

# Phytoremediation of Radiocesium-Contaminated Soil in the Vicinity of Chernobyl, Ukraine

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Remediation of soil contaminated with <sup>137</sup>Cs remains one of the most challenging tasks after the Chernobyl 1986 accident. The objectives of this research were to (1) identify extractants that may be used to solubilize <sup>137</sup>Cs in soil solution, (2) study the effect of soil amendments on <sup>137</sup>Cs accumulation by plants, and (3) evaluate the applicability of phytoextraction for environmental restoration of soil contaminated with <sup>137</sup>Cs. The availability of <sup>137</sup>Cs to the plants in Chernobyl soil was limited, because this radionuclide was tightly bound to exchange sites of soil particles or incorporated into the crystalline structure of primary and secondary minerals. Out of 20 soil amendments tested to increase <sup>137</sup>Cs desorption/solubility in the soil, ammonium salts were found to be the most practical soil amendment that can potentially increase <sup>137</sup>Cs bioavailability. Among the screened plants, Amaranth cultivars had the highest <sup>137</sup>Cs accumulation. Three sequential crops of Indian mustard grown in one vegetation season at the experimental plot resulted in a small decrease of <sup>137</sup>Cs specific activity within the top 15 cm of soil. Further improvements are necessary to make phytoremediation technology a feasible option for restoration of <sup>137</sup>Cs-contaminated territories.

## Introduction

Radioactive contamination of the environment is a problem humanity cannot afford to ignore. The total activity of all radioactive material released in the Chernobyl Nuclear Power Plant, Ukraine (ChNPP) accident is presently estimated to have been  $3.7 \times 10^{18}$  (1) to  $12 \times 10^{18}$  Bq (2). The presence of radionuclides in soil and water often jeopardizes ecosystem stability and poses serious risk to human health (3, 4).

A variety of environmental restoration methods for radioactively contaminated sites have been developed and used with some success (5). However, these technologies may be prohibitively costly if large areas of land or volumes of water are involved. Hence, there is a great need for reliable and inexpensive technologies that are capable of reducing radiation to environmentally acceptable levels. Such tech-

nologies might also be effectively used in pollution prevention and waste reduction programs.

Recently, significant attention has been drawn to phytoremediation, an emerging technology using plants to remove pollutants from the environment. Phytoremediation could provide an affordable way to restore the economical value of contaminated land. This technology employs a plant's natural ability to concentrate essential and nonessential elements in their tissues. Plants are not capable of distinguishing isotopes of the same element. Radioactive isotopes such as <sup>14</sup>C, <sup>18</sup>O, <sup>32</sup>P, <sup>35</sup>S, <sup>64</sup>Cu, and <sup>59</sup>Fe are widely used as tracers in plant physiology and biochemistry. In some cases, plants react analogously to ions with similar physicochemical properties. It is known that Sr is an analogue of Ca in living organisms (6), and the effect of K on <sup>137</sup>Cs accumulation in plants is well documented (7). The ability of plants to tolerate elevated levels of heavy metals and to accumulate them to unusually high levels has been shown in a number of different plant species (8, 9). However, the value of metal-accumulating plants for environmental remediation has been fully realized only recently (10–13).

Several subsets of phytoremediation technology are being developed (14). The most advanced are phytoextraction (15, 16)—the use of metal-accumulating plants, which can transport and concentrate metals from the soil in the roots and above ground shoots; rhizofiltration (17)—the use of plant roots to absorb, concentrate, and precipitate toxic metals from aqueous streams; and phytostabilization—the use of plants to eliminate the bioavailability of toxic metals in soils. The objectives of this research were to (1) identify extractants that may be used to solubilize <sup>137</sup>Cs in soil solution, (2) study the effect of soil amendments on <sup>137</sup>Cs accumulation by plants, and (3) evaluate the applicability of phytoextraction for environmental restoration of soil contaminated with <sup>137</sup>Cs.

## Materials and Methods

**Extraction of <sup>137</sup>Cs from Soil.** Soil for this study was collected from the top 15 cm at the experimental plot within the Chernobyl Exclusion Zone in Chernobyl, Ukraine. The soil was air-dried in the laboratory, sieved to 2 mm, mixed thoroughly, and then analyzed for <sup>137</sup>Cs activity. The soil was classified as a sod podzolic with a loamy-sand texture derived from sandy fluvio-glacial deposits. The soil had 2.5% organic matter, pH<sub>KCl</sub> 5.5, and an electric conductivity at 0.20 dS m<sup>-1</sup>.

Solubilization of <sup>137</sup>Cs from the Chernobyl soil was studied in batch experiments. A soil sample of 133 g was placed in a plastic bottle and then mixed with 1 L of a treatment solution. These suspensions were sealed and placed on an end-over-end shaker at room temperature for 24 h. The slurry was filtered through cheesecloth filter, and the filtrate was centrifuged at 2000 rpm for 12 min. The resulting supernatant was used for <sup>137</sup>Cs activity determination. Ammonium acetate (0.1 M) was used to successively extract the soil sample with gradually increasing equilibration times (1, 3, 7, and 14 days). Three replicates were used for all treatments.

Different surfactants (Triton X-100, triethanolamine hydrochloride, hydroxylamine hydrochloride, sodium lauryl sulfate, sodium laurate, Calgon), organic (oxalic acid, citric acid) and inorganic (HCl, HNO<sub>3</sub>) acids, and salts with cations similar to Cs in physicochemical properties (NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, CsNO<sub>3</sub>, KCl, RbCl, FeCl<sub>3</sub>·6H<sub>2</sub>O) were used to desorb <sup>137</sup>Cs from the soil. All chemicals were obtained from Sigma, U.S.A.

**Field Experiments.** An experimental plot was established on the heavily contaminated soil at the Northwest border of Chernobyl, Ukraine, approximately 10 km south of the ChNPP

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TABLE 1. Desorption of <sup>137</sup>Cs from the Chernobyl Soil<sup>a</sup>

treatment solution	concn of active ingredient	specific activity (10 <sup>-12</sup> Ci L <sup>-1</sup> )	% of initial activity removed
deionized water	N/A	28 ± 6	0.3
Triton X-100	0.5%	28 ± 0.3	0.3
triethanolamine hydrochloride	1%	31 ± 3.6	0.3
hydroxylamine hydrochloride	0.1 M	41 ± 3.1	0.4
sodium lauryl sulfate	1%	53 ± 0.5	0.5
sodium laurate	1%	142 ± 6	1.3
oxalic acid	1 M	144 ± 18	1.3
citric acid	1 M	190 ± 9	1.8
sodium lauryl sulfate, citric acid	1%, 1M	195 ± 11	1.8
hydrochloric acid	1.0 N	268 ± 17	2.5
ammonium acetate	0.1 M	435 ± 66	4.1
calgon	1%	463 ± 13	4.3
ammonium nitrate	0.1 N	492 ± 13	4.6
potassium sulfate	0.1 M	496 ± 21	4.6
cesium nitrate	0.01 M	530 ± 12	5.0
potassium nitrate	0.5 N	615 ± 63	5.7
hydrochloric acid, potassium chloride, ferric chloride	0.1 M each	733 ± 31	6.9
ammonium sulfate	0.1 M	909 ± 25	8.5
rubidium chloride	1 M	1170 ± 67	10.9
nitric acid	5 M	2220 ± 9	20.7

<sup>a</sup> A soil sample of 133 g was placed in a plastic bottle and mixed with 1 L of a treatment solution. The bottles with the soil/extractant suspension were sealed and placed on an end-over-end shaker at room temperature for 24 h. The slurry was filtered through cheesecloth filter, and the filtrate was centrifuged at 2000 rpm for 12 min. Average ± standard deviation of three replicates is shown in the table.

fourth reactor that was damaged in 1986. The soil within the plot was classified as a sod podzolic with a loamy-sand texture derived from sandy fluvio-glacial deposits. The soil had pH<sub>KCl</sub> of 5.5, 2.5% organic matter content, and electric conductivity of 0.20 dS m<sup>-1</sup>. Soil fertility was characterized by nitrogen (N) 96 kg ha<sup>-1</sup>, phosphorus (P<sub>2</sub>O<sub>5</sub>) 30 kg ha<sup>-1</sup>, potassium 28 kg ha<sup>-1</sup>, Mn 29.1 mg kg<sup>-1</sup>, Cu 1.4 mg kg<sup>-1</sup>, and Zn 3.3 mg kg<sup>-1</sup>. To improve soil fertility at the experimental plot, lime (5000 kg ha<sup>-1</sup>), ammonium nitrate (100 kg ha<sup>-1</sup>), triple super phosphate (288 kg ha<sup>-1</sup>), potassium chloride (190 kg ha<sup>-1</sup>), and ammonium sulfate (190 kg ha<sup>-1</sup>) were applied to the soil surface and incorporated to a depth of 15 cm prior to planting. The bioaccumulation coefficient, calculated as a ratio of <sup>137</sup>Cs specific activity in the plant versus <sup>137</sup>Cs specific activity in the soil, was used to evaluate <sup>137</sup>Cs phytoextraction.

**Screening of Plants for <sup>137</sup>Cs Accumulation.** A portion of the experimental plot was subdivided into 2 m × 2 m blocks with 1 m borders and was used to screen high biomass crops for <sup>137</sup>Cs accumulation. A variety of Amaranth species (*Amaranthus bicolor* L., *A. caudatus* L., *A. cruentus* L., *A. hybridus* L., *A. retroflexus* L.), Indian mustard (*Brassica juncea* (L.) Czern.), corn (*Zea mays* L.), peas (*Pisum sativum* L.), Jerusalem artichoke (*Helianthus tuberosus* L.), sunflower (*Helianthus annuus* L.), and sunflower x Jerusalem artichoke hybrid (*H. tuberosus* L. x *H. annuus* L.) were used in the screening. Plants were seeded by hand in rows and were weeded and watered as needed. After 9 weeks, plants were harvested, air-dried, and analyzed for <sup>137</sup>Cs activity.

**<sup>137</sup>Cs Compartmentalization in Plants.** To study the radiocesium distribution within the plant, in addition to harvesting above-ground parts, the roots of corn, sunflower, and Indian mustard were dug out, washed in tap water, air-dried, and analyzed for <sup>137</sup>Cs activity.

**Impact of Soil Amendments on <sup>137</sup>Cs Accumulation by Plants.** A portion of the experimental plot was subdivided into 2 m × 2 m blocks with 1 m borders and was used to evaluate the effect of soil amendments on <sup>137</sup>Cs accumulation by plants in their above-ground biomass. Triplicates were used in each treatment. Soil amendments were applied either before planting, when no plant toxicity was expected, or 1 week before harvest, when the amendments may interfere with plant growth. To the plots with Indian mustard and sunflower, the following amendments were added: (a) excess

of potassium (incorporated to the soil before planting at the rate of KCl – 1150 kg ha<sup>-1</sup> and KNO<sub>3</sub> 3000 kg ha<sup>-1</sup>); (b) potassium salt of DTPA (diethylenetrinitriropentaacetic acid, 0.5 M solution sprayed on the soil surface 1 week before harvesting at the rate 1 L m<sup>-2</sup>); (c) potassium salt of EDTA (ethylenedinitrirotetraacetic acid, 0.5 M solution sprayed on the soil surface 1 week before harvesting at the rate 1 L m<sup>-2</sup>); and (d) biogumus (organic fertilizer, incorporated to the soil before planting at the rate 6250 kg ha<sup>-1</sup>). The effect of NH<sub>4</sub><sup>+</sup> on <sup>137</sup>Cs accumulation in plants was also tested on *A. retroflexus* cv. myronivka. One week before harvest (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or NH<sub>4</sub>NO<sub>3</sub> was applied to the test plots as a water solution at the rate of 1500 kg ha<sup>-1</sup>.

**Phytoextraction Field Experiment.** A 40 m<sup>2</sup> plot was established for the phytoextraction (defined as the removal of metals from soil by plants) trial. Soil was tilled to 15 cm depth. Indian mustard was planted by hand in rows spaced 12.5 cm apart at a depth of 1.5 cm. A press wheel was used to firm the soil around the seed. After 6 weeks, all above-ground biomass was harvested, and the plot was then tilled and replanted. Three sequential Indian mustard crops were grown during one vegetation period. Ammonium nitrate (50 kg ha<sup>-1</sup>), triple super phosphate (144 kg ha<sup>-1</sup>), potassium chloride (100 kg ha<sup>-1</sup>), and ammonium sulfate (100 kg ha<sup>-1</sup>) were applied to the soil surface and incorporated to a depth of 15 cm prior to planting the second and third crops. The specific activity of <sup>137</sup>Cs was measured at 14 sampling points in the soil at the beginning of the experiment and in the soil and plants after each crop. All harvested biomass was removed from the plot.

**Determination of Radionuclides.** Soil and plant samples were air-dried prior to analyses. Plants were cut to <2 cm. The activity of <sup>137</sup>Cs in the soil and plants was determined directly by gamma-spectrometry using a HPGe detector, coupled to a multichannel. The efficiency of the system was 30% as determined with a <sup>152</sup>Eu standard source. The systems were calibrated with soils and plant material containing known amounts of <sup>137</sup>Cs in appropriate standard containers. All results were decay corrected to May 1, 1996.

**Statistical Procedures.** All experiments were done at least in three replicates. All data were subject to ANOVA. Fisher's least significant test (*P* < 0.05) was used to evaluate differences between treatments and changes in <sup>137</sup>Cs activity in soil

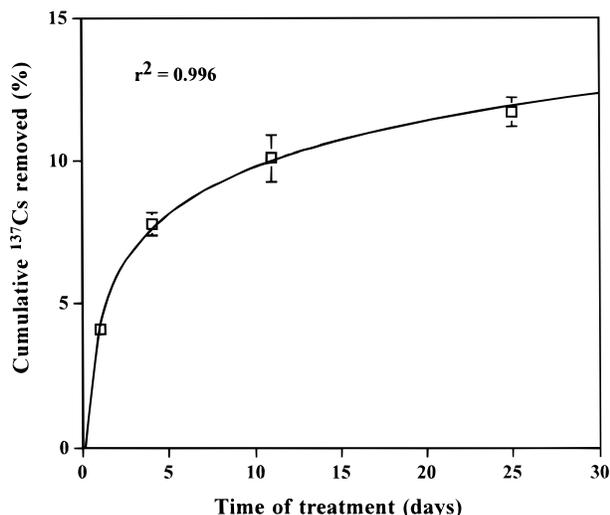


FIGURE 1. Sequential desorption of <sup>137</sup>Cs from the Chernobyl soil with ammonium acetate (0.1 M). A soil sample of 133 g was placed in a plastic bottle and then mixed with 1 L of a treatment solution. The bottles with the soil/extractant suspension were sealed and placed on an end-over-end shaker at room temperature for 1, 3, 7, and 14 days, respectively. After the equilibration, the slurry was filtered through cheesecloth filter, and the filtrate was centrifuged at 2000 rpm for 12 min. The resulting supernatant was used for <sup>137</sup>Cs activity determination. Remaining soil was used for sequential extraction.

following phytoremediation. The soil surface maps were produced using Surfer 6.04 software (Golden Software, Inc.) and were based on linear kriging of sampling points data.

## Results

**Extraction of <sup>137</sup>Cs from Soil.** Radiocesium (<sup>137</sup>Cs) was strongly adsorbed by soil particles and was difficult to extract

(Table 1). Only a small fraction (<0.3%) of <sup>137</sup>Cs was water soluble. The majority of the surfactants tested did not affect <sup>137</sup>Cs desorption greatly (<2.0%). Organic acids were also ineffective in mobilizing <sup>137</sup>Cs into solution. Even application of 5 M nitric acid resulted in the extraction of only 20.7% of radiocesium from the soil. Ammonium, potassium, and rubidium salts demonstrated a propensity to enhance Cs desorption from the soil. Stable Cs isotope was also effective in replacing radiocesium from the binding sites.

Ammonium acetate (0.1 M) was used for four successive extractions with gradually increasing time of equilibration. Almost half of the <sup>137</sup>Cs removed from the soil sample during the experiment was extracted at the first equilibration (1 day) of the soil/extractant suspension. Effectiveness of extraction was significantly reduced with the number of extractions (Figure 1).

**Screening of Plants for the <sup>137</sup>Cs Accumulation.** Sixteen high biomass cultivars of 10 species were screened for <sup>137</sup>Cs accumulation. Indian mustard, a common plant for remediation of Pb-contaminated soils, had the lowest yield among the tested cultivars. A large group of plants, including the majority of the Amaranth cultivars, peas, and sunflower, had an overall yield close to 500 g of dried biomass per m<sup>2</sup> (Figure 2). Cesium-137 specific activity within this group of species ranged from several hundred Bq kg<sup>-1</sup> in peas and sunflower up to 3000 Bq kg<sup>-1</sup> for *A. retroflexus* cv. *belozernii*. Another group of cultivars that included corn, Jerusalem artichoke, and sunflower x Jerusalem artichoke hybrid had a high yield in conjunction with relatively low <sup>137</sup>Cs accumulation. *Amaranthus retroflexus* cvs. *aureus* and PT-95 were the leading cultivars in total radioactivity removal from the soil (Table 2). These cultivars combined high biomass production with the high level of <sup>137</sup>Cs accumulation in the above-ground biomass.

**<sup>137</sup>Cs Compartmentalization in Plants.** Radiocesium compartmentalization within the plant was studied in corn, sunflower, and Indian mustard. Roots of these species had

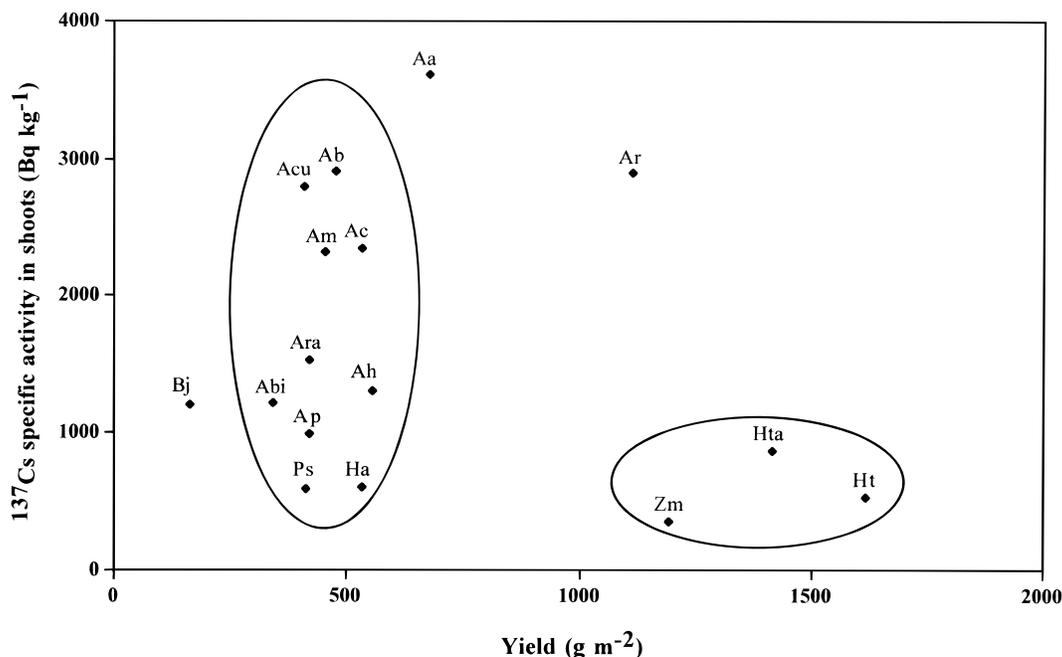


FIGURE 2. Screening results. Yield and <sup>137</sup>Cs activity in shoots. Plants were grown at the experimental plot at the Northwest border of Chernobyl, Ukraine, approximately 10 km south of the ChNPP fourth reactor that was damaged in 1986. Aa – *Amaranthus retroflexus* L. cv. *aureus*; Ab – *Amaranthus retroflexus* L. cv. *belozernii*; Abi – *Amaranthus bicolor* L.; Ac – *Amaranthus cruentus* L.; Acu – *Amaranthus caudatus* L.; Ah – *Amaranthus hybridus* L.; Am – *Amaranthus cruentus* L. cv. *myronivka*; Ap – *Amaranthus cruentus* L. cv. *paniculatus*; Ar – *Amaranthus retroflexus* L. cv. PT-95; Ara – *Amaranthus retroflexus* L. cv. *Antey*; Bj – *Brassica juncea* (L.) Czern.; Ha – *Helianthus annuus* L.; Ht – *Helianthus tuberosus* L.; Hta – *Helianthus tuberosum* L. x *Helianthus annuus* L.; Ps – *Pisum sativum* L.; Zm – *Zea mays* L.

TABLE 2. Bioaccumulation Coefficient and Total <sup>137</sup>Cs Removal from Soil<sup>a</sup>

species and cultivars	bioaccumulation coeff	total removal (Bq m <sup>-2</sup> )
<i>Amaranthus retroflexus</i> L. cv. PT-95	1.50	3225
<i>Amaranthus retroflexus</i> L. cv. aureus	1.90	2440
<i>Amaranthus retroflexus</i> L. cv. belozernii	1.41	1392
<i>Amaranthus cruentus</i> L.	1.32	1251
<i>Helianthus tuberosum</i> L. x <i>Helianthus annuus</i> L.	0.49	1221
<i>Amaranthus caudatus</i> L.	2.03	1144
<i>Amaranthus cruentus</i> L. cv. myronivka	1.07	1053
<i>Helianthus tuberosus</i> L.	0.30	846
<i>Amaranthus hybridus</i> L.	0.60	719
<i>Amaranthus retroflexus</i> L. cv. Antey	1.07	641
<i>Amaranthus bicolor</i> L.	0.59	417
<i>Amaranthus cruentus</i> L. cv. paniculatus	0.53	412
<i>Zea mays</i> L.	0.28	409
<i>Helianthus annuus</i> L.	0.24	319
<i>Pisum sativum</i> L.	0.48	244
<i>Brassica juncea</i> (L.) Czern.	0.47	194

<sup>a</sup> Plants were grown at the experimental plot at the Northwest border of Chernobyl, Ukraine, approximately 10 km south of the ChNPP fourth reactor that was damaged in 1986. Bioaccumulation coefficient was calculated as a ratio of <sup>137</sup>Cs specific activity in the plant versus <sup>137</sup>Cs specific activity in the soil.

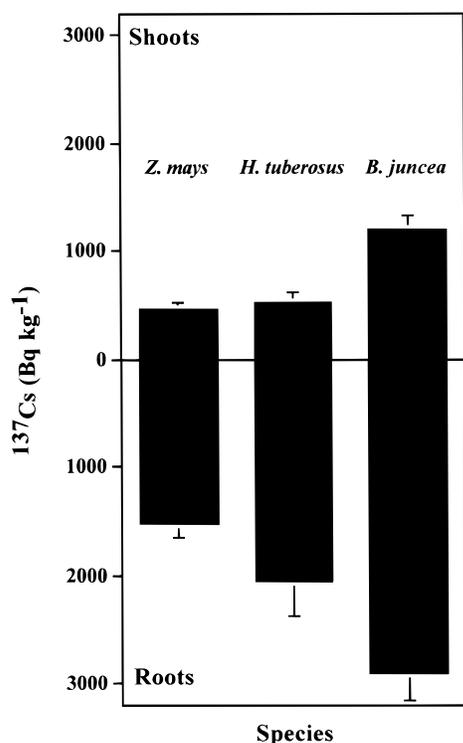


FIGURE 3. Radiocesium specific activity in above-ground and underground parts of selected plants. Shoots were harvested 2 cm above ground, air-dried, and analyzed for <sup>137</sup>Cs activity. Roots were dug out, washed in tap water, air-dried, and analyzed for <sup>137</sup>Cs activity.

2.5–3.4 times greater <sup>137</sup>Cs activity compared to the above-ground parts (Figure 3). A positive correlation was found between <sup>137</sup>Cs activity in the roots and <sup>137</sup>Cs activity in the shoots.

**Impact of Soil Amendments on <sup>137</sup>Cs Accumulation by Plants.** A number of soil amendments including the addition of exchange ions, chelating agents, and organic matter were tested for further influence on <sup>137</sup>Cs accumulation in plants. Biogumus, EDTA, and DTPA did not significantly affect the accumulation of <sup>137</sup>Cs by Indian mustard. However, the introduction of potassium into the soil as 1150 kg ha<sup>-1</sup> KCl coupled with 3000 kg ha<sup>-1</sup> KNO<sub>3</sub>, resulted in a slightly greater bioaccumulation coefficient compared to the control and

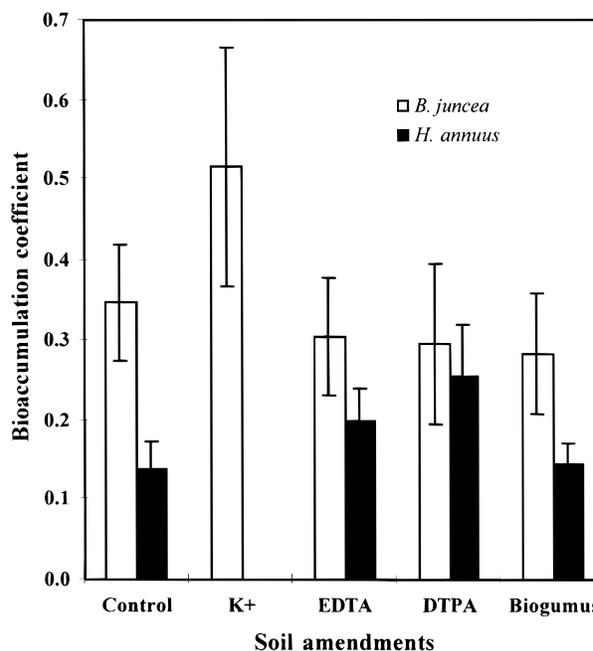


FIGURE 4. Effect of soil amendments on <sup>137</sup>Cs accumulation in Indian mustard (*B. juncea*) and sunflower (*H. annuus*). Triplicates were used in each treatment. The following amendments were added: K<sup>+</sup> – an excess of potassium, incorporated to the soil before planting at the rate KCl – 1150 kg ha<sup>-1</sup> and KNO<sub>3</sub> 3000 kg ha<sup>-1</sup>; DTPA – potassium salt of DTPA, diethylenetrinitriolpentaacetic acid, 0.5 M solution sprayed on the soil surface 1 week before harvesting at the rate 1 L m<sup>-2</sup>; EDTA – potassium salt of EDTA, ethylenedinitrioltetraacetic acid, 0.5 M solution sprayed on the soil surface 1 week before harvesting at the rate 1 L m<sup>-2</sup>; and Biogumus – organic fertilizer, incorporated to the soil before planting at the rate 6250 kg ha<sup>-1</sup>.

other treatments (Figure 4). Sunflower generally had lower bioaccumulation coefficients than Indian mustard. Biogumus and chelating agents did not dramatically affect <sup>137</sup>Cs accumulation in sunflowers (Figure 4). Similarly, no statistically significant difference in <sup>137</sup>Cs accumulation in Amaranthus was observed at the levels of ammonium salts soil amendment used for this experiment (Figure 5). However, incorporating 1500 kg (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> per ha resulted in a slight increase in the average bioaccumulation coefficient.

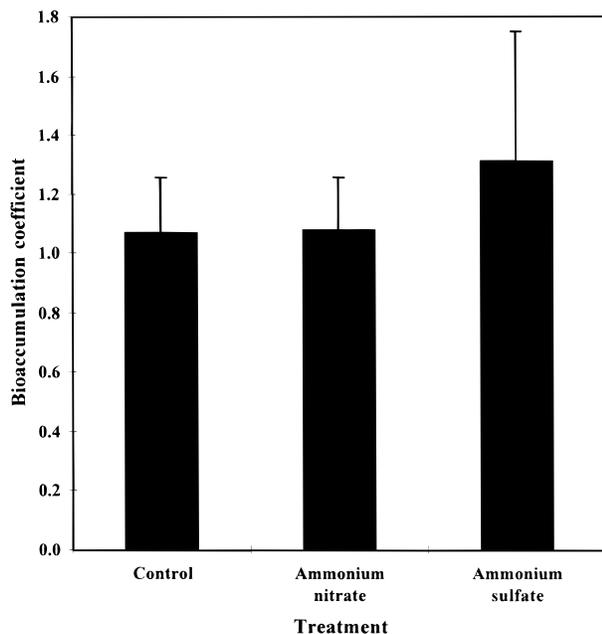


FIGURE 5. Effect of ammonium soil amendments on  $^{137}\text{Cs}$  accumulation in Amaranth (*A. retroflexus* cv. myronivka). Ammonium sulfate or ammonium nitrate was applied to the test plots as a water solution at the rate of  $1500 \text{ kg ha}^{-1}$  1 week before harvest.

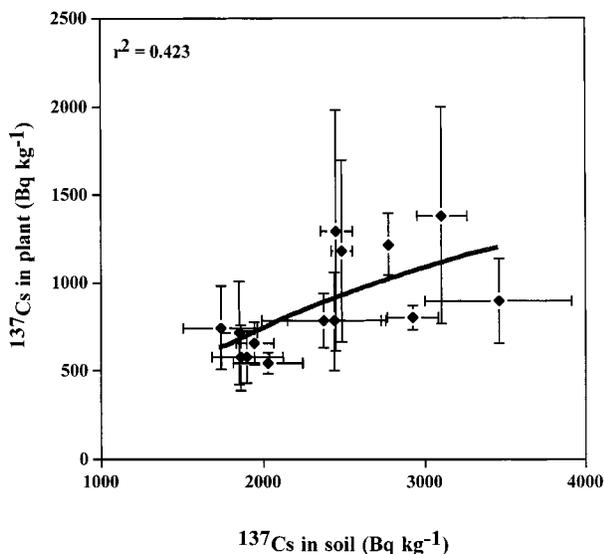


FIGURE 6. Radiocesium activity in Indian mustard shoots versus radiocesium activity in soil.

**Phytoextraction Field Experiment.** Radiocesium activity in the soil and the corresponding plants was measured for each of three Indian mustard crops at 14 sampling points. Significant variability of  $^{137}\text{Cs}$  concentrations in the plants and soil was observed. Nevertheless, a positive linear correlation for  $^{137}\text{Cs}$  specific activity in the soil and in the plants was established (Figure 6).

There was a general trend for  $^{137}\text{Cs}$  in soil to decline, starting at an average of  $2558 \text{ Bq kg}^{-1}$  in spring and gradually dropping to an average of  $2239 \text{ Bq kg}^{-1}$  after the harvest of third crop. Although, the difference between means of  $^{137}\text{Cs}$  specific activity in soil measured at the beginning of the experiments and measured after each crop was not statistically significant at  $P < 0.05$ , visible changes in the  $^{137}\text{Cs}$  surface distribution were found (Figure 7). Areas having  $^{137}\text{Cs}$  levels  $> 3000 \text{ Bq kg}^{-1}$  shrank from 29.4% of the total plot area before treatment to 7.7% after treatment. After the final harvest of

the phytoremediation crop, areas having  $^{137}\text{Cs}$  levels  $< 2000 \text{ Bq kg}^{-1}$  increased to 33.3% compared to 27.4% before treatment.

## Discussion

The laboratory and field experiments demonstrated that plants may be used to remove  $^{137}\text{Cs}$  from soil contaminated with radionuclides during the Chernobyl Nuclear Power Plant accident in 1986. It was shown that plants significantly differ in their ability to accumulate  $^{137}\text{Cs}$ . Additions of soil amendments to help mobilize  $^{137}\text{Cs}$  from soil particles may increase  $^{137}\text{Cs}$  accumulation by the plants; however, our study uncovered that phytoremediation of  $^{137}\text{Cs}$  in the Chernobyl region has certain limitations.

The experimental plot was located in the area contaminated with  $^{137}\text{Cs}$  from the ChNPP accident in 1986. Radioactive aerosols deposited on the soil surface during the accident had a heterogeneous structure (18). Radiocesium was partially associated with coarse and fine dispersed fragments of irradiated fuel having a mixed uranium oxide core (fuel type of deposition). Another type of aerosol consisted of a core, covered by recondensed cesium (condensed type of fallout). Both types of radiocesium deposition to the soil contributed evenly to the contamination of the experimental plot (19). Field observations showed that the majority of the  $^{137}\text{Cs}$  remained in the top 5 cm of the soil (20) several years after deposition. It is generally accepted that condensed radionuclides migrate faster than radionuclides from fuel type of deposition (1). However, a migration of the  $^{137}\text{Cs}$  to the deeper soil layers is a very slow process (21), and the velocity of  $^{137}\text{Cs}$  vertical migration usually remains sufficiently below  $1 \text{ cm year}^{-1}$  (22). A long-term restraining of surface deposited  $^{137}\text{Cs}$  within the rooting zone (top 0–15 cm) is an important precondition for effective phytoremediation.

The accumulation of  $^{137}\text{Cs}$  in plants is a complex process that is determined by an interaction of numerous factors (23). Soil type and soil physicochemical properties (18, 24, 25), timing from the  $^{137}\text{Cs}$  deposition (25, 26), type of radionuclide deposition (18), and plant species physiology (27) are among the major factors affecting radiocesium accumulation in plants. In this study, a combination of soil properties and aging time determined the behavior of  $^{137}\text{Cs}$  in the soil and its potential bioavailability. Radiocesium speciation in the soil during the 10 years after the Chernobyl accident was affected by radionuclide release from the fuel particles and its incorporation into soil phases. Weathering and chemical leaching of the fuel particles under the natural conditions released  $^{137}\text{Cs}$  in the soil solution. It has been shown that soil microorganisms and root exudates may play important roles in accelerating the destruction of fuel particles (28). Once released, radiocesium ions moved to exchange sites of soil particles or were incorporated into the crystalline structure of primary and secondary minerals. Kinetics of the  $^{137}\text{Cs}$  bounding to the soil matrix prevail the release from the fuel particles. The overall rate constant for cesium fixation in the sod podzolic soil was estimated at about  $8 \times 10^{-4} \text{ day}^{-1}$  (19). By the time of the phytoremediation experiments in 1996, the majority of the  $^{137}\text{Cs}$  was tightly fixed in the soil with a diminutive portion of total  $^{137}\text{Cs}$  in the soil solution, and only about 10% was potentially bioavailable (extractable and labile fractions) (19). Agapkina with colleagues (29) found that a significant amount of  $^{137}\text{Cs}$  in the soil solution in the upper layer of the forest soil was associated with organic matter, evenly distributed across fractions with different molecular weight. Consequently, bounding with organic matter may also affect  $^{137}\text{Cs}$  accumulation by plants.

Ploughing leads to a more even redistribution of the radionuclide contaminants through the soil profile, thus reducing the  $^{137}\text{Cs}$  concentration in the top 0–5 cm layer (1,

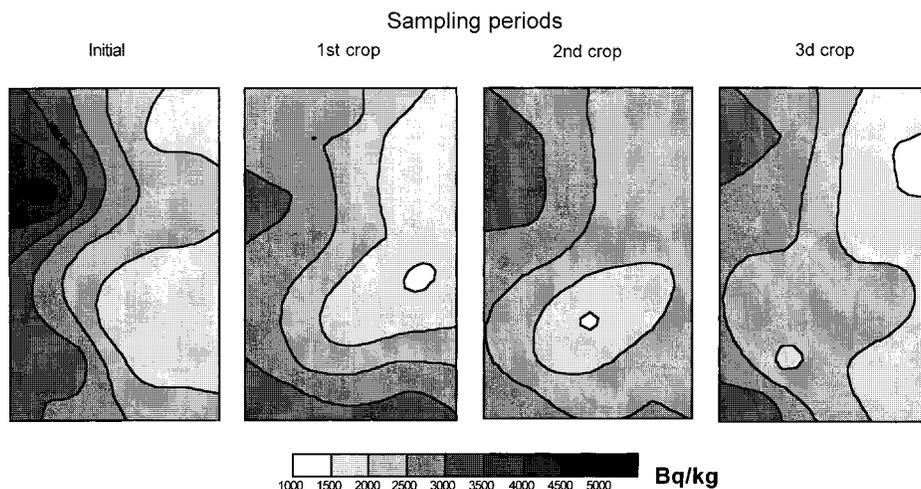


FIGURE 7. Top 15 cm  $^{137}\text{Cs}$  distribution at 40 m<sup>2</sup> (5 m × 8 m) phytoextraction experimental plot at Chernobyl. Soil was tilled to 15 cm depth. Indian mustard was planted by hand in rows spaced 12.5 cm apart at a depth of 1.5 cm. A press wheel was used to firm the soil around the seed. After 6 weeks all above-ground biomass was harvested, and the plot was tilled and replanted. Three sequential Indian mustard crops were grown during one vegetation period. Radiocesium specific activity was measured at 14 sampling points in soil at the beginning of the experiment and in the soil and plants after each crop. Maps were produced using Surfer 6.04 software (Golden Software, Inc.) and were based on linear kriging of 14 sampling points.

30). Ploughing is also usually associated with a significant reduction in  $^{137}\text{Cs}$  accumulation by plants (26).

In general,  $^{137}\text{Cs}$  bioavailability to plants was relatively higher in the Chernobyl region during the first two years after the accident (25) and sharply declined afterward. Low bioavailability of radiocesium in the Chernobyl soil may significantly limit  $^{137}\text{Cs}$  accumulation by roots. It was shown that  $^{137}\text{Cs}$  accumulation by plants is determined by the content of exchangeable and mobile forms of radionuclide in the soil (18). Soil amendments are widely used in the phytoremediation technology to increase bioavailability and enhance accumulation of heavy metals (31) and radionuclides (13) in plants. In a search for a potential soil amendment, we screened 20 different chemicals and their combinations for the ability to desorb  $^{137}\text{Cs}$  from soil. It is generally agreed that  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  form a homologous series of ions with considerable physicochemical similarity. In coherence with previous studies (32), it was found that the addition of monovalent cations similar to  $\text{Cs}^+$  physicochemical properties resulted in the most significant levels of  $^{137}\text{Cs}$  desorption from the Chernobyl soil. In our experiments, ammonium was superior to potassium for displacing  $^{137}\text{Cs}$  from bounding sites and releasing  $^{137}\text{Cs}$  into solution. Therefore, ammonium salts were selected as the primary soil amendment for the field experiments. In the pot experiments, treatment of soil with ammonium nitrate stimulated  $^{137}\text{Cs}$  accumulation in the above-ground biomass (32); however, in the field experiments, the addition of ammonium salts to the soil did not affect  $^{137}\text{Cs}$  accumulation by plants (33) (Figure 5). Failure to increase  $^{137}\text{Cs}$  accumulation by plants in the field experiments may be partially attributed to a relatively lower amount of  $\text{NH}_4^+$  introduced to the soil in the field experiments. It is also probable that  $\text{NH}_4^+$  cations not only helped to release  $^{137}\text{Cs}$  in the soil solution but also competed with cesium cations for plant uptake.

Even though the high bioaccumulation ratio for Cs was reported in earlier hydroponic experiments (32, 34), radiocesium activity in the shoots of the plants grown in  $^{137}\text{Cs}$ -contaminated areas were usually significantly lower than in the soil (23, 35). Our data showed that radiocesium concentration in the roots was about four times higher than the radiocesium concentration in the shoots (Figure 3). These data correlated well with other results obtained hydroponi-

cally (34) and suggests that for effective phytoremediation of  $^{137}\text{Cs}$  it is necessary to induce radionuclide transport to the above-ground parts.

The ability of plant species to accumulate  $^{137}\text{Cs}$  in the above-ground parts may differ by an order of magnitude (27). The difference in  $^{137}\text{Cs}$  accumulation varied from 2–4-fold within cereals and reached 27-fold for all field crops (26). Significant variation in radiocesium accumulation was observed in the cultivars of the same species (Figure 2). We found *Amaranthus* species *A. cruentus*, *A. retroflexus*, and *A. caudatus* were able to concentrate radiocesium in the above-ground parts. Lasat et al. (33) reported a bioaccumulation coefficient of >2 for *A. retroflexus* grown on a  $^{137}\text{Cs}$ -contaminated soil at Brookhaven National Laboratory, U.S.A. These data compared favorably to the bioaccumulation coefficients of <1 for Indian mustard and tepary bean (*Phaseolus acutifolius* A. Gray) at the same plot (33). In the laboratory experiments, with readily available  $^{137}\text{Cs}$  in sphagnum moss/perlite growth medium, a bioaccumulation coefficient close to one was obtained in Ponderosa and Monterey pine seedlings (36).

The developmental stage of the plant may also play an important role in radionuclide accumulation. In laboratory experiments (34), radiocesium shoot concentration followed changes in K concentrations during plant development. Radiocesium content rapidly increased between 11 and 28 days after sowing and reached a maximum at 35 days. After that, a slight decrease in concentration was observed.

Light sandy soils are characterized by relatively high level of available forms compared to heavy clay soils for  $^{137}\text{Cs}$ . Overall, the accumulation of  $^{137}\text{Cs}$  in plants dropped 2–3 times over 7 years after the Chernobyl accident (26). The residence half-time of the  $^{137}\text{Cs}$  content in grassland plants was observed to be 2.0–2.2 years for the initial period after the accident and increased to 4–12 years in following period (26). Phytoremediation has the greatest potential as a land restoration technology for  $^{137}\text{Cs}$ -contaminated areas during the first few years after radionuclide deposition, when  $^{137}\text{Cs}$  remains bioavailable.

For successful restoration of radioactively contaminated territories, it is crucially important that plants be able to remove a significant portion of radioactivity from the soil. In addition to high biomass production, a potential phytoremediation crop should have the ability to accumulate

radionuclide in the above-ground parts to the concentration exceeding the soil concentration (i.e. bioaccumulation coefficient >1). A major obstacle limiting phytoremediation of <sup>137</sup>Cs is that after deposition, <sup>137</sup>Cs is rapidly incorporated into soil clay minerals and becomes unavailable for plants. Currently, phytoremediation at Chernobyl may target only the bioavailable <sup>137</sup>Cs which represent 10–25% of the total <sup>137</sup>Cs. Phytoremediation may be a valuable option during the first years after <sup>137</sup>Cs deposition, providing cultivars with high bioaccumulation coefficients will be found and/or mechanisms for inducing <sup>137</sup>Cs translocation from the roots to the shoots will be discovered.

### Acknowledgments

The authors thank the Administration of the Chernobyl Exclusion Zone for valuable assistance and Dr. Mark Elless for his critical review. The authors also thank Ms. Kathy Makowski for her assistance in manuscript preparation.

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Received for review July 31, 1998. Revised manuscript received October 20, 1998. Accepted October 29, 1998.

ES980788+