

## Desorption of $^{137}\text{Cs}^+$ from mosses

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*Abstract:* Mosses are biomonitors that accumulate large amounts of various pollutants, including radionuclides. In this work we investigated the possibility of  $^{137}\text{Cs}$  extraction from mosses, as well as the significance of species specificity on the efficiency of  $^{137}\text{Cs}$  desorption. Salt and acid solutions were used as extraction media. It was shown that a 5 % solution of both ammonium oxalate and phosphoric acid was able to desorb 81.8 % of  $^{137}\text{Cs}^+$  from *Homalothecium sericeum*, which was 39.9 % more than desorption from water. At the same time, most of the desorbed  $^{137}\text{Cs}^+$  was incorporated in crystals that precipitated from the solution. An interspecies difference in respect to  $^{137}\text{Cs}^+$  desorption was noticed.

*Keywords:* moss,  $^{137}\text{Cs}^+$ , extraction.

### INTRODUCTION

Mosses have certain characteristics that meet the specific requirements for a biological monitor. They spread over large geographical ranges, allowing comparison of the pollutant content in ecosystems from diverse regions. Their morphology does not vary with season, the accumulation occurs throughout the year and they have considerable longevity which has led to their use as long-term integrators of atmospheric deposition.<sup>1</sup> Mosses have the ability to accumulate metals to levels that severalfold exceed their expected physiological needs. This characteristic is explained by the ion-exchange properties of the plant, as well as particular plant surface, the structure and roughness of which facilitate the interception and retention of metals, including radionuclides.<sup>2</sup> In addition, mosses have morphological features that enhance metal uptake. They do not have a well developed cuticle, thus minimizing any physical resistance to the entry of contaminants into the plant interior. Mosses, unlike higher plants, do not have a well developed root structure. They are strongly dependent on material falling through wet and dry deposition onto the surface.<sup>1</sup> In the case of release of radionuclides into the atmosphere, the concentrations in mosses may reach potentially toxic levels without apparent damage to the species.<sup>3</sup>

After the Chernobyl accident in 1986 an increased level of radioactive cesium in the environment was detected. Soil activities of  $^{137}\text{Cs}$  in excess of  $30 \text{ Bq cm}^{-3}$  still persist over large areas in Russia and the Ukraine.<sup>4</sup> There is considerable interest in remediating

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sites contaminated by Cs radioisotopes and, because of the lack of alternative technologies that are practicable, effective and affordable, the use of plants to extract and concentrate Cs is one option.<sup>5</sup> The other side of the problem is an understanding of the mechanism of Cs uptake, distribution, binding to cellular structures and release. There have even been attempts to use special cloth-monitors, impregnated with resinous material, that resemble biomonitors.<sup>6</sup> Therefore, there is both interest and necessity to understand the mechanism of cesium accumulation in biomonitors. In this work the specificity of  $^{137}\text{Cs}$  binding in mosses was investigated, as well as the strength of those bonds using aqueous solutions of salts and acids. Four moss species were analysed and compared.

#### EXPERIMENTAL

The extraction of  $^{137}\text{Cs}^+$  was carried out with twelve different types of solutions, including an investigation of the effect of increasing concentrations of solutes (1 %, 2 % and 5 %). Dry moss samples (15 g) were treated with the following fluids ( $3 \times 300$  mL): distilled water ( $\text{H}_2\text{O}$ ), and aqueous solutions of: ammonium chloride ( $\text{NH}_4\text{Cl}$ ), sodium chloride ( $\text{NaCl}$ ), potassium chloride ( $\text{KCl}$ ), cesium chloride ( $\text{CsCl}$ ), ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ), ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ), ammonium oxalate ( $(\text{NH}_4)_2(\text{COO})_2$ ), hydrochloric acid ( $\text{HCl}$ ), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), boric acid ( $\text{H}_3\text{BO}_3$ ) and phosphoric acid ( $\text{H}_3\text{PO}_4$ ). After each extraction step (20 °C, 24 h) the solutions were filtered and the samples were dried at room temperature. Their masses and specific radioactivities were measured (gammaspectrometer CANBERRA ORTEC, 8192 channels; NaI crystal). The resolution power was 6.8 % and the efficiency of counting was 8.7 %. The experiments were performed on *Homalothecium sericeum* (specific activity 1000 Bq kg<sup>-1</sup>), *Hypnum cupressiforme* (2350 Bq kg<sup>-1</sup>), *Leskella nervosa* (1815 Bq kg<sup>-1</sup>) and *Hylocomium splendens* (1780 Bq kg<sup>-1</sup>).

#### RESULTS AND DISCUSSION

The efficiency of  $^{137}\text{Cs}^+$  extraction with each salt and acid solution is presented in Table I. In the first part of the experiment the possibility of ion-exchange between  $^{137}\text{Cs}^+$  and the cations from the first analytical group ( $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ ) was examined. The applied solutions were chlorides and the moss *H. sericeum* was used as a model system. The effect of specific extraction was compared with a simple solution of  $^{137}\text{Cs}^+$  in water, which extracted 41.9 %  $^{137}\text{Cs}^+$  from *H. sericeum*, 45.7 % from *H. cupressiforme*, 22.4 % from *L. nervosa* and 28.7 % from *H. splendens*. The most efficient extractions were achieved by applying 5 % aqueous solutions and ammonium chloride as the solute. The desorption effect, when 5 % ammonium chloride was used, was a 21.9 % increment for *H. sericeum*. After the third extraction step, the activity level of  $^{137}\text{Cs}$  in the moss residue reached a constant value, *i.e.*, the next extraction did not desorb more cesium.  $\text{NH}_4^+$  proved to be the most suitable cation to substitute  $^{137}\text{Cs}^+$  in moss, followed by  $\text{Na}^+$  (20.2 % increment).

The influence of the anion was further tested. Solutions of inorganic and organic ammonium salts were assayed as extractants. The greatest increment was achieved with 5 % ammonium oxalate solution (33.0 %), followed by ammonium chloride. When inorganic acids were used for desorption the most successful was 5 % phosphoric acid (30.0 % more  $^{137}\text{Cs}^+$  was extracted than in distilled water), followed by sulphuric acid (24.2 %). When hydrochloric and sulphuric acids were the extraction media, significant decreases of plant mass also occurred (approximately 16–17 %). As these two acids are strong, they probably caused acid hydrolysis of plant material.

TABLE I. The efficiency of  $^{137}\text{Cs}^+$  extraction with salt and acid solutions (the percentage increment of a specific solution compared to water)

Solution	Conc. %	<i>H. sericeum</i>	<i>H. cupressiforme</i>	<i>L. nervosa</i>	<i>H. splendens</i>
$\text{NH}_4\text{Cl}$	1	8.9	–	–	–
	2	18.6	–	–	–
	5	21.9	19.0	17.3	21.4
NaCl	1	12.2	–	–	–
	2	13.4	–	–	–
	5	20.2	11.3	14.7	18.2
KCl	1	14.1	–	–	–
	2	15.5	–	–	–
	5	15.9	8.5	7.6	13.4
CsCl	1	13.5	–	–	–
	2	15.0	–	–	–
	5	16.4	7.7	5.9	14.4
$(\text{NH}_4)_2\text{SO}_4$	5	10.3	8.4	7.9	9.8
$\text{CH}_3\text{COONH}_4$	5	11.7	9.3	8.8	10.7
$(\text{NH}_4)_2(\text{COO})_2$	5	33.0	26.0	25.3	30.1
HCl	1	9.1	–	–	–
	2	11.3	–	–	–
	5	19.4	22.0	10.6	11.4
$\text{H}_2\text{SO}_4$	1	6.3	–	–	–
	2	17.2	–	–	–
	5	24.2	14.2	11.3	9.2
$\text{H}_3\text{BO}_3$	1	7.6	–	–	–
	2	12.1	–	–	–
	5	14.1	16.4	7.9	13.6
$\text{H}_3\text{PO}_4$	1	11.9	–	–	–
	2	17.4	–	–	–
	5	30.0	32.1	27.0	33.1
$(\text{NH}_4)_2(\text{COO})_2 + \text{H}_3\text{PO}_4$	5 + 5	39.9	32.6	32.8	37.5

In order to determine the specificity of moss species in respect to  $^{137}\text{Cs}^+$  extraction, the experiment was carried out with three more species: *H. cupressiforme*, *L. nervosa* and *H. splendens*. As can be seen in Table I, radiocesium in the examined species exhibited different behaviour upon extraction, although a general trend was kept. It is obvious that biodiversity is another variable that must be taken into consideration when discussing the type and strength of  $^{137}\text{Cs}^+$  binding. The common feature of all examined species was that they most readily released  $^{137}\text{Cs}^+$  in ammonium oxalate and phosphoric acid solutions.

The effect of 5 % ammonium oxalate ranged from 33.0 % (*H. sericeum*) to 25.3 % (*L. nervosa*) and that of 5 % phosphoric acid from 33.1 % (*H. splendens*) to 27.0 % (*L. nervosa*).  $^{137}\text{Cs}^+$  in *H. sericeum* and *H. splendens* seemed to be the most easily exchangeable. The results shown in Table I demonstrate that in some solutions (e.g., potassium chloride, cesium chloride, hydrochloric acid) there was significant interspecies difference. This variation in  $^{137}\text{Cs}^+$  behaviour is most probably due to the specific type of chemical interaction between radiocesium and the binding sites in each moss.

As ammonium oxalate and phosphoric acid appeared to be the most powerful in terms of  $^{137}\text{Cs}^+$  removal from moss, this combination was tested further. The mixture which contained 5 % ammonium oxalate and 5 % phosphoric acid exhibited an additional potential for  $^{137}\text{Cs}^+$  extraction. After three successive steps the amount of extracted  $^{137}\text{Cs}^+$  ranged from 81.8 % of the initial radiocesium in *H. sericeum* (39.9 % more than in pure water) to 55.2 % in *H. cupressiforme* (32.6 %). The final mass of the moss was only slightly decreased after this procedure (approximately 5 %), indicating that the desorption was achieved without significant destruction of plant structure. The combination of ammonium oxalate and phosphoric acid in one solution led to unexpected crystallization. At room temperature this phenomenon was only initiated and it was fully expressed after cooling. The crystallization occurred in the chemical mixture regardless of the moss extraction. Transparent, colourless crystals sedimented from the solution upon storage at 4 °C for 24 h. These crystals contained  $^{137}\text{Cs}^+$  (approximately 65–79 % of the total amount extracted). Therefore, effect of  $^{137}\text{Cs}^+$  desorption from mosses was amplified by the combination of ammonium oxalate and phosphoric acid. The incorporation of  $^{137}\text{Cs}^+$  into the crystal lattice was a new phenomenon, which made the combined system superior to those that contained only one chemical. The crystals that were formed could not be identified by crystallographic analysis using published data,<sup>7</sup> but ammonium phosphates (including known hydrates) were excluded. Ammonium dodecamolybdo-phosphate (AMP) is the most frequently used inorganic exchanger for determination of cesium in water<sup>8</sup> and it is possible that some kind of heteropolyacid was formed in this experiment as well.

Cesium has chemical properties similar to potassium. There is no known role for cesium in plant nutrition, but excessive cesium can be toxic to plants. Physiological studies demonstrated that  $\text{K}^+$  and  $\text{Cs}^+$  competed for influx, suggesting that the influx of these cations is mediated by the same mechanism(s).<sup>9</sup> Plant membrane transport has frequently been reviewed in recent years.<sup>10</sup> Ion channels are integral components of all membranes and they can be viewed as dynamic transport systems coupled *via* membrane electrical activities.<sup>11</sup> Many  $\text{K}^+$  channels are also permeable to other monovalent cations, like  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{NH}_4^+$ ,  $\text{Tl}^+$ .<sup>12,13</sup> The sizes of these cations (0.19–0.30 nm) are similar to that of  $\text{K}^+$  (0.27 nm) and  $\text{K}^+$  channels conduct these ions at different rates.<sup>13</sup> The selectivity among the ions is thought to occur by different affinities at binding sites within the pore and different rates of translocation to and from these sites.<sup>13</sup>

## CONCLUSION

<sup>137</sup>Cs is located in mosses in a water-soluble form, as one or more salts or metal complexes. <sup>137</sup>Cs<sup>+</sup> can be exchanged with all cations from the first analytical group and it can form salts with solvated inorganic and organic anions. Different moss species exhibited distinct behaviour in the analysed solutions. Thus, the structural and chemical specificities of each species play a role in determining the strength of <sup>137</sup>Cs<sup>+</sup> binding. Incorporation of the extracted <sup>137</sup>Cs<sup>+</sup> into a crystal lattice allows more efficient removal of radiocesium from the moss, without destruction of the plant itself.

## ИЗВОД

ДЕСОРПЦИЈА <sup>137</sup>Cs<sup>+</sup> ИЗ МАХОВИНА

СНЕЖАНА ДРАГОВИЋ, СЛОБОДАНКА СТАНКОВИЋ и ОЛГИЦА НЕДИЋ

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Маховине су биомонитори који акумулирају велику количину различитих загађивача, укључујући и радионуклиде. У овом раду испитивали смо могућност екстракције <sup>137</sup>Cs из маховина, као и значај специфичности биљне врсте за ефикасност десорпције <sup>137</sup>Cs. Као екстракциони медијуми коришћени су раствори соли и киселина. Показано је да се 5 % раствором амонијум-оксалата и фосфорне киселине може екстраховати 81,8 % <sup>137</sup>Cs<sup>+</sup> из врсте *Homalothecium sericeum*, што је 39,9 % више у односу на екстракцију дестилованом водом. Највећи део раствореног <sup>137</sup>Cs<sup>+</sup> је био уграђен у кристал добијен таложењем из раствора. Уочене су разлике између врста испитиваних маховина у погледу десорпције <sup>137</sup>Cs<sup>+</sup>.

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