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## STRONTIUM AND CALCIUM RELATIONS IN PLANT AND SOIL SOLUTION ON CHORNOBYL-AFFECTED AREAS

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*Ratios Sr/Ca for natural total strontium and <sup>90</sup>Sr/Ca in plants and in the corresponding soil solutions for three experimental lands with the "fuel" type of pollution for several plants under natural conditions are determined. These lands with three different types of soil are at the Exclusion Zone of the Chornobyl Nuclear Power Plant. The obtained experimental results show that the ratio Sr/Ca in plant is equal to this ratio in the corresponding soil solution for all investigated lands and plants. Ratio <sup>90</sup>Sr/Ca in plant exceeds this ratio in the corresponding soil solution. The ratio in the plant has positive correlation with the soil humidity for every experimental land.*

*Keywords:* total strontium; <sup>90</sup>Sr; calcium; transition of strontium to plant; strontium-calcium ratio; soil solution; ICP-spectrometry; radiochemistry.

### 1. Introduction

Studying the transfer of <sup>90</sup>Sr to plants has been carried out for half a century. It became especially important after the Chornobyl Accident. Today, some researchers agree, that the Sr/Ca ratio in plant is equal to this ratio in the corresponding equilibrium soil solution (Russell [1], Nisbet *et al.* [2], Prorok *et al.* [3]). This equality or OR-value should help to predict the uptake of strontium to plants. Other researchers disagree, however, with the above assertion (Papanicolaou *et al.* [4]). They showed that the calculated OR-values varied considerably. To make clear this problem, we investigated strontium/calcium relations in soil and plants. We determined the activity concentrations of <sup>90</sup>Sr and the concentrations of Sr and Ca in plants and soil solutions by direct measurements. From these measurements, we calculated the <sup>90</sup>Sr/Ca and Sr/Ca ratios in plant and a soil solution, respectively, and two corresponding OR-values.

### 2. Material and Methods

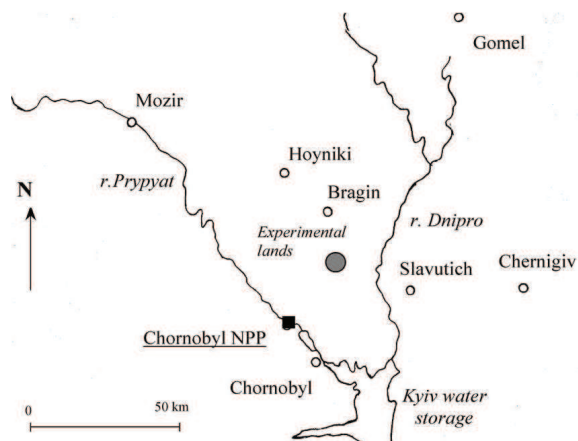
We carried out our investigations under field conditions on three different lands situated 30 km from

the Chornobyl Nuclear Power Plant in the north-east direction (see Fig. 1).

There were three lands: land A – glacial-water sand soddy-podzol middle podzol silt sand soil; land B – decomposed middle thick sedge, rush and wood peat low-lying type peaty soil; land C – glacial-water sand loam soddy-podzol middle podzol sand loam with the signs of temporal excess humidification soil. According to Sandalls *et al.* [5], the lands in this region were polluted mostly with fuel particles. Every area had the dimension 2 × 4 meters. We sowed the fast-ripening plants on lands A, B, and C that were as distinct from one another as possible. These were radish (*Raphanus sativus*), salad (*Lactuca sativa*), watercress (*Lepidium sativum*), and coriander (*Coriandrum sativum*). There were mixed sowing. The roots of plants grew side-by-side in soil. We selected samples several times. Every time, we took samples of soils, samples of sowed plants, if they had grown, and samples of wild plants. The wild plants were couch grass (*Elytrigia repens*), timothy grass (*Phleum pratense*), smartweed (*Polygonum hydropiper*), nettle (*Urticaceae dioica*), winter cress (*Barbarea vulgaris*), and marsh betony (*Stachys palustris*). We took samples of barley (*Hordeum vulgare*) on land C as well. We selected all the plants before they blossomed. All the plant samples were

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Location of the experimental lands

washed and dried. Soil solution was extracted from the soil using a centrifuge RS-6 (former USSR) with a centripetal acceleration of 3,000 g. We extracted the soil solution from some samples immediately after sampling, from some samples after the addition of distilled water and treating with a rotator for an hour. Our estimation showed that the addition of water to the soil changes the  $^{90}\text{Sr}$  concentration by less than 5%, if the soil humidity do not exceed the humidity of water saturated soil. We can describe this concentration  $\mathbf{B}_1$  as  $\mathbf{B}_1 = \mathbf{B}_s / \mathbf{K}_d^{\text{ex}}$ , where  $\mathbf{B}_s$  is the concentration of solid exchangeable  $^{90}\text{Sr}$  in the soil,  $\mathbf{K}_d^{\text{ex}}$  is the  $^{90}\text{Sr}$  exchangeable sorption distribution coefficient for the soil (Ageyetz [6]). Our experimental data showed that the addition of water at a so low concentration does not change  $^{90}\text{Sr}/\text{Ca}$  and  $\text{Sr}/\text{Ca}$  ratios in soil solution. We determined the humidity and the moisture saturation of soil, as described by Dospheov *et al.* [7]. Then we determined the relative humidity of the soil as the ratio of the moisture content in the soil at the moment of sampling to the moisture content in soil saturated with water. The centrifuged solution was filtered through a glass filter Whatman GF/A and through a filter TU 6-09-1678-86 (former USSR). The filtrate was clear. To conserve the obtained soil solution, we added 1 ml of concentrated nitric acid per 500 ml of the soil solution and heated it to boiling. We determine the chemical compositions of extracted soil solutions and plants with an atom emission spectrometer, inductively coupled plasma (ICP) “Spectro” (FRG). We prepared samples to determine the chemical content of plants in the fol-

lowing way. We homogenized a dry plant to particles less than  $2 \times 2 \times 2$  mm. Then we took 1 g of the obtained blend and placed it in a teflon beaker. We mineralized it with nitric acid (65%) and hydrogen peroxide (30%) in ratio 5:2 using a microwave module MLS-1200 MEGA (Italy). We treated the samples at the next power of a microwave radiator: 250 W – 5 min, 400 W – 5 min, 500 W – 5 min, 600 W – 1 min according to the instruction for a module. We also treated the soil solutions with a module according to the above-described program and used the obtained samples for ICP-measurements. Atomization of the samples at this spectrometer occurs in the high-frequency inductive discharge in argon at the atmospheric pressure using a high-frequency generator (the maximum power 2.5 kW) for the argon plasma ignition. The frequency of a generator was 27.12 MHz. The range of working wavelengths of a spectrometer was 1600 Å–8000 Å.

The  $^{90}\text{Sr}$  content in plants and in soil solutions were determined with the radiochemistry extraction method. The method is described by Tuzova *et al.* [8]. Dicyclohexyl-18-crown-6 was used for the extraction of strontium from acid extract. Then the obtained sediment of  $\text{SrCO}_3$  was measured with a low-background installation UMF-1500M (former USSR).

### 3. Results and Discussion

The results of measurements are presented in Tables 1–3. The tables show the relative humidity at sampling occasion, concentrations of  $^{90}\text{Sr}$ , Ca and Sr in plant and soil solution, and the results of mathematical treatment of the data.

They are:  $^{90}\text{Sr}/\text{Ca}$  ratio of the concentration of  $^{90}\text{Sr}$  to the concentration of calcium;  $\text{Sr}/\text{Ca}$  ratio of the concentration of strontium to the concentration of calcium; OR-values of  $((\text{Sr}/\text{Ca})_p / (\text{Sr}/\text{Ca})_{ss})$  and  $(^{90}\text{Sr}/\text{Ca})_p / (^{90}\text{Sr}/\text{Ca})_{ss}$ . Rh = Relative humidity, Note = Plant or soil solution, Ns = Number of samples. The content of water in capillary saturated soil of land A was 63 g per 100 g of dry soil, of land B – 347 g per 100 g of dry soil, and of land C – 38 g per 100 g of dry soil. Soil humidity of land C was not measured in 2003, but we have no doubts, that it was less than in 2002. According to X-ray fluorescence analysis, the concentration of Sr in soil of land A is 22 microgram per gram, in soil of the land B – 28 mcg/g, and in soil of the land C – 30 mcg/g. The error of de-

**Table 1. Land A – Based on glacial-water sand loam soddy-podzol middle podzol sand loam. Content of Ca, Sr and  $^{90}\text{Sr}$  in 2002 and 2003 and results of mathematical treatment of these data. Plants – mg/g, Bq/g per g dry weight; soil solutions – mg/l, Bq/l**

Date	Rh	Note	Ns	$^{90}\text{Sr}$	Sr	Ca	$^{90}\text{Sr}/\text{Ca}$	$\text{Sr}/\text{Ca}$	$(^{90}\text{Sr}/\text{Ca})\text{p}/$ $(^{90}\text{Sr}/\text{Ca})\text{ss}$	$(\text{Sr}/\text{Ca})\text{p}/$ $(\text{Sr}/\text{Ca})\text{ss}$
12May02	1	Soil solution	6	10.40	0.1580	23.42	0.444	0.00675		
12May02	0.37	Timothy-grass	57	1.28	0.0100	1.43	0.893	0.00699	2.01	1.04
22June02	1	Soil solution	18		0.2160	34.21		0.00631		
22June02	0.098	Radish roots	55	7.51	0.0380	6.16	1.220	0.00617		0.98
22June02	0.098	Radish leaf	65	19.34	0.1330	15.54	1.245	0.00856		1.36
08June03	0.46	Soil solution	5	42.00	0.2240	53.62	0.783	0.00418		
08June03	0.025	Radish	35	14.28	0.1090	13.81	1.034	0.00789	1.32	1.89
08June03	0.025	Water-cress	36	7.04	0.0506	8.36	0.842	0.00605	1.08	1.45
08June03	0.025	Salad	37	5.94	0.0507	7.41	0.802	0.00684	1.02	1.64
08June03	0.025	Marsh betony	38	4.36	0.0292	5.21	0.837	0.00560	1.07	1.34
13July03	0.47	Soil solution	8	46.80	0.3641	59.30	0.789	0.00614		
13July03	0.05	Salad	21	7.01	0.0474	12.18	0.576	0.00389	0.73	0.63
13July03	0.05	Smart weed	22	10.27	0.0656	7.60	1.351	0.00863	1.71	1.41
13July03	0.05	Coriander	23	8.09	0.0388	9.29	0.871	0.00418	1.10	0.68
13July03	0.05	Marsh betony	24	4.75	0.0355	5.57	0.852	0.00637	1.08	1.04

**Table 2. Land B – Based on decomposed middle thick sedge, rush and wood peat low-lying type peat soil. Content of Ca, Sr and  $^{90}\text{Sr}$  in 2002 and 2003 and results of mathematical treatment of these data. Plants – mg/g, Bq/g per g dry weight; soil solutions – mg/l, Bq/l**

Date	Rh	Note	Ns	$^{90}\text{Sr}$	Sr	Ca	$^{90}\text{Sr}/\text{Ca}$	$\text{Sr}/\text{Ca}$	$(^{90}\text{Sr}/\text{Ca})\text{p}/$ $(^{90}\text{Sr}/\text{Ca})\text{ss}$	$(\text{Sr}/\text{Ca})\text{p}/$ $(\text{Sr}/\text{Ca})\text{ss}$
12May02	0.86	Soil solution	10	34.00	0.1070	27.90	1.219	0.00384		
12May02	0.86	Coach gr.blades	51	9.25	0.0160	5.16	1.793	0.00310	1.47	0.81
12May02	0.86	Coach gr.roots	52	7.77	0.0170	3.96	1.962	0.00429	1.61	1.12
09June02	0.68	Soil solution	24	43.00	0.0810	33.65	1.278	0.00241		
09June02	0.68	Smart weed	60	16.02	0.0360	8.55	1.874	0.00421	1.54	1.75
22June02	1	Soil solution	19		0.4090	145.00		0.00282		
22June02	0.59	Radish roots	54	14.11	0.0280	8.95	1.577	0.00313		1.11
22June02	0.59	Smart weed	69	28.50	0.0720	13.80	2.065	0.00522		1.85
08June03	0.40	Soil solution	6	201.00	0.5090	268.00	0.750	0.00190		
08June03	0.13	Salad	39	13.90	0.0390	18.24	0.763	0.00214	1.02	1.13
08June03	0.13	Coriander	40	15.37	0.0310	14.25	1.079	0.00218	1.44	1.15
08June03	0.13	Coach gr.blades	41	6.49	0.0120	3.80	1.708	0.00316	2.28	1.66
08June03	0.13	Nettle	42	53.21	0.0770	37.99	1.401	0.00203	1.87	1.07
08June03	0.13	Smart weed	43	24.06	0.0520	21.40	1.125	0.00243	1.70	1.28
13July03	0.21	Soil solution	9	282.00	0.8350	305.00	0.925	0.00274		
13July03	0.078	Coriander	25	15.46	0.0370	13.83	1.118	0.00268	1.21	0.98
13July03	0.078	Salad	26	17.24	0.0450	16.43	1.049	0.00274	1.13	1.00
13July03	0.078	Radish	27	29.61	0.0790	30.58	0.969	0.00258	1.05	0.94
13July03	0.078	Smart weed	28	30.55	0.0680	21.49	1.422	0.00316	1.54	1.15
13July03	0.078	Coach gr.blades	29	5.31	0.0160	5.27	1.008	0.00304	1.09	1.11

**Table 3. Land C – Based on glacial-water sand loam soddy-podzol middle podzol sand loam with the signs of temporal excess humidification soil. Content of Ca, Sr and  $^{90}\text{Sr}$  in 2002 and 2003 and results of mathematical treatment of these data. Plants – mg/g, Bq/g ; soil solutions – mg/l, Bq/l**

Date	Rh	Note	Ns	Sr	$^{90}\text{Sr}$	Ca	$^{90}\text{Sr}/\text{Ca}$	Sr/Ca	$(^{90}\text{Sr}/\text{Ca})_p/$ $(^{90}\text{Sr}/\text{Ca})_{ss}$	$(\text{Sr}/\text{Ca})_p/$ $(\text{Sr}/\text{Ca})_{ss}$
09June02	1	Soil solution	12	0.3570	14.00	51.30	0.2729	0.00696		
09June02	0.18	Winter-cress	61	0.0648	3.52	7.41	0.4750	0.00874	1.74	1.26
09June02	0.18	Barley	70	0.0105	0.65	1.33	0.4910	0.00789	1.80	1.13
08June03		Soil solution	4	0.1350	5.60	23.10	0.2424	0.00584		
08June03		Radish	31	0.0811	5.81	12.48	0.4655	0.00650	1.92	1.11
08June03		Water-cress	32	0.0251	1.45	3.96	0.3657	0.00634	1.51	1.09
08June03		Barley	33	0.0173	1.14	3.35	0.3412	0.00516	1.41	0.88
3July03		Soil solution	7	0.1305	5.30	17.79	0.2979	0.00734		
13July03		Radish	16	0.0855	3.55	9.96	0.3562	0.00858	1.20	1.17
13July03		Water-cress	17	0.0364	2.13	5.26	0.4055	0.00692	1.36	0.94
13July03		Barley	18	0.0123	0.63	1.62	0.3901	0.00759	1.31	1.03
13July03		Winter-cress	20	0.0967	2.94	9.94	0.2962	0.00973	0.99	1.33

termination of the  $^{90}\text{Sr}$  concentration for the majority of samples was 15–30% and, for the concentrations of Ca and strontium, 1%. Temperature and humidity of soil change under field conditions. We can see from the data presented by Prorok *et al.* [3] for the experimental areas that the ratio Sr/Ca in the soil solutions, as a rule, changes not more than by 30% from its average value with changes of temperature and humidity of soils. We can see from Tables 1–3 that, for all our experimental lands and for all investigated plants, the ratios Sr/Ca differ not more than by 30% from the average value Sr/Ca of the soil solution, i.e. it changes in the same limits. The obtained results confirm that the ratio Sr/Ca in the soil solution is an adequate criterion for the prediction of this ratio in a plant. The exception is smartweed. According to our data (Tables 1–3), the ratio for this plant exceeds the ratio in the corresponding soil solution approximately by a factor of 1.49 (sample standard deviation  $\sigma = 0.30$ ). Nisbet *et al.* [2] showed such differences for some plants as well. The reason for this deviation is not yet known. Our experimental results (Tables 1–3) have shown that the average magnitude of values  $(^{90}\text{Sr}/\text{Ca})_p/({}^{90}\text{Sr}/\text{Ca})_{ss}$  in 2002 and 2003 for land A is 1.24,  $\sigma = 0.39$ ). For land B, it equals 1.48,  $\sigma = 0.37$ ), and it equals 1.47,  $\sigma = 0.30$ ) for land C. We can see that the excess of the values over 1 is not essential. They are near to the sample standard deviation and to the declared er-

ror of determination of the  $^{90}\text{Sr}$  content at the investigated samples. But, in 2002 for lands A + B + C, the average value  $(^{90}\text{Sr}/\text{Ca})_p/({}^{90}\text{Sr}/\text{Ca})_{ss}$  (without smartweed) was 1.73,  $\sigma = 0.20$ ). This value exceeds 1 essentially. The average magnitude of values  $(\text{Sr}/\text{Ca})_p/(\text{Sr}/\text{Ca})_{ss}$  for the same samples (lands A + B + C in 2002) is 1.07,  $\sigma = 0.17$ ). OR-values for  $^{90}\text{Sr}$  were essentially more than OR-values for natural total strontium in 2002. At the moment, only the ingredients of a soil solution are available for the plant nutrition. The transition soil solution-plant coefficients for the plant may differ for the different isotopes of strontium only in the case where these isotopes are in different physico-chemical forms in the soil solution. We consider that the reason why the ratio  $^{90}\text{Sr}/\text{Ca}$  in the investigated plant is more than that in the corresponding soil solution for our experimental lands is the permanent dissolving of fuel particles in the soil of the lands. Consequently, the soil solutions in the soil of the lands are non-equilibrium. In 2002, the relative humidity of soil on our experimental lands was essentially more than that in 2003, especially on lands A and C. So, the dissolving of fuel particles in 2002 was more intense than in 2003. So, soil solutions were more non-equilibrium in 2002 than in 2003. This question should be investigated additionally in more details. We think that the difference in the ratios strontium-calcium in plant and in the corresponding soil solution marked by Papanicolaou

*et al.* [4] and earlier by another researchers may be explained in two ways. First, the content of soil solution was determined there by the chemical analysis of soil, but not by the direct measurement of soil solution. Perhaps, this yields an error in the final result. Second, not in all the cases, the soil solution is in equilibrium with respect of the investigating strontium isotope. We consider that the transition coefficients for soil solution-plant are equal for all strontium isotopes, if we have equilibrium for all these isotopes in soil solution. In this case, we can obtain this coefficient for total natural strontium from the results of high-precision optical measurements. It will be equal to the coefficients for other strontium isotopes. If the soil solution is not in equilibrium with respect to some isotope, then, to determine the transition coefficient for this isotope, we must measure just this isotope in a plant and in a soil solution.

#### 4. Conclusions

For the investigated lands and plants, the ratio Sr/Ca in a plant is equal to the ratio in the corresponding soil solution. For the same samples, the ratio  $^{90}\text{Sr}/\text{Ca}$  exceeds the ratio in the corresponding soil solution. This excess correlates with the relative humidity of the soil.

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#### СПІВВІДНОШЕННЯ СТРОНЦІЙ-КАЛЬЦІЙ У РОСЛИНИ ТА У ВІДПОВІДНОМУ ҐРУНТОВОМУ РОЗЧИНІ НА ЗАБРУДНЕНІЙ ЧОРНОБИЛЬСЬКІЙ ТЕРИТОРІЇ

#### Резюме

Визначено відношення Sr/Ca для валового стронцію та  $^{90}\text{Sr}/\text{Ca}$  у рослинах та у відповідних ґрунтових розчинах для трьох дослідних ділянок з "паливним" типом забруднення для кількох видів рослин у природних умовах. Вказані ділянки з трьома різними типами ґрунтів знаходяться в зоні відчуження Чорнобильської АЕС. Отримані експериментальні результати показують, що для всіх досліджуваних рослин та експериментальних ділянок відношення Sr/Ca у рослині дорівнює цьому відношенню у відповідному ґрунтовому розчині. Відношення  $^{90}\text{Sr}/\text{Ca}$  у досліджуваній рослині перевищує це відношення у відповідному ґрунтовому розчині. Це відношення у рослині позитивно корелює з вологістю ґрунту для кожної експериментальної ділянки.