agronomic Institute of Campinas, state of São Paulo, Brazil. This cultivar is characterized by early (cycle of 55–60 days) and small size (maximum of 50 cm), ideal for the development of experiments in greenhouse.

Soil types

Among 317 different soils in the State of São Paulo, 21 were selected for preliminary analyzes. The choice of these soils was due to differences in mineralogical composition, cation exchange capacity (CEC) and occurrence range in the State

of São Paulo, agronomic importance, and pedological classification. The selection of the eight soils used to perform the laboratory and pot experiments was based on the data related to the results of the mineralogical analysis by X-ray diffraction, results of potentiometric titration curves and pH effect on the adsorption of radioactivity, soil radioactivity, and its interception potential.

Soils used in the experiment were collected in the following cities of the state of São Paulo: Ribeirão Preto (Oxisol and Udox 2), Cravinhos (Psamment), São Simão (Ochrept, Aquoll and Udox-1) and Leme (Udult), SP, Brazil. Clay mineral composition was assessed with an X-ray diffractometer for all soil types (Table 1), and chemical analyses were performed (Table 2).

Setting up and conduction of the experiment

Pots containing 2 kg of sieved soil (5 mm) were used in the experiment. After sieving, soils were contaminated with radio-caesium (¹³⁷Cs) by addition of 50 mL of aqueous solution prepared with a specific activity of 1 KBq mL⁻¹. To promote a specific activity of about 25 KBq kg⁻¹, soil samples received the treatments and remained under incubation for 180 days. Before starting the greenhouse experiments, soils were again crumbled, fertilized (Table 4), and sown.

Four treatments of cesium chloride (0, 2.5, 5 and 10 mg L⁻¹ of Cs) and in a solution containing 100 mmol L⁻¹ of calcium chloride were used to observe the effect of stable Cs on radio-caesium adsorption. The mass of one mole of cesium chloride is 168.363 g and the atomic mass of the element cesium is 132.91 g. Thus, solutions correspond to concentrations of 0.015, 0.030 and 0.060 mmol L⁻¹ ¹³⁷Cs.

Dry matter analysis and chemical analysis of K in bean grains

The dry mass and grains were dried at 65°C and weighed, ground and stored in the same way as the plant samples. Subsequently, the yield of grains and dry matter in the cultivated plants was quantified. The analysis of potassium concentrations in bean grains was performed by nitric-perchloric digestion and determined by emission flame photometry.

Determination of ¹³⁷Cs transfer factor of tropical soils for common bean

Sample preparation

After drying, soil inside pots was crumbled, homogenized, sampled and passed through a 1 mm sieve. Subsequently, these samples were put into vials of 24.0 mm in outer diameter, weighed and taken to account. Aiming at determining ¹³⁷Cs transfer factor values from soil to bean, plant samples (shoot and grains) were dried in forced ventilation oven at 65°C to constant weight (48–72 hours), ground and packed into paper bags. Then, the sub-samples were placed in vials of 24.0 mm in outer diameter, weighed and conducted to count.

Counts conducted in soils and plants to study the effect of stable Cs

Samples were taken for counting in a sodium iodide detector

well type coupled with a single-channel electronic equipment, with potential difference application of 1000 V. Coarse gain was set to 100 times and the fine gain was 1.07. Using a sealed ^{137}Cs source, counts were performed between channels from 0.1 to 5.0 V at sub-ranges of 0.1 V for 0.4 minutes, being established the interval from 3.0 to 5.0 V to carry out the counts of samples containing ^{137}Cs . For plant samples, counts were performed for 10 minutes. For soil samples, counting time was one minute. At every 20 samples submitted to counting, background radiation detection was performed, subsequently deducted from the total counts.

Conversion of soils and plants into specific activity values

After counting, the soil and plant samples were dried again in an oven to reach a constant weight to remove water adsorbed by hygroscopicity which helps to correct the count data for activity values per kilogram of dry material. The standard used for plants was IAEA-156 (forage clover), whose specifications are 264 Bq kg⁻¹ in ^{137}Cs , the degree of uncertainty of 4%, reference date of 08/01/1986 and IAEA Laboratory Seibersdorf as certification laboratory. For ^{137}Cs count in soils, 10 secondary standards were used, which was adjusted to 1998 based on the standard Soil 6, also from IAEA. Conversion of counting values per minute to Bq.kg⁻¹ was performed by using the correlation between counts and activity existent in the standards (linear regression), with a correlation coefficient (R²) of 0.9997. Corrections were also carried out to the effect of detection geometry. The difference in relative efficiency for the minimum (0 mm) and maximum (50 mm) heights was 20.02%. Because the vial presented irregular shape (funneled neck), the equation that best expressed the relative efficiency as a function of height was not a straight line. Thus, two different equations were used as a function of sample height in the vial. By using a sealed ^{137}Cs source placed at a half depth of the detector's well, the absolute efficiency of equipment was obtained for the energy range of gamma radiation emitted by $^{137}\text{Ba}^m$ (661.70 keV), which allowed the calculation of measurement of detection and geometry efficiency.

Thus, the number of counts per minute obtained in the detector could be converted into a specific activity (becquerel per kilogram of dry material). From these results, the transfer factor was calculated by using Equation 1.

$$\text{TRANSFER FACTOR} = \frac{\text{ACTIVITY IN THE PLANT (Bq kg}^{-1}\text{ DRY MATTER)}}{\text{ACTIVITY IN THE SOIL (Bq kg}^{-1}\text{ DRY SOIL)}}$$

Equation 1. Transfer factor calculation of a radionuclide for plants

After mathematical simplification, transfer factor has as a unit kilogram of dry soil per kilogram of dry matter. It represents the dry soil mass with total activity corresponds to the activity in a unit mass of plant dry matter developed in that soil (Harada et al., 2014).

Statistical analysis

Initially, the individual effect of each variable was assessed. Seven soil types were used in the Oxisol, Udox, Psamment, Ochrept; Aquoll; Udox and Udult with the application of four doses of ^{133}Cs of 0, 5, 10 and 20 mg/pot in each treatment in a factorial design (soils x Cs rates). The statistical design was completely randomized, in a factorial scheme (7 soil types x 4 doses of ^{133}Cs) with three replicates.

The results with cesium levels for each soil type were submitted to statistical analysis using the statistical software SAS – System for Windows 6.11 (SAS, 1996). The treatment effect was assessed by the F test for analysis of variance and the means by the Tukey's test, which is multiple mean comparison test (P<0.05).

In addition, respecting the dependence structure contained in the original set of variables, two multivariate statistical methods were used: cluster analysis by a hierarchical method in an attempt to assess the structure of groups contained in an initial set of sample and principal component analysis. All multivariate analyses were performed after standardizing variables, in which each of them had zero mean and unit variance. Cluster analysis by hierarchical method (Sneath and Sokal, 1973) was processed with Euclidean distance as a similarity measure between accessions using eleven variables and with Ward algorithm as a group connection method. The structure of groups formed is presented in a graphic called dendrogram, which assisted identification of the groups of accessions. For identification of figures, the type of soil and doses were mentioned as follows: PSAMMENT-0 (control); PSAMMENT-15 (0.015 mmol L⁻¹ ^{133}Cs); PSAMMENT-30 (0.030 mmol L⁻¹ ^{133}Cs); PSAMMENT-60 (0.060 mmol L⁻¹ ^{133}Cs).

Principal component analysis allows to condense a greater amount of original information contained in p variables (in this study, p =6 : the activity of ^{137}Cs in the soil and ^{137}Cs transfer factor of the soil for the plant and for the grain, dry mass of the plants and grains and concentration of potassium in the bean grains) into new orthogonal latent variables called principal components, which are eigenvectors of the covariance matrix and linear combinations of original variables created with the eigenvalues of the covariance matrix of accessions (Hair, 2005). Thus, the initial set of eleven variables became characterized by new latent variables that enable identifying patterns contained in accessions and variables. Only the eigenvectors generated with eigenvalues higher than the unity are considered because they retain relevant original information (Kaiser, 1958). All statistical analyses were performed by using the software STATISTICA version 7.0 (Statsoft, 2004).

Conclusion

Psamment soil presented higher specific activity of ^{137}Cs and transfer coefficient to the plant and the bean grains. The addition of ^{133}Cs was effective in increasing transfer of ^{137}Cs to the plant regardless of soil type proving to be an effective practice for remediation of soils contaminated with radioactive Cs. Common bean appears to be efficient as a plant for use in phytoremediation. Soil application at ^{133}Cs did not reduce dry matter yield of the plant, except for grains in plants cultivated in Ochrept soil.

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