

Acid extraction as a predictive tool of Radiocaesium Interception Potential (RIP) in a worldwide scale

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Abstract. The extent of radiocaesium in soil is very important to appreciate the risk of its recycling by the vegetation and thus the risk of food chain contamination. An intrinsic soil parameter, the radiocaesium interception potential (RIP), could be used to measure this retention. In this study, we tested the possibility to predict the RIP starting from a simple acid extraction in widely different soils coming from the whole world and pertaining to various soil reference groups of the WRB/FAO world soil classification. Our results show that a simple acid extraction could be used as an operational test to estimate the RIP whatever the soil type.

1. INTRODUCTION

After atmospheric deposition, radiocaesium accumulates rapidly in the topsoil because of its selective adsorption on soil particles, largely ruled by weathered micaceous minerals [1]. The extent of ¹³⁷Cs retention in soil is very important in order to appreciate the risk of its recycling by the vegetation and the potential of foodchain contamination. Various experimental approaches were used to quantify that retention leading to different conceptual coefficients. One of them, the Radiocaesium Interception Potential (RIP – [2]), initially established to measure the radiocaesium fixation on soil particles, has the particularity to be an intrinsic soil parameter that can be rapidly determined in standardized experimental conditions.

The RIP method was initially used to characterize the ¹³⁷Cs adsorption capacity of temperate soils containing micas. In a first time, tropical and sub-tropical soils were largely overlooked. However, Joussein et al. [3] have showed that African volcanic soils devoid of micas could also selectively retain radiocaesium and thus have a RIP. In this study, we verify the relation between RIP and retention properties of radiocaesium. We also test the possibility to predict the RIP starting from a simple acid extraction.

2. MATERIALS AND METHODS

2.1 A worldwide soil collection

A collection of 88 surface soil samples from the International Soil Reference and Information Center (ISRIC, Wageningen) was used to measure ¹³⁷Cs retention properties and also RIP. These soils were chosen to be representative of major soil types in agriculture on a worldwide scale and to cover different climatic zones. These soils came from 24 lands and pertained to 17 different soil reference groups according to the World Reference Base for Soil Resource [4].

2.2 RIP measurements

RIP was measured in a well defined ionic scenario according to a procedure adapted from [5]. One g of each soil sample (3 replicates) was introduced in a dialysis bag with 5 ml of a KCl 0,5 M-CaCl₂ 10⁻⁴ M equilibration solution (Potassium Adsorption Ratio (PAR) = 0,05 mmol^{1/2} L^{-1/2}). The solution was changed 10 times during 7 days. During equilibration, all PE bags were agitated 2 hours each 12 hours. Each dialysis bag was then transferred in a 100 ml PE bag filled with 95 ml of the KCl-CaCl₂ solution labeled with carrier-free ¹³⁷CsCl. These bags were shaken 2 hours each 12 hours. After 5 days, aliquots of 20 ml were taken and ¹³⁷Cs activity was determined by gamma-counting.

The RIP ($\mu\text{mol} \cdot \text{g}^{-1}$) was defined by the relation:

$$\text{RIP} = K_C * [\text{FES}] = K_D^{\text{Cs}} * [\text{K}^+] \quad (1)$$

where [FES] is the capacity of Frayed Edge Sites with high adsorption selectivity for Cs⁺, K_C is the ¹³⁷Cs-K selectivity coefficient on these sites, K_D^{Cs} is the ¹³⁷Cs solid-liquid distribution coefficient and [K⁺] is the concentration of K in solution.

2.3 Acid extraction

A sub-sample of the 88 soils was also contaminated by hand shaking. In order to quantify ¹³⁷Cs retention in the long term, each soil sample was submitted to 10 drying-wetting cycles in order to simulate the ¹³⁷Cs ageing in soil [6]. The fraction of acid extractable ¹³⁷Cs was determined following ¹³⁷Cs desorption with HCl 10⁻¹ M during 24 hours.

3. RESULTS AND DISCUSSION

3.1 Range of measured RIP values

The soil collection we used involved a large set of soil groups with very diverse properties and was found to cover a maximum range of adsorption selectivity for radiocaesium in terms of RIP. In fact, the measured RIP values extended on five orders of magnitude. These RIP values ranged from 1.8 $\mu\text{mol} \cdot \text{g}^{-1}$ in a Malaysian humic podzol to 13343 $\mu\text{mol} \cdot \text{g}^{-1}$ in a Nicaraguan ferric luvisol, which are respectively the smallest and the highest RIP values never found for a soil to our knowledge. Figure 1 represents the confidence interval ($\alpha = 0.05$) and optima of RIP for each major reference soil group represented in our collection. Obviously only 3 groups of soil were characterized by a very low RIP: Podzols, Andosols and Ferralsols.

3.2 Relation between RIP and ¹³⁷Cs retention in the soil

Figure 2 presents the fraction of acid-extractable radiocaesium (AER) as a function of RIP values for the different soils considered. The desorption yields decreased with increasing RIP, the decrease being particularly important in acid extraction for RIP values < 2000.

Results shown in Figure 2 implied the existence of a relationship between RIP and AER and thus confirmed the link between the RIP and the radiocaesium retention in soil. Using transformations to normalize at once the RIP and the AER, we observed effectively a highly significant (P-Value < 0.001) linear relation between the square root of RIP and the logarithm of AER. This relationship, shown in Figure 3, is characterized by a correlation coefficient of R = -0.905 (N = 88).

According to the results of the linear regression, the RIP could be estimated from the equation:

$$\text{RIP} = (-31.701 * \log(\text{AER}) + 58.886)^2 \quad (2)$$

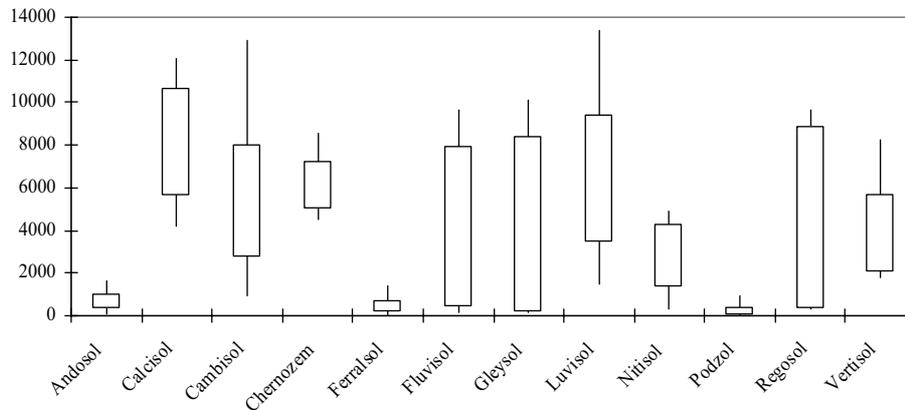


Figure 1. Confidence interval and optima of RIP [$\mu\text{mol} \cdot \text{g}^{-1}$] for major reference soil groups.

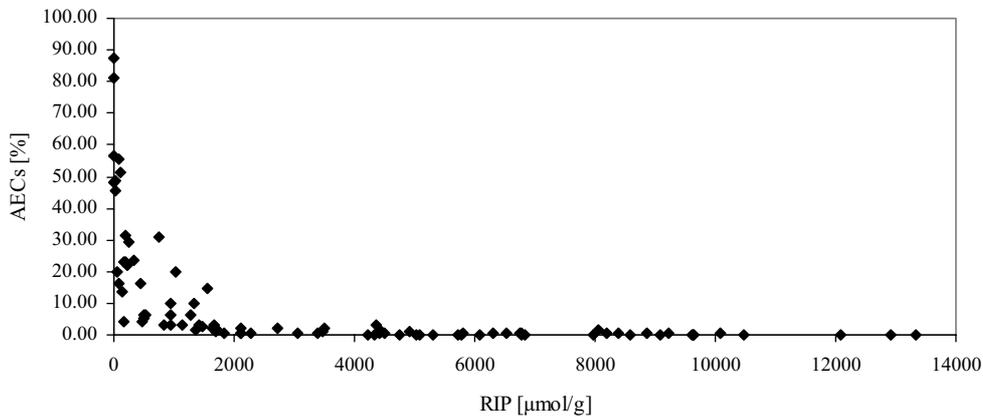


Figure 2. Relation between RIP [$\mu\text{mol} \cdot \text{g}^{-1}$] and percentage of acid-extractable ^{137}Cs .

Comparison of measured and modeled RIP values resulted in a determination coefficient R^2 of 0.736 ($N = 88$). We defined the error percentage (% error) as the ratio:

$$(\text{RIP}_{\text{predicted}} - \text{RIP}_{\text{observed}}) / \text{RIP}_{\text{observed}} * 100 \quad (3)$$

A positive % error meant an over-estimation of the RIP while a negative % error resulted in an underestimation of the RIP. The % error goes from -87% to 764% . The largest error percentages were observed in the lowest range of RIP. Indeed, the % error goes from -87% to $+764\%$ for the range of $\text{RIP} < 2000 \mu\text{mol} \cdot \text{g}^{-1}$ while it goes from -65% to $+123\%$ for the range of $\text{RIP} > 2000 \mu\text{mol} \cdot \text{g}^{-1}$. This finding could be explained by the fact that below a RIP of $2000 \mu\text{mol} \cdot \text{g}^{-1}$, the quantities of radiocaesium desorbed by the HCl solution were higher and more variable than for a RIP above $2000 \mu\text{mol} \cdot \text{g}^{-1}$.

The range of error percentages which characterize 50% of the predicted RIP values may be defined by the interval between the first and the third quartile. This range of % error goes from -29 to $+67$. When considering only the RIP values higher than $2000 \mu\text{mol} \cdot \text{g}^{-1}$, the interval of % error is reduced between -31 and $+26\%$. However, this interval increased from -21 to $+128\%$ for the RIP less than $2000 \mu\text{mol} \cdot \text{g}^{-1}$. That would mean that deducing a realistic estimation of RIP whatever the soil

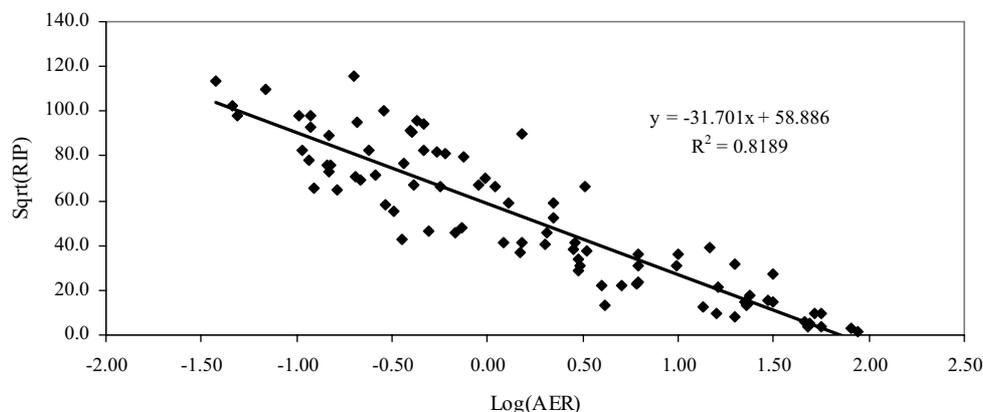


Figure 3. Plot of the square root of RIP as a function of log(AER).

properties could be achieved through a simple acid extraction. All these results must be confirmed by an independent data base.

4. CONCLUSIONS

The proposed scale of RIP values was higher than those previously published. It was shown to embrace all possible cases of agricultural soils contamination including those areas, and especially the developing countries, where data is scarce or missing. Our results showed for the first time that a simple acid extraction could be used as an operational test to estimate the RIP whatever the soil type and the origin of the soil.

A next step will imply the link between RIP, AER and ^{137}Cs transfer to plant.

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