Concentration of Strontium-90 at Selected Hot Spots in Japan

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Abstract

This study is dedicated to the environmental monitoring of radionuclides released in the course of the Fukushima nuclear accident. The activity concentrations of β-emitting ⁹⁰Sr and β/γ-emitting ¹³⁴Cs and ¹³⁷Cs from several hot spots in Japan were determined in soil and vegetation samples. The ⁹⁰Sr contamination levels of the samples were relatively low and did not exceed the Bq g⁻¹ range. They were up four orders of magnitude lower than the respective ¹³⁷Cs levels. This study, therefore, experimentally confirms previous predictions indicating a low release of ⁹⁰Sr from the Fukushima reactors, due to its low volatility. The radioesesium contamination could be clearly attributed to the Fukushima nuclear accident via its activity ratio fingerprint (¹³⁴Cs/¹³⁷Cs). Although the correlation between ⁹⁰Sr and ¹³⁷Cs is relatively weak, the data set suggests an intrinsic coexistence of both radionuclides in the contaminations caused by the Fukushima nuclear accident. This observation is of great importance not only for remediation campaigns but also for the current food monitoring campaigns, which currently rely on the assumption that the activity concentrations of β-emitting ⁹⁰Sr (which is relatively laborious to determine) is not higher than 10% of the level of γ-emitting ¹³⁷Cs (which can be measured quickly). This assumption could be confirmed for the samples investigated herein.

Methods

Samples

Samples were taken between December 2011 and July 2012 from several spots on the eastern Japanese coast (Fig. 1). All samples were taken from public areas, hence no permits from private land owners were necessary. Apart from the sampling in the restricted areas (for which permission was obtained from the mayor of Okuma town), no specific permits were required for the described field studies. Some of the spots have already been investigated previously with respect to short-lived γ-emitting radionuclides [17]. On most sites two types of samples were taken: soil and vegetation (leaves, grass, conifer needles etc.). The studies did not involve protected or endangered species. The sampling sites included highly contaminated spots such as the gate of the Fukushima Daiichi nuclear power plant (NPP), locations in the close vicinity of the NPP, but also more remote sites such as...
Kashiwa (some 200 km south of the NPP). For exact locations and sampling dates, please see Table S1.

Strontium separation and measurement

Liquid scintillation counting (LSC) was applied for the radiometric analysis of $^{90}\text{Sr}$. It requires a chemically pure strontium sample in order to avoid contributions to the counting signal by other radionuclides in the sample.

It was assumed that Fukushima fallout $^{90}\text{Sr}$ was adsorbed on the surface of the soil particles and not immobilized, e.g. by incorporation into the crystals of the mineral components of the soil. Complete dissolution of the soil samples was hence not deemed necessary. In order not to immobilize the surface-adsorbed radiostrontium, the samples were not dried by heating, but carefully air dried in a desiccator. Before radiostrontium extraction, the activity concentrations of $^{134}\text{Cs}$ and $^{137}\text{Cs}$ were deemed necessary. In order to not immobilize the surface-soil. Complete dissolution of the soil samples was hence not necessary especially with the plant samples for complete dissolution.

Strontium was extracted from the soil and vegetation materials using the following procedure. The samples were treated with a mixture of 2.5 mL concentrated $\text{HNO}_3$ (65%; Roth®, p.a.), 2.5 mL of an aqueous Sr carrier solution ($c_{\text{Sr}} = 1.2$ mg mL$^{-1}$) stable Sr in distilled $\text{H}_2\text{O}$; Sr($\text{NO}_3$)$_2$ by Riedel de Haen®, extra pure) and 1 mL $\text{H}_2\text{O}_2$ (30%; Roth®, p.a.). If necessary, additional $\text{HNO}_3$ and $\text{H}_2\text{O}_2$ were added during the procedure (which was necessary especially with the plant samples for complete dissolution). The samples were stirred and heated to boil under the reflux of a cooler for 30 min. The mixture was filtered using Schleicher & Schuell® 595 filters and washed with several mL of 8 M $\text{HNO}_3$. The yellow filtrate was collected and steamed off to dryness. The yellow color, in part, proved to be $\text{Fe}^{(III)}$ compounds. The residue was taken up in 4 mL 8 M $\text{HNO}_3$ and stirred until complete dissolution.

For the separation of radiostrontium from other radionuclides, strontium selective SR-resin-B (100–150 $\mu$m) by Eichrom®/Triskem International® was used. The columns for this ion chromatography were produced by Carlo Erba® and fulfill Euratom standards. An amount of 380–420 mg fresh Sr resin was equilibrated in 8 M $\text{HNO}_3$ at least 90 min before loading with the sample extract onto the column. After loading, the flask was rinsed four times with 0.5 mL 8 M $\text{HNO}_3$. This rinsing solution was also loaded onto the column. Then the column was rinsed five times with 1 mL of a solution of 3 M $\text{HNO}_3$ and 0.05 M oxalic acid (Merck®, p.a.). In this washing procedure the yellow color could be removed from the column to the greatest extent. Subsequent elution of Sr was performed with ten times 1 mL of 0.05 M $\text{HNO}_3$. Any residual yellow color on the column was also retained by the column during the elution, providing a clear and colorless product, which is important for LSC (avoiding color quenching). The product was collected in a flask, evaporated to dryness and taken up in four times 1 mL of 0.01 M $\text{HNO}_3$ that were pipetted into the LSC counting vials sequentially for the sake of rinsing the flask. Sixteen mL of Ultima Gold™ LSC cocktail (Perkin Elmer®) were added to the 4 mL of aqueous Sr extract, which proved to be the optimum ratio between aqueous phase and LSC cocktail in our case.

The measurements were conducted with a Packard® Tri-Carb 2700TR Liquid Scintillation Analyzer. Each measurement lasted for 1000 min. The samples were measured twice, once immediately after the chemical separation, once after at least two weeks, i.e. after ingrowth of the daughter nuclide $^{85}\text{Y}$ ($T_{1/2} = 64.1$ h) into radioactive equilibrium with its mother $^{90}\text{Sr}$.

The efficiency of the Sr extraction (i.e., the total Sr recovery after dissolution and extraction) was determined using a 3 mg Sr aliquot of a solution of Sr($\text{NO}_3$)$_2$, which was activated in the Atominstitut’s TRIGA Mark II reactor. The resulting $^{85}\text{Sr}$ tracer was pipetted onto an aliquot of approximately 200 mg of each sample and carefully dried at 55°C. Then the procedure of Sr extraction was performed as described above. The $\gamma$-emitting radioisotope $^{85}\text{Sr}$ ($T_{1/2} = 64.9$ d; $\gamma$-line at 514 keV) allows straightforward quantification before and after the procedure using $\gamma$-spectrometry. The utilization of $^{85}\text{Sr}$ is regarded as the most suitable technique for the quantification of the strontium extraction yield in this type of radioecological study [28]. The recoveries were in the range of 92.4–98.2%. They were used to extrapolate the results of the analyses to the total activity concentration of $^{90}\text{Sr}$ in the respective samples.

For $^{90}\text{Sr}$ quantification in the LSC, IAEA-373 (Radionuclides in Grass) was used as a reference material. The standard’s grass matrix was treated in the identical way like the vegetation samples in order to obtain a pure Sr fraction. All nuclear data in this paper are taken from the National Nuclear Data Center [29].

Results and Discussion

The results of the measurements are illustrated in Fig. 2 and tabulated in Table S1. The $^{90}\text{Sr}$ levels were generally relatively low (up to approximately 1 Bq g$^{-1}$), and 1 to 4 orders of magnitude lower than the $^{137}\text{Cs}$ levels in the respective sample. This experimentally confirms the modeling by Schwantes and colleagues [18], who predicted only very low releases of radiostrontium via the gas phase. In general, a contamination of the land surface occurs via dry deposition of radionuclides, but it is much enhanced through rainfall causing wet deposition. Southern wind directions and rainfall explain the relatively high activity levels in the remote hot spot in Kashiwa (spot code I) and Yokohama (spot code J), which are located close to Tokyo. Accordingly, also local environmental conditions seem to be responsible for the surprisingly low contamination levels at spots E and G that are located not only quite close to the damaged reactors of Fukushima NPP (distance 8.7 and 16.4 km, respectively), but also in or next to the highly contaminated strip in (north)northwestern direction from the NPP that, even outside the restricted area (20 km radius), had
been declared as “deliberate evacuation area” [3]. In this special case, probably the local lack of rainfall as well as a specific soil composition led to low contamination levels at spots E and G and/or prevented the retention of both radiostrontium and radiocesium in the top soil at these locations. Our results once again evidence that distance from the source alone is no sufficient factor for the prediction of a contamination level at a certain spot after a nuclear accident.

One has to take into account that pre-Fukushima events (mainly atmospheric nuclear explosions of the 20th century as well as previous nuclear accidents) also contribute to the inventory of both radionuclides $^{137}$Cs and $^{90}$Sr. In case of radiocesium, the presence of the shorter-lived reactor nuclide $^{134}$Cs allows the assignment to the Fukushima accident. Any $^{134}$Cs from previous nuclear accidents typically has decayed below the limit of detection in environmental samples due to its relatively short half-life ($T_{1/2} = 2.07$ yr). Previous studies on the Fukushima nuclear accident indicated an activity ratio of $^{134}$Cs/$^{137}$Cs of approximately 1 or just below 1 at the time of the accident (11 March 2011) [12,30], which also was found in the present study (see Table S1).

In addition to absolute contamination data for $^{90}$Sr, a possible correlation between the $^{90}$Sr and radiocesium levels is worth more in-depth discussion. In the ideal case, this should make a rough estimation of the activity concentration of $^{90}$Sr possible via the straightforward γ-spectrometric determination of $^{137}$Cs, just as it has been proposed by Japanese authorities with respect to food safety [31]. The authorities assumed intrinsic co-existence of both radionuclides in the environment (including foodstuffs) as well as a maximum $^{90}$Sr activity of 10% of the respective $^{137}$Cs activity. The correlations between the activity concentration data of $^{90}$Sr and $^{137}$Cs in this study are shown in Fig. 3. Although this correlation is quite weak, a certain trend between the both radionuclides can be observed in this figure. Previous studies showed a reliable correlation of the concentrations of isotopes of the same element, e.g. $^{134}$Cs/$^{137}$Cs [30], $^{134}$Sr/$^{137}$Cs [18], or (in a different topic) $^{239,240}$Pu/$^{238}$Pu [32], which even allowed source identification.

Radionuclide correlations between two different elements always involve problematic factors such as different volatilities in the course of the release as well as chemical fractionation in the environment after the release. The above correlation between $^{90}$Sr and $^{137}$Cs hence does not provide more information than a rough estimation of the maximum $^{90}$Sr activity concentration via the respective $^{137}$Cs activity concentration, as suggested by the Japanese authorities [31]. Also, one has to take into account, that even after deposition this correlation cannot be regarded as constant over time due to different diffusion, adsorption, and washout behavior of the two elements Cs and Sr. This fact also becomes obvious from Fig. 2, indicating that the relative contamination levels of soil and vegetation at one spot are not always fully comparable. Both soil and vegetation samples from spot B, for example, exhibited a comparable $^{90}$Sr activity concentration, whereas the $^{137}$Cs concentration in this location is more than an order of magnitude higher in soil than with the vegetation sample. For a long-term assessment of the radiological risk, the effective ecological half-lives of radiostrontium and radiocesium will have to be determined in the various types of soil in the next years.

![Figure 2. Activity concentrations of $^{90}$Sr and sum activity concentrations of $^{90}$Sr + $^{137}$Cs at the investigated spots. Sample codes include the code of the sampling locations (see Fig. 1) and the type of sample material, soil (S) or vegetation (V). At the spots G and J, two soil samples were taken (indicated by 1 and 2). Error bars are due to counting statistics. Activities were decay corrected to the time of the accident. Please note the logarithmic scale.](doi:10.1371/journal.pone.0057760.g002)
Although the correlation proved to be weak (as reflected by the R-squared value of 0.264), the power trend line was found to fit the data set presented in Fig. 3 best. Please note that the limited data set introduces a considerable uncertainty. The relative 90Sr activity concentration in highly contaminated areas in close vicinity to the reactors showed to be higher than in more remote areas. It is likely that both dry and wet deposition of less volatile elements such as Sr is enhanced compared with the more volatile Cs. Therefore, it is reasonable to predict that the more remote hot spots northwest of the NPP site will exhibit lower relative 90Sr contributions to the total activities than the hot spots next to the reactors. To a minor extent, distinct features of the four different sources (i.e. the four reactors) may be partly responsible for the poor correlation, as characteristics such as the type of fuel, the burn-up rate, the type of damage, as well as the temperature and coolant profiles inside the damaged reactors may have influenced the releases from the four distinct sources [18]. The present data set, however, does not allow identification of these sources in distinct areas as other mechanisms such as chemical fractionation in the environment has concealed such minute differences.

As indicated above, some uncertainty could also have been introduced by the contributions of previous fall-out from nuclear explosions that affects low-contaminated samples to a greater extent than highly contaminated spots. For instance, this could be the case with sample G-V, which has a relatively high 90Sr content, whereas the radiocesium content is relatively low. Although the 134Cs/137Cs activity ratio (0.97) tells us that the radiocesium in this sample is virtually completely due to Fukushima fallout, we can hypothesize that the [low] radiostanum contamination, in part, could be old fall-out 89Sr that has been retained in the soil and taken up by the plant (whereas any old radiocesium may not have been retained by the soil as efficiently). If this sample G-V is omitted in Fig. 3, the R-squared of the resulting power trend line (y = 0.0066 x^0.5204) “improves” to a value of 0.41, which is still not comparable to the neat correlations between radionuclides of the same element, though.

The presence of bone-seeking 90Sr in food or potable water poses a big threat after nuclear accidents. The determination of 90Sr in environmental samples such as foodstuffs, however, requires a relatively time-consuming radiochemical separation as illustrated above, whereas γ-emitters can be quantified quickly. In order to still address the 90Sr issue properly to a dense network of samples taken from different regions, Japanese authorities assumed the intrinsic co-existence of radiostrontium together with γ-emitting radiocesium. As stated above, the activity of 90Sr was assumed to be 10% of the activity of 137Cs for the assessment of the regulatory limits. Obviously, this value originated from the experience with fallout radiostrontium and radiocesium from atmospheric nuclear explosions, for which the 90Sr:137Cs activity ratio of 1:10 was reported e.g. in contaminated rice [33]. Our study indicates the correctness of this conservative approach: in no Japanese sample investigated herein, the 90Sr level was higher than 10% of the 137Cs level. In most samples, the 137Cs activity concentrations was several orders of magnitude higher than the 90Sr the activity concentrations (see Figs. 2 and 3).

**Conclusions**

Several hot spots in Japan were investigated with respect to the activity concentrations of β–-emitting 90Sr and β–/γ-emitting 134Cs and 137Cs in soil and vegetation samples. Although the 137Cs activity levels were partly as high as in the kBq g⁻¹ range, the 90Sr contamination levels of any sample did not exceed the Bq g⁻¹ range. The radiocesium contamination could be clearly attributed to the Fukushima nuclear accident via its activity ratio fingerprint (134Cs/137Cs). Since short-lived 90Sr could no longer be determined, the source of the 90Sr theoretically could, in part, also be...
fallout from the nuclear explosions of the 20th century or previous nuclear accidents. In any case, it is likely that releases from the Fukushima nuclear accident contributed much of the 90Sr that was measured at the hot spots.

The low contamination levels confirmed previous simulations by Schwantes et al. [15], who predicted that most of the radiostrontium was retained inside the reactors. In fact, the 90Sr activity concentrations were partly four orders of magnitude lower than the respective 137Cs activity concentrations.

The data set (though limited in terms of sample numbers) suggests an intrinsic coexistence of 137Cs and 90Sr in the contaminations caused by the Fukushima nuclear accident. This observation is of great importance for the current food monitoring campaigns, which currently rely on the assumption that the activity concentrations of β-emitting 90Sr (which is relatively laborious to determine) is not higher than 10% of the level of γ-emitting 137Cs (which can be measured quickly). This assumption could be confirmed for the samples investigated herein.

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Supporting Information

Table S1 Samples, sample locations and activity concentrations of the investigated radionuclides. Uncertainties are due to counting statistics. Data were decay corrected to the time of the accident (11 March 2011).

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Author Contributions

Conceived and designed the experiments: GS VS KS. Performed the experiments: GS VS. Analyzed the data: GS VS. Contributed reagents/materials/analysis tools: KS. Wrote the paper: GS.