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Fukushima's Forgotten Radionuclides: A Review of the Understudied Radioactive Emissions

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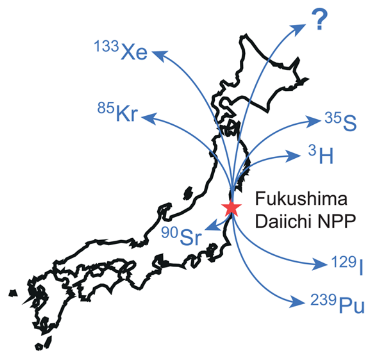
Ⓢ *Supporting Information*

ABSTRACT: In environmental monitoring campaigns for anthropogenic radionuclides released in the course of the Fukushima nuclear accident (2011), most focus had been on gamma-emitting radionuclides. More than 99% of the released activity was due to radionuclides of the elements Kr, Te, I, Xe, and Cs. However, little work had been done on the monitoring of radionuclides other than ^{131}I, ^{132}Te, ^{134}Cs, ^{136}Cs, and ^{137}Cs. Radionuclides such as those of less volatile elements (e.g., ^{89}Sr, ^{90}Sr, ^{103}Ru, ^{106}Ru, plutonium), pure beta-emitters (^{3}H, ^{14}C, ^{35}S), gaseous radionuclides (^{85}Kr, ^{133}Xe, ^{135}Xe) or radionuclides with very long half-lives (e.g., ^{36}Cl, ^{99}Tc, ^{129}I, some actinides such as ^{236}U) have been understudied by comparison. In this review, we summarize previous monitoring work on these "orphan" radionuclides in various environmental media and outline further challenges for future monitoring campaigns. Some of the understudied radionuclides are of radiological concern, others are promising tracers for environmental, geochemical processes such as oceanic mixing. Unfortunately, the shorter-lived nuclides of radioxenon, ^{103}Ru, ^{89}Sr and ^{35}S will no longer exhibit detectable activities in the environment. Activity concentrations of other radionuclides such as tritium, ^{14}C, or ^{85}Kr will become blurred in the significant background of previous releases (nuclear explosions and previous accidents). Isotope ratios such as ^{240}Pu/^{239}Pu will allow for the identification of Fukushima plutonium despite the plutonium background.



■ INTRODUCTION

On March 11, 2011, after the most powerful earthquake in Japanese history, a gigantic tsunami hit the eastern coast of Japan and killed almost 20 000 people. The tsunami destroyed the emergency cooling facilities of the Fukushima Daiichi nuclear power plant (NPP), which caused partial meltdown of the nuclear fuel. Pressure release operations from the reactor pressure vessels (RPV) resulted in the release of radionuclides in amounts that have only been exceeded by the Chernobyl accident. Consequently, hardly any environmental disaster has received as much public attention in recent years like the Fukushima nuclear accident.

Almost three years after the accident, the public interest still has not declined. After an unprecedented global monitoring campaign for radionuclides,[1] the scientific focus on this accident will also keep radioecologists and nuclear scientists busy for many years to come. The importance of radionuclide monitoring after the Fukushima nuclear accident is not only given by obvious radiological considerations and basic data for the Japanese remediation and decontamination campaigns but also by the fact that many radionuclides are suitable geochemical tracers that will provide valuable information about hydrological, atmospheric, and geochemical processes.

A significant part of the extensive Japanese monitoring campaign is not yet sufficiently "visible" or accessible to the global scientific community, as it has been stockpiled in governmental databases only without sufficient interpretation or discussion. Moreover, much of these data is available in Japanese language only. Important data were also recorded by the Comprehensive Nuclear-Test-Ban Treaty Organization (CTBTO), but these data remain confidential. In any case, much of the governmental monitoring efforts focused on easy-to-measure radionuclides. Here we would like to spotlight the understudied radionuclides. Without these important "pieces of the puzzle", the environmental impact of the Fukushima nuclear accident is far from being completely studied or understood.

One may argue that many of the understudied radionuclides are hardly radiologically relevant. However, their monitoring will be important also with respect to many other scientific questions. In any case, the great public interest in the Fukushima accident will make it necessary to study and assess emitted radionuclides even at low levels. This will help, partly restoring public trust in the scientific work-up of the accident as well as accident-related political decisions that are based on such scientific results.

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■ THE FORGOTTEN RADIONUCLIDES

Radionuclides are formed in a nuclear reactor by both nuclear fission and neutron activation. These nuclear processes yield numerous radionuclides of more than two dozens of elements. The total atmospheric releases from the damaged reactors was recently estimated as high as 520 PBq (1 PBq = 10^{15} Bq), excluding noble gases.[2] The fact that the vast majority of Fukushima's radioecological studies reported on the monitoring of radionuclides of iodine (e.g., ^{131}I), cesium (^{134}Cs, ^{136}Cs, ^{137}Cs), and tellurium (e.g., ^{132}Te) is explained by four basic physical, chemical or nuclear characteristics of these elements or nuclides:

- Only gaseous elements and I, Cs, and Te are sufficiently volatile to escape from the RPVs in significant amounts under the conditions encountered at Fukushima. More than 99% of the released radioactivity was due to radionuclides of these volatile elements.[2]
- The above listed radionuclides have half-lives long enough to allow for their monitoring after days and weeks. At the same time, their half-lives are short enough to cause high activities that are needed for their radioanalytical detectability.
- These radionuclides also have great cumulative fission yields or production rates by neutron capture and hence exhibit dominant activities.
- These radionuclides are potent γ-emitters, which allows for their identification and quantification with minimumal sample preparation by simple and straightforward γ-spectrometry.

These radionuclides were detected and monitored in air,[1,3] rainwater,[4−6] seawater,[7,8] soil,[9] plant material,[10−12] and animal tissue.[13−16] Gamma-emitters are the radionuclides of choice when activity data are needed immediately, for example, when it comes to the design of evacuation areas or food safety.[17−19] Unfortunately, the sole focus on γ-emitting radionuclides disguises the environmental impact of the accident on a holistic level. In the following we discuss some yet understudied isotopes that, if possible, need to be addressed in future studies for a complete assessment of the Fukushima nuclear accident (see Table 1).

Table 1. Orphan Radionuclides after Fukushima[a]

radionuclide	half-life	decay radiation	nuclear origin	biological relevance
^{3}H	12.32 y	low energy β^-	FP & AP	contained in water and all biomolecules
^{14}C	5730 y	β^-	FP & AP	contained in all biomolecules
^{35}S	87.37 d	β^-	AP	contained in many biomolecules
^{36}Cl	3.0 × 10^5 y	β^-, (ε)	AP	essential electrolyte, contained in digestive juices
^{85}Kr	10.75 y	β^-, (γ)	FP	none
^{89}Sr	50.53 d	β^-, (γ)	FP & AP	mistaken for Ca (bone-seeker)
^{90}Sr	28.90 y	β^-	FP	
^{99}Tc	2.1 × 10^5 y	β^-, (γ)	FP	TcO_4^- is mistaken for I^- and concentrated in thyroid
^{103}Ru	39.4 d	β^-, γ	FP	none (heavy metal)
^{106}Ru	373.6 d	β^-[b]	FP	
^{129}I	1.57 × 10^7 y	β^-, (γ)	FP	concentrated in thyroid
^{131m}Xe	11.9 d	γ, e^-	FP	none
^{133m}Xe	2.2 d	γ, e^-	FP	
^{133}Xe	5.25 d	β^-, γ, e^-	FP	
^{135}Xe	9.1 h	β^-, γ	FP	
^{235}U	7.038 × 10^8 y	α, γ	nuclear fuel	none, but poisonous heavy metal
^{236}U	2.342 × 10^7 y	α, (γ)	AP	
^{238}U	4.468 × 10^9 y	α, (γ)	nuclear fuel	
^{238}Pu	87.7 y	α, (γ)	AP	none, but accumulated in bone tissue
^{239}Pu	24 110 y	α, (γ)	AP & nuclear fuel	
^{240}Pu	6561 y	α, (γ)	AP	
^{241}Pu	14.33 y	low energy β^-, α, (γ)	AP	
^{241}Am	432.6 y	α, γ	AP	none, but accumulated in bone tissue

[a] FP, fission product; AP, activation product; (γ), low intensity γ rays; ε, electron capture; e^-, conversion electron. [b] In secular equilibrium with γ-emitting ^{106}Rh.

■ TRITIUM (T)

Tritium (^{3}H) is a low-energy β^--emitter with a relatively long half-life (12.32 y). It is produced naturally by interaction of cosmic rays with air, for example, though the reaction ^{14}N(n,^{3}H)^{12}C. In nuclear reactors, anthropogenic ^{3}H is formed not only from nuclear fission as a ternary fission product with a fission yield of approximately 0.01% but also as an activation product from ^{2}H(n,γ)^{3}H (cross section for thermal neutron capture 0.51 mb) in the primary coolant circuit and from trace lithium impurities via ^{6}Li(n,α)^{3}H.[20] With such a nuclear "history", it can be expected that most of the ^{3}H inventory of the damaged reactors was released quickly after fuel melt-down and in the course of the venting operations. The inventory of ^{3}H in the Fukushima Daiichi reactor Units 1 and 3 (presumably ternary fission product fraction only) was calculated to be 1.81 × 10^{13} Bq as of 12 March 2011.[21]

Only little information is yet available in English scientific literature on findings of ^{3}H in the environment after Fukushima. Although the releases of ^{3}H undoubtedly exceeded the activities of less volatile radionuclides, the lack of monitoring data is probably only explainable by the adverse nuclear properties of ^{3}H in radiometric measurement, in particular the lack of γ-rays and the very low energies of the emitted β^- particles (max. 18.6 keV). Although gas proportional counting methods can be applied for the determination and quantification of ^{3}H,[22,23] modern environmental monitoring laboratories usually rely on liquid scintillation counting (LSC) as the radioanalytical method of choice. LSC is susceptible for color and chemical quenching and hence requires a (water) sample free of chemical contaminants. Purification of a water sample for LSC can be achieved by distillation, freeze-drying, ion exchange and other methods. Since HTO behaves chemically almost identically with its H_2O-matrix no chemical enrichment can be applied prior to measurement. However, since HTO exhibits a slightly higher binding energy than HDO and H_2O, it can be concentrated by electrolysis of the water. Using this method, more than 90% of the tritium can be found in the remaining water. However, since this laborious process takes 5−7 days for completion, it is usually not applied as a routine method for large sample numbers.[24] One of the most sensitive techniques uses the ingrowth of ^{3}He by beta decay of ^{3}H, which is applied most efficiently for aqueous samples.[25] The water sample is stored in a steel vessel and degassed by applying underpressure. The sample is stored for several months to wait for the ingrowth of ^{3}He. Helium-3 is then collected and analyzed with a dual collector noble gas mass spectrometer. This method may be time-consuming, but it reaches sensitivities down to 0.01 Tritium Units (TU).[26] Environmental tritium is often quantified in TU, which is defined as 0.118 Bq ^{3}H per kg of H_2O or 7.19 decays per minute of ^{3}H per L of H_2O or a ratio of 1 atom ^{3}H per 10^{18} atoms of ^{1}H. For special analytical purposes also accelerator mass spectrometry (AMS) can also be applied to the analysis of tritium, however, this is probably not the method of choice for routine environmental analyses.[27]

Tritium has been found in plants around the Fukushima power station in levels significantly higher than the previous background concentration (Free Water Tritium, FWT < 1.5 Bq/L).[28] Kakiuchi et al.[28] also showed a rough dependence of ^{3}H concentrations in the FWT concentrations in plants with distance to the NPP, with a maximum FWT concentration of 167 Bq/L 20 km northwest of the NPP. This distance dependence has been examined in detail and confirmed by Matsumoto et al. (see Figure 1).[29] Based on their result of the HTO concentration in atmospheric moisture (5.6 kBq/L), Kakiuchi et al. estimate the dose due to ^{3}H inhalation on the order of a few microsieverts. It is important to note that ^{3}H has a short biological half-life of only few days.[30] Matsumoto et al.[29] determined ^{3}H levels in precipitation, coming to the conclusion that the first rain at Tsukuba had ^{3}H levels 30 times higher (160 TU) than preaccident rain (6 TU), yet still not exceeding the regulatory limit for potable water (85 000 TU). The atmospheric ^{3}H level at source during the earliest stage of the accident was estimated to 1500 Bq/m^3.[29]

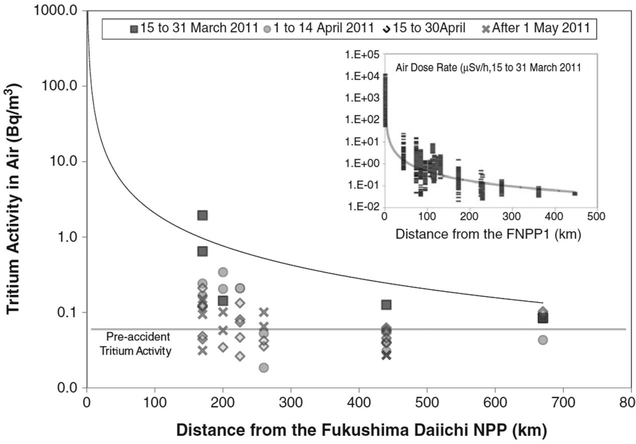

Figure 1. Plot of sampling distance from the Fukushima Daiichi NPP versus ^{3}H activity in air (Bq/m^3) deduced from washout ratio of 1×10^4 as a generic value. Data are grouped by sampling periods. A curve shown is a least-squares fit (power law) of the 15−31 March data with a constraint that the tritium activity decreases with distance in proportional to the air dose rates as shown in the imposed diagram in which the air dose rates (μSV/h) between the same time period recorded at monitoring stations along the SW to SSW direction from the Fukushima NPP. A curve in the imposed diagram is a regression of the median value of each locality versus distance from the source. See ref 29 for sources of the monitoring data. Taken from ref 29. Reprinted with permission from Elsevier, 2013.

Although tritium with its high exemption limit and the rapid dilution in the environment is unlikely to cause significant health hazards, it is surely suitable as a tracer nuclide to study environmental processes, in particular for groundwater processes[31] and water circulation in the oceans.[26,32−34] Moreover, the Fukushima nuclear accident impressively revealed the need for published environmental radionuclide data so that the impact of future accidents or releases can be assessed correctly against the background of long-lived radionuclides. The Fukushima nuclear accident surely impacted the ^{3}H background in Japan, however, apart from one study,[29] it has not been determined so far with sufficient effort.

The effect of the tritium release from the damaged Fukushima Daiichi reactors has to be set into relation with previous emissions to allow for a better assessment of their environmental ecological relevance. The greatest amount of anthropogenic ^{3}H was released from nuclear weapon tests in the 20th century: 186 000 PBq.[26,35] The Fukushima nuclear accident contributed relatively little to the marine tritium inventory: 0.1−0.5 PBq (liquid discharges into the Pacific Ocean plus atmospheric deposition; based on samples taken in June 2011).[26] The discrepancy of this number with the above-mentioned inventory of 0.0181 PBq[21] is probably due to the fact that this inventory is just for reactor Units 1 and 3, and would be higher if Units 2 (and 4) were taken into account. Furthermore, we suspect that the inventory only includes fission-product ^{3}H but not activation-derived ^{3}H in the coolant water. The ^{3}H background (pre-Fukushima) activity in the NW Pacific surface water was estimated to 0.6 ± 0.1 TU.[26] The surface ocean water samples taken in June 2011 exhibited ^{3}H levels in the range of 0.4−1.3 TU. The background is largely dominated by the nuclear weapons tests which contributed a total of 13 300 PBq (total ocean inventory as of year 2000).[36] The natural ^{3}H inventory is just 2000 PBq. The peak activity in atmospheric moisture in 1963 exceeded the natural, cosmogenic background by a factor of 1000.[26]

■ CARBON-14

Carbon-14 is a long-lived β^- emitting radionuclide (156 keV max.) that is produced naturally in the upper atmosphere in the nuclear reaction ^{14}N(n,p)^{14}C. In nuclear reactors it is produced not only through neutron action on N impurities of materials exposed to the neutron flux, but also by neutron capture of stable carbon, ^{13}C(n,γ)^{14}C or the reaction ^{17}O(n,α)^{14}C. Lastly, it is also a fission product of (ternary) nuclear fission with a cumulative fission yield of 1.6×10^{-4}% (thermal ^{235}U fission).

Environmental levels of ^{14}C can be determined by LSC and AMS, with typical detection limits of 30 mBq[20] and 10^{-7} Bq,[37] respectively. Due to the extensive sample preparation and the low accessibility of AMS, environmental monitoring is still frequently conducted using radiometric methods, whereas for radiocarbon dating purposes AMS has established as the method of choice. For details on analytical procedures, the reader is referred to the extensive literature on this topic, for example, refs 37 and 38.

In contrast to the Fukushima's boiling-water reactors, the RBMK reactor type used in Chernobyl had a significant carbon source exposed to high neutron fluxes in the form of the graphite moderator. However, an even more important ^{14}C source was ^{14}N impurities in the graphite. Carbon-14 produced in Chernobyl's moderator was partly released in the form of $^{14}CO_2$ and graphite particles when the graphite caught fire in the course of the accident.[2] The total release of ^{14}C from Chernobyl was estimated to 44 TBq.[39] Inside the Fukushima reactors, activation of ^{14}N and ^{13}C could only take place on trace impurities of both elements in the materials used. During fabrication, the fuel rods of this reactor type are evacuated and backfilled with dry helium to improve the thermal conductivity across the pellet-cladding gap, hence excluding most of the ^{14}N.

Carbon-14 remains one of Fukushima's most understudied radionuclides. So far, monitoring of ^{14}C and the possible influence of the Fukushima nuclear accident has been addressed only once in (English) literature. From 1945 to 1963, the ^{14}C/^{12}C ratio in atmospheric carbon increased rapidly due to atmospheric nuclear explosions, since the implementation of the Partial Nuclear-Test-Ban Treaty in 1963 it is steadily decreasing. A Korean AMS study[40] observed a decrease in the average ^{14}C/^{12}C atomic ratio for the main clean air sites between 2010 and 2011 which was smaller than that of between 2009 and 2010, which, in part, could be a contribution of ^{14}C releases from Fukushima, which needs further investigation.

Based on the experience from Chernobyl, which, at least at some distance to the NPP,[41,42] did not impact the ^{14}C levels in Europe, it remains unlikely that a measurable emission of ^{14}C from Fukushima Daiichi can be observed on a global scale. Local effects, as shown after Chernobyl,[39] may be detectable with sensitive methods (AMS).

■ SULFUR-35

Sulfur-35 is another pure β^- emitter (167 keV max.) and an interesting radionuclide with respect to its nuclear origin. It is a naturally occurring radionuclide that is formed by action of cosmic rays on argon. Sulfur-35 atoms produced in this reaction are quickly oxidized to $^{35}SO_2$ and further to $^{35}SO_4^{2-}$ by the atmospheric $^\bullet$OH radical. The sulfate is scavenged by water droplets or bound to aerosols, on which it is removed from the atmosphere by dry and wet deposition. Owing to its short half-life (87.5 days) nuclear methods are used to determine the activity of ^{35}S in environmental samples. Quantification of ^{35}S can be performed by a Geiger-Müller counter with a very thin entrance window or, more frequently, LSC.[43] As for any pure beta emitter, chemical separation from other radionuclides is crucial. This is usually achieved by precipitation in the form of $Ba^{35}SO_4$, followed by reduction of the sulfate ion to sulfide and release to the gas phase in the form of $H_2{}^{35}S$. The H_2S is absorbed in dilute NaOH solution and mixed with the LSC cocktail for measurement.[44] However, also analytical protocols for a direct, highly sensitive LSC measurement of the $BaSO_4$ precipitate have been developed.[45]

Sulfur-35 has been monitored soon after the Fukushima accident in California in the form of $^{35}SO_4^{2-}$ and $^{35}SO_2$ (Figure S1 in the Supporting Information (SI)).[46] There is common agreement that the main source of ^{35}S is most likely an (n,p) nuclear reaction on chlorine, ^{35}Cl(n,p)^{35}S, which prevails over the activation by neutron capture of ^{34}S by a factor of 200.[46] The source of the chlorine inside the reactor has been debated. Priyadarshi et al.[46,47] argued that the cooling operations from March 13 using several hundred tons of seawater mixed with boric acid (to inhibit the nuclear chain reaction) are the source of ^{35}Cl. Although Priyadarshi et al. did not comment on the source of the neutrons at the time of seawater injection, it is likely that only spontaneous fission of heavy nuclides could have been the source, as the nuclear chain reaction in the reactors was inhibited by the control rods and the injection of borated (sea) water. Upon release in the course of the ventings, ^{35}S was expected to oxidize to $^{35}SO_2$ and further to $^{35}SO_4^{2-}$ (Figure 2). Both substances were transported across the Pacific Ocean in the gas and aerosol phase, respectively, and were detected in significantly elevated concentrations on the U.S. west coast in mid/late March 2011 (see SI Figure S1). The natural atmospheric background of ^{35}S, the source of which is dominated by spallation processes of cosmic rays on ^{40}Ar, was exceeded by a factor of 3 or more (or more than a factor of 2 higher than the spring average) for both $^{35}SO_2$ and $^{35}SO_4^{2-}$.[46]

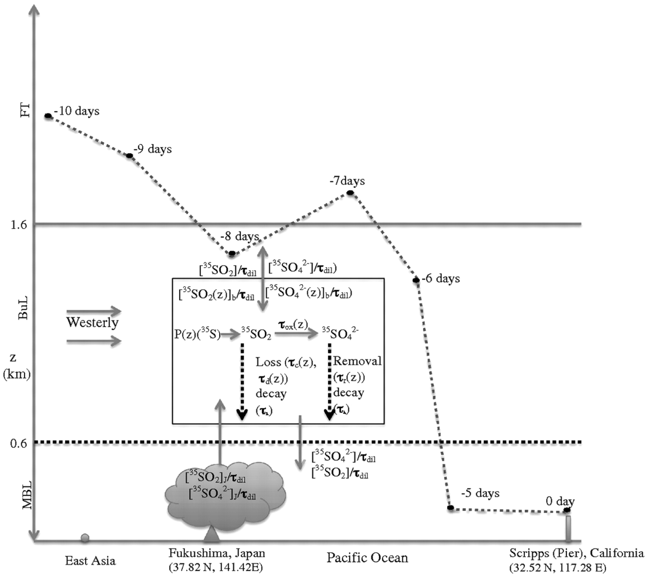

Figure 2. Schematic description of a moving box model developed to calculate the concentration of $^{35}SO_4^{2-}$ and $^{35}SO_2$ at Scripps pier, La Jolla (California) due to the long-range transport of radiation plume from Fukushima. The atmosphere is divided into three layers: marine boundary layer (MBL), buffer layer (BuL), and free troposphere (FT). τ_{dill} is the dilution lifetime of the radiation plume. τ_{ox} is the oxidation lifetime of $^{35}SO_2$, whereas τ_c and τ_d are the cloud scavenging and dry depositional lifetime of $^{35}SO_2$, respectively. τ_r is the removal lifetime of $^{35}SO_4^{2-}$. The dotted line represents the mean transit altitude at which air mass transport occurred. The model parameters in the box were changed according to its transit altitude. From ref.[46] Reprinted with permission from the National Academy of Sciences, 2011.

Although this is a remarkable result of a rather exotic radionuclide monitored in a remote station, the suggested creation path of ^{35}S caused some dispute.[48] Strub et al. argue that the technically unavoidable chlorine content (typically ~0.1 ppm) of the primary coolant is a more relevant source of chlorine. Although this is 5 orders of magnitude below the chlorine concentration of seawater, the neutron flux density of an operating reactor is 6 orders of magnitude higher than in shut-down state. An even more relevant source of ^{35}S, according to Strub et al.,[48] is the chlorine impurities in the nuclear fuel itself. In any case, the link of elevated atmospheric ^{35}S concentrations with the Fukushima nuclear accident stands beyond debate.

Sulfur-35 was also detected in aerosol and rainwater samples from several Japanese prefectures in a sampling campaign that lasted until September 2011.[49] Maximum aerosol ^{35}S activity concentrations in surface air were 6 mBq/m^3, which was said to be 100 times higher than the natural background. Maximum concentration of ^{35}S in rainwater reached up to 90 mBq/L.[49]

■ RADIOACTIVE NOBLE GASES

The noble gases, per definition, are characterized by the greatest volatility among the fission products. Owing to their chemical inertness, they are unlikely to contribute to internal exposure, however they may contribute to the external exposure until dilution in the air. In any case, some nuclides of krypton (^{85}Kr) and xenon (^{131m}Xe, ^{133m}Xe, ^{133}Xe, and ^{135}Xe) are of great importance in nuclear forensics and for the verification of the Comprehensive Nuclear-Test-Ban Treaty (CTBT). Therefore, it is crucial that their background activity is known and contributors to the background are identified and understood.[50−53]

Krypton-85. The typical fission products of radiokrypton are usually very short-lived, with the exception of long-lived ^{85}Kr ($T_{1/2}$ = 10.8 y). It is produced by fission with a cumulative fission yield of 1.3% (thermal ^{235}U fission) and to a minor extent by neutron capture in the reaction ^{84}Kr(n,γ)^{85}Kr. The natural ^{85}Kr levels, as determined in prenuclear era air samples, were several orders of magnitude below modern levels and hence contribute negligibly to the current global ^{85}Kr background.[54] Krypton-85 is a β^--emitter (0.7 MeV max.), but a poor γ-emitter (γ-efficiency at 514 keV is 0.43%). A radiometric method for the determination of ^{85}Kr is low-level counting (LLC) using a gas proportional counter operated at increased pressure; see ref 55 for a detector design. Often krypton, together with other dissolved gases, is degassed from large amounts of environmental water samples. In an alternative approach,[56] atmospheric krypton can be enriched and purified by cryogenic absorption on activated charcoal (cooled with liquid N_2), desorption and gas chromatography (for the determination of the stable krypton fraction), followed by counting in a gas proportional counter. Mobile and automated systems have a detection capability (i.e., the smallest concentration of analyte that can be reliably distinguished from zero) of ^{85}Kr down to 0.1 Bq·m^{-3},[57] which is approximately a tenth of the current atmospheric ^{85}Kr background.

From a nuclear forensics point of view, ^{85}Kr is of special interest because it allows for the detection of clandestine activities (e.g., reprocessing of spent fuel for the extraction of possibly weapons-grade plutonium) or information on whether or not a nuclear fuel reprocessing plant (NFRP) is operational.[57−59] The production of 1 kg weapons-grade ^{239}Pu is associated with the onset of an estimated activity of 1.5−2.0 × 10^{13} Bq ^{85}Kr,[60] that can be detected if air is sampled at a sufficiently short distance. Like ^{3}H in oceanography, ^{85}Kr is also a suitable tracer radionuclide to study atmospheric processes (air circulation).[61−63]

It can safely be assumed that virtually the entire ^{85}Kr inventory of reactor cores of Fukushima Units 1−3 have been released into the environment. Concerning the inventory, there is some disagreement in literature. Ahlswede et al.[58] estimated a total ^{85}Kr inventory of 44.1 PBq, which is significantly higher than the estimate of Schwantes et al.[21] (0.364 PBq in Units 1 and 3). Even if this value was (more than) doubled to account for the inventories contained in Units 2 and 4, the authors' estimation would be more than 1 order of magnitude lower than the estimate by Ahlswede et al. This discrepancy illustrates the need for experimental validation of the ^{85}Kr source term from Fukushima.

Although the atmospheric content of ^{85}Kr (today more than 5000 PBq, leading to an average activity concentration of 1.3 Bq·m^{-3} in air)[63] has been dominated by the emissions of NFRPs, nuclear accidents also contribute to this background. It is noteworthy that no experimentally validated data on Fukushima's contribution to the environmental presence of this important radionuclide have been published up to now. The estimate of Ahlswede et al.[58] (44 PBq, see above) would have exceeded the ^{85}Kr releases from Chernobyl (33 PBq).[2] The ^{85}Kr source term of the Three Mile Island accident was 1.3 PBq.[64] Especially with respect to its importance for the IAEA's safeguards activities, well-founded data on ^{85}Kr are needed.

Radioxenon. In contrast to ^{85}Kr, more (experimental) information is available on environmental Fukushima-derived radioxenon, in particular ^{133}Xe. This is also due to the International Monitoring System of the CTBTO, because the above-mentioned radioxenon nuclides ^{131m}Xe, ^{133m}Xe, ^{133}Xe, and ^{135}Xe are of key importance for CTBT verification.

Radioxenon isotopes are prominent fission products with variable cumulative fission yields (thermal ^{235}U fission): 0.046% (^{131m}Xe); 0.19% (^{133m}Xe); 6.76% (^{133}Xe); 6.97% (^{135}Xe). For its detection, atmospheric radioxenon is generally trapped in activated charcoal traps, for example,[65] for preconcentration. The measurement is generally either performed with β/γ-coincidence spectrometry, high-resolution γ-spectrometry, proportional counters or gas chromatography−mass spectrometry.[66] Gas chromatography−mass spectrometry, however, is both time and cost intensive and, due to the short half-lives of the radioxenon nuclides, usually outperformed by radiometric methods.

Literature on the ^{133}Xe inventories of the Daiichi Fukushima reactors and source terms again shows some discrepancies. Schwantes et al.[21] published an inventory of 4.83 × 10^{16} Bq for Units 1 and 3. This is approximately 2 orders of magnitude lower than early inventory estimates by Stohl et al.[67] The overall release of ^{133}Xe was first estimated to 1.53 × 10^{19} Bq by Stohl et al.[67] and later re-discussed and refined to 1.42 × 10^{19}Bq.[68] Both values are in quite good agreement with another estimate (1.2 × 10^{19} Bq).[69] One must note that ^{133}I decay ($T_{1/2}$ = 20.8 h) adds to the ^{133}Xe releases which explains that the release estimates even exceeded the sole ^{133}Xe inventory.

Radioxenon stations around the globe harnessed the Fukushima plume to test their systems under "real conditions".[67−72] Even new methods for the monitoring of CTBT-relevant nuclides were developed.[73]

In western Canada, ^{133}Xe activity concentrations were in the range of 30−70 Bq/m^3, which still not significantly increased the ambient dose rate levels.[72] In the northwest U.S., Bowyer et al.[69] monitored a maximum of 40 Bq/m^3, which is in agreement with the observations from western Canada. These ^{133}Xe activity concentrations are much higher than activity concentrations of other radionuclides in air (e.g., particulate ^{131}I or ^{134,137}Cs) around the globe, which rarely exceeded a range of a few mBq/m^3 outside of Japan.[1−4] However, the combined radioxenon activities in the northwest U.S. caused a maximum daily effective dose of 0.0056 μSv/d, which is approximately 1/1500 of the local daily effective background dose (8.52 μSv/d).[69] Xenon-133 activity concentrations in China (max. 5.5 Bq/m^3) were one decade lower than in North America.[71]

Whereas ^{133}Xe has been studied relatively intensively, only few studies reported on the monitoring of one of the other CTBT-relevant radioxenon nuclides ^{131m}Xe (e.g., ref 69), ^{133m}Xe (e.g., ref 69) or ^{135}Xe. On 1 November 2011, traces (2.7 × 10^{-2} Bq/cm^3) of short-lived ^{135}Xe ($T_{1/2}$ = 9.1 h) were detected at a monitoring station in Fukushima Daini. Early concerns of a continued chain reaction could be disproved as spontaneous fission of heavy actinide nuclei proved to be the source of this radioxenon emission.[74]

STRONTIUM-89 AND -90

The radiostrontium isotopes ^{89}Sr and ^{90}Sr are prominent fission products (cumulative fission yields 4.9 and 5.9%, respectively). Strontium is categorized as a fission product with intermediate volatility. Strontium-89 has a relatively short half-life (50.5 days), and it is a weak γ-emitter (909 keV with a very low intensity of 0.0096%, which makes γ-spectrometric detection in environmental monitoring impossible). Strontium-90 is a pure β^- emitter with a long half-life (by human dimensions) of 28.9 years, which is still short enough to cause a great specific activity. More importantly, due to its chemical similarity with calcium, radiostrontium is a bone seeker and may exhibit long retention times in the body. Possible consequences of ^{90}Sr (and ^{89}Sr) uptake are bone cancer and leukemia. Due to all these characteristics, ^{90}Sr was known to often "dictate risk over longer periods of time" after previous incidents.[21]

Unfortunately, ^{89}Sr, ^{90}Sr and its daughter nuclide ^{90}Y ($T_{1/2}$ = 64 h; a poor γ-emitter with 1.4×10^{-6}% efficiency at 2186 keV) cannot be determined in straightforward γ-spectrometry. The determination of radiostrontium hence requires laborious chemical isolation of the Sr fraction from other radionuclides (primarily radiocesium). This makes ^{90}Sr an important but "inconvenient" radionuclide and partly explains why ^{90}Sr is one of the severely understudied radionuclides after the Fukushima nuclear accident. Another reason for this phenomenon is the fact that only a small fraction of the radiostrontium inventory was emitted through the gas phase from the damaged reactors owing to its low volatility.[21] Special attention will have to be paid on ^{90}Sr with respect to the liquid discharges from the reactors in future studies.

Determination of radiostrontium in environmental samples usually involves the chemical separation of strontium from other radionuclides, followed by (radiometric) analysis. The separation nowadays usually involves extraction chromatography using strontium specific resins. For simple sample matrices such as water samples, this extraction chromatography may be a sufficient separation method, or it can be applied in combination with precipitation techniques.[75] Such precipitation techniques include the historic but still used $Sr(NO_3)_2$ precipitation technique using fuming nitric acid,[76] which helps separating Sr from Ca, the latter of which is often present in environmental samples in great excess. Then Sr is separated from Ba, Ra, and Pb by precipitation of $SrCrO_4$. Coprecipitation with $Fe(OH)_3$ eliminates Y and Ru; finally, Sr is precipitated as $SrCO_3$.[75] Sometimes slightly modified precipitation techniques are used and proposed in literature.[77,78] Alternative to the above protocol, Sr may be separated from Ca, Ba, and Ra by means of $Ca(OH)_2$ and $Ba(Ra)SO_4$ precipitation for the separation of interfering matrix elements and radionuclides, which is especially useful in samples with high Ca content.[79] The strontium specific resin faces limitations when dealing with samples with high Sr contents, which becomes a relevant restraint in the determination of low ^{90}Sr concentrations, where large sample sizes have to be worked up. Here precipitation techniques remain the separation method of choice. In any case, the application of Sr specific resins accelerates the analysis and provides good Sr recoveries. Due to similar ionic radii, β^--emitting, naturally occurring ^{210}Pb will also be retained by the Sr specific resin. This possible interference does not pose a problem as long as the elution reagent is sufficiently acidic, which will elute strontium but not the absorbed lead.[80] Radiometric measurement may be performed with LSC or gas ionization detectors, the latter of which provides higher sensitivity. The counting efficiency of the LSC is approximately twice as high; however, the background level in LSC is usually 10 times higher than in gas flow counters. However, LSC allows for the spectral distinction between ^{89}Sr and ^{90}Sr, taking advantage of the higher maximum β^- energy of ^{89}Sr (1.5 MeV) compared with ^{90}Sr (0.5 MeV). In particular, ^{89}Sr can be determined using Cherenkov counting, if the sample is measured in aqueous media without a scintillation cocktail. The energy threshold for Cherenkov radiation in water is 256 keV. Due to the lower energy β^- energy, only a very small fraction of the β^- particles of ^{90}Sr will produce a Cherenkov radiation signal, but ^{89}Sr will produce a much more intense Cherenkov signal.[37] The same method can be used for determination of ^{90}Sr after (partial) ingrowth of ^{90}Y into radioactive equilibrium (which is completed after approximately 3 weeks). The ingrowth of the daughter nuclide ^{90}Y also allows for a simple QC of the analysis, as the LSC signal should increase with time until equilibrium is reached.

Also nonradiometric methods, in particular ICP-MS can be used for the determination of radiostrontium.[27,37,81−86] The main focus is on the monitoring of ^{90}Sr, because the determination of short-lived ^{89}Sr by ICP-MS suffers from the much lower atom number compared with ^{90}Sr. At identical activity levels of ^{89}Sr and ^{90}Sr, the number of ^{89}Sr atoms is approximately lower by a factor of 200. One major problem in the mass spectrometry of ^{90}Sr is caused by isobaric interference of ubiquitous $^{90}Zr^+$ and other ions, for example, $^{50}Ti^{40}Ar^+$, $^{54}Fe^{36}Ar^+$, and many others. This problem can be reduced chemically, by preconcentration and pretreatment of the sample; and instrumentally, by reaction with a reaction gas (O_2) in a dynamic reaction cell (ICP-DRC-MS). Using this approach, the interference caused by $^{90}Zr^+$ could be reduced by a factor of 10^7.[85] This method is capable of determining ^{90}Sr levels down to the 1 $Bg \cdot g^{-1}$ range or even slightly below. Although ICP-MS cannot compete with radiometric methods with respect to sensitivity and detection limits, ICP-MS is superior in terms of time-efficiency and potential sample throughput.[84]

The radiostrontium inventories of the Fukushima Daiichi Units 1 and 3 were reported as 2.87×10^{15} Bq (^{90}Sr) and 2.55×10^{16} Bq (^{89}Sr).[21] The authors predicted that the majority of ^{90}Sr remained inside the reactors, which was confirmed by the few (published) investigations of ^{90}Sr in Japan.[87] A recent study[88] investigated soil and plant material samples for radiocesium and radiostrontium and found 1.14 kBq ^{90}Sr per kg in plant samples from the gate of the Fukushima Daiichi NPP. Soil from the same spot contained 1.07 kBq ^{90}Sr per kg. In both cases, radiocesium activity concentrations exceeded the ^{90}Sr activity concentration by more than 3 orders of magnitude. Due to chemical fractionation processes, the correlation between ^{137}Cs and ^{90}Sr, however, was found to be relatively poor (Figure 3).

In regard to food safety, the Japanese authorities relied on the assumption that the activity concentrations of β^- -emitting ^{90}Sr (which is relatively laborious to determine) in any food sample is not higher than 10% of the level of γ-emitting ^{137}Cs (which can be measured quickly), which helped increasing the sample throughput.[17−19] This conservative correlation hypothesis, despite the relatively poor correlation between these radionuclides, was confirmed for the environmental samples

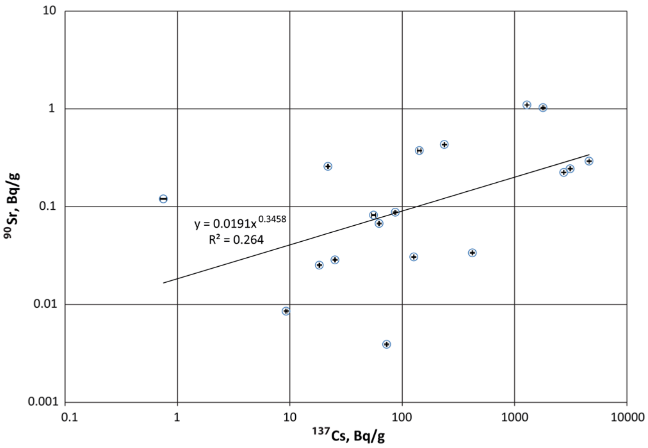

Figure 3. Correlation of the activity concentrations of ^{90}Sr vs ^{137}Cs. Taken from ref 88. Reprinted according to the Creative Commons Attribution License.

investigated in ref 88. Dissimilar chemical behavior in the environment, however, will cause fractionation of the two elements over time. Such effects may affect the assumption of the intrinsic coexistence of Sr and Cs in food, calling for independent radiostrontium monitoring.

Several studies investigated ^{90}Sr in seawater of the Pacific Ocean. One study determined activity concentrations of ^{90}Sr (range from 0.8 ± 0.2 to 85 ± 3 Bq/m^3) and ^{89}Sr (9 ± 6 to 265 ± 74 Bq/m^3) in surface seawater.[89] The pre-Fukushima ^{90}Sr-background is about 1.2 Bq/m^3. The authors also present evidence via correlation factors with ^{137}Cs that direct liquid discharges of ^{90}Sr to the ocean exceeded atmospheric deposition as the main source of Fukushima-derived radiostrontium in the Pacific. The ^{90}Sr releases (up to 400 Bq/m^3) into the Pacific partly and in some areas even exceeded the ^{137}Cs releases.[90] In a 2011 study, a significant increase of ^{90}Sr in seawater around the Korean peninsula, however, could not (yet) be determined (activity concentration range in surface waters 0.63−1.24 mBq/kg).[91]

According to ref 92, the maximum dissolved inventory for ^{90}Sr was 58 TBq (for 10 April 2011) as found by numerical modeling. Casacuberta et al.[89] estimated the range of the total released ^{90}Sr to the Pacific Ocean between 90 and 900 TBq. Povinec et al. estimate that the total release of ^{90}Sr could reach 1 PBq.[90]

Data on ^{90}Sr in air are very sparse. In the European monitoring campaign,[3] [89,90]Sr was monitored in air filters by some stations, however, no abnormal values were detected.

■ TECHNETIUM-99

Technetium-99 is a prominent, long-lived fission product (cumulative fission yield 6.11% for thermal neutron fission of ^{235}U; $T_{1/2} = 2.1 \times 10^5$ y). It is a β^- emitter with a maximum energy of 294 keV. Technetium exhibits a unique chemistry among the fission products. Oxidation states from +1 to +7 are known, of which +4 and +7 are the only environmentally relevant ones. In heptavalent form, Tc forms the stable pertechnetate (TcO_4^-) ion, which makes ^{99}Tc(VII) very water-soluble and mobile. Due to its anionic nature, TcO_4^- is not adsorbed or retained by synthetic or natural cation exchangers (such as clay/silt barriers). Under reducing conditions, Tc exists in the form of sparingly soluble Tc(IV), in particular $TcO_2 \cdot n\ H_2O$. Presence of (organic) ligands, however, increases the solubility of Tc(IV).[93] The ionic radius of TcO_4^- (2.40 Å)[94] is similar to the one of I$^-$ (2.20 Å), which explains its accumulation in the thyroid.

Several analytical techniques are applied for the determination of Tc in environmental samples. Due to very low environmental concentrations, preconcentration and separation are usually required. Preconcentration is typically performed with anion exchange columns, which have a high affinity for the TcO_4^- anion, whereas most other radionuclides are eluted and thereby removed.[37] Further purification is performed by solvent extraction or coprecipitation techniques, as described in ref 37. The extraction chromatography technique using Eichrom's TEVA resin is especially useful to purify ^{99}Tc and remove ^{106}Ru (interference in radiometric measurements) or ^{99}Ru (interference in ICP-MS).[37,95,96] Gamma-emitting ^{95m}Tc is a suitable radiotracer to determine the recovery of the separation. Radiometric methods for the determination of ^{99}Tc include gas ionization detectors (MDC 1.5 mBq), LSC (MDC 17 mBq), AMS (MDC 6−10 μBq), NAA (2.5 mBq) as well as various ICP-MS-based methods with MDCs between 10 and 0.16 mBq.[37] Please find details one the analytical methods and procedures elsewhere.[37,97]

Monitoring data of the Tc releases (or releases of ^{99} Mo with subsequent decay to ^{99m}Tc) from Fukushima are rare. Moreover, those few reports in scientific literature reported exclusively on γ-emitting ^{99m}Tc. In not a single study long-lived ^{99g}Tc was detected or investigated. The activity ratio of ^{99m}Tc to ^{137}Cs in soil from the Fukushima NPP site was reported to be 0.227 at one site and 0.417 on another site (decay-corrected to shutdown), which appears relatively high.[98] In any case, the decay characteristics of the ^{99m}Tc corresponded more to the decay of its mother ^{99}Mo, which indicates that primarily ^{99}Mo (not ^{99m}Tc itself) was released, followed by ingrowth of ^{99m}Tc into its secular equilibrium.

Some studies only reported the presence of the characteristic ^{99m}Tc peak at 141 keV in the γ-spectra, for example, in Iitate,[99] Chiba,[100] or Tsukuba;[101] but did not quantify the ^{99m}Tc levels. Another study from Tsukuba quantified activity concentrations in air, with a maximum for ^{99}Mo/^{99m}Tc of 0.462 Bq/m^3 in the period from 20 to 22 March 2011.[102] Cesium-137 activity concentrations were 7.01 Bq/m^3 in this time window, hence challenging the ratio Yamamoto found closer to the source. Doi et al. also found large variations in the ^{99}Mo-^{99m}Tc/^{137}Cs ratio and concluded that the atmospheric behavior of ^{99}Mo/^{99m}Tc was "notably different" from that of ^{137}Cs and ^{132}Te.[102] For Wako, maximum ^{99}Mo/^{99m}Tc activity concentrations (air) of 1.3 Bq/m^3 were reported (together with 8.8 Bq/m^3 for ^{137}Cs).[103] The CTBTO station at Takasaki reported generally much lower activity concentrations, but a relatively high contribution from ^{99m}Tc of 4.4 mBq/m^3 during 25−26 March 2011. In this filter, the ^{99m}Tc activity concentration was only exceeded by ^{131}I (23.2 mBq/m^3), but not by ^{137}Cs (3.0 mBq/m^3).[104] In contrast, in situ measurements in Fukushima City revealed that the ^{99m}Tc contamination (~1 Bq/cm^2) of a 2 × 2 m^2 plot was exceeded by all other γ-emitting radionuclides.[105] Perhaps future monitoring campaigns can shed some light on those large variations in the ^{99}Mo-^{99m}Tc/^{137}Cs ratio.

Due to its high solubility and mobility, monitoring of ^{99}Tc in the marine environment will be one important future challenge. In a few samples taken in the period of 21−31 March, approximately 100 Bq/L ^{99m}Tc were determined in a few seawater samples—this is the only report we could find for Fukushima-Tc in seawater.[106]

■ IODINE-129

Iodine-129 is one of the very long-lived fission products of uranium or plutonium ($T_{1/2}$ = 1.6 · 10^7 a).[107−109] It is also produced by natural processes such as the interaction of high-energetic cosmic rays with natural xenon, as well as (spontaneous) fission of heavy nuclides.[108,110] The sources of the environmental ^{129}I inventory are illustrated in SI Figure S2.[108,111,112] In contrast to many other man-made radionuclides, anthropogenic releases were dominated not so much by nuclear accidents or nuclear weapons testing, but mainly by releases from NFRPs.[108,109,113] According to a recent study, the ^{129}I releases from Fukushima (estimated 1.2 kg) remained slightly below those from Chernobyl (estimated 1.3−6 kg).[114] However, SI Figure S2 illustrates that the contribution of both accidents to the global ^{129}I inventory is rather negligible.

Primarily due to its low specific activity, the radiological hazards of ^{129}I upon intake are generally regarded as low.[115,116] However, because of its nearly identical chemical behavior with ^{131}I, ^{129}I has been proposed and used as a long-lived proxy for the retrospective monitoring and dosimetry of ^{131}I from previous nuclear accidents, when short-lived ^{131}I has decayed completely.[117−120] The impact of a certain nuclear incident is assessed via the atomic ratio between the target nuclide ^{129}I and the natural isotope ^{127}I. The natural ^{129}I/^{127}I background of the prenuclear era (1.5×10^{-12} for the hydrosphere, which has not been confirmed for the terrestrial biosphere, though[121,122]) has been increased by anthropogenic inputs to 10^{-11} to 10^{-4}.[109] Fortunately, the pre-Fukushima background of ^{129}I in Japan is quite well documented and investigated.[123] The isotopic ratio between ^{129}I/^{131}I in the releases from Fukushima was determined by Miyake et al. as 31.6 ± 8.9 as of 15 March 2011.[124] Xu et al.[125] found an ^{129}I/^{131}I isotopic ratio of 16 ± 1 as of 11 March 2011, which is in decent agreement with the value of Miyake et al., when the decay of ^{131}I in 4 days is taken into account.

Several methods can be deployed to the determination of ^{129}I, but only neutron activation analysis and accelerator mass spectrometry, until recently, have been regarded to be capable of measuring ^{129}I at an environmental level.[110] Innovative analytical developments are likely to make ICP-MS a competitive tool in the future (especially for Fukushima samples with relatively high ^{129}I content). Due to the low specific activity of ^{129}I, radiometric determination such as γ-spectrometry (39.6 keV with a low-intensity of 7.5%)[126] or LSC cannot compete with the aforementioned methods and will not play an important role in the work-up of the Fukushima accident.[108] For details on the established analytical procedures for ^{129}I, the reader is referred to refs 109 and 110.

For a long time, neutron activation analysis (NAA) used to be the method of choice for the determination of ^{129}I. It takes advantage of the neutron capture reaction ^{129}I(n,γ)^{130}I and subsequent γ-measurement of the activation product ^{130}I ($T_{1/2}$ = 12.4 h). Interferences from short-lived activation products of stable elements (primarily high-energy γ-ray emitting ^{24}Na and ^{82}Br) often impede the applicability of instrumental NAA (INAA) by increasing the Compton background in the measurement of ^{130}I (γ-peak at 536 and 669 keV). This problem can be overcome by application of chemical separation of iodine from other impurities (separation in the form of MgI_2/I_2 on charcoal) in a radiochemical NAA. RNAA exhibits a detection limit of 1 μBq ^{129}I or a ^{129}I/^{127}I ratio of 10^{-10}, respectively.[110] For the determination and quantification of stable ^{127}I, INAA exhibits great sensitivity with detection limits down to the subμg per kg level (under ideal conditions).[127] NAA is still applied for the determination of ^{129}I,[112] but meanwhile accelerator mass spectrometry is used more frequently as it exhibits greater sensitivity.[114,116,128,129] With AMS, detection limits of 1 nBq ^{129}I or a ^{129}I/^{127}I ratio of 10^{-13}, respectively, can be achieved.[110] The detection limit depends on the procedure blank value and the purity (^{129}I content) of the stable iodine carrier.[37] AMS requires separation of ^{129}I, for which several techniques are available, depending on the sample matrix, the expected concentration of the analyte(s) ^{127}I and/or ^{129}I and the species of iodine. For aqueous samples, anion-exchange resins can be applied for preconcentration in sample matrices such as seawater, milk or urine. The iodine species is converted to I^-, concentrated on the resin, eluted as IO_3^- with NaOCl, converted to iodine and purified by extraction into $CHCl_3$. A ^{125}I tracer (or stable iodine) can be used to trace iodine through the process and to quantify the losses during the pretreatment. As the final step prior to AMS measurement, I^- is precipitated in the form of AgI, and mixing with conductive materials, such as Ag or Nb powder.[109,110] Organically bound iodine, for example, in soil samples, first needs to be decomposed prior to extraction by alkali fusion or ashing at 800 °C. The liberated I_2 is trapped in NaOH or on activated charcoal cooled with liquid nitrogen (cryogenic adsorption). Acid digestion has also been used to decompose soil samples and separate iodine.[121] For ICP-MS, isobaric interferences from the stable noble gas $^{129}Xe^+$ as well as $^{127}IH_2^+$, $^{127}ID^+$, $^{89}Y^{40}Ar^+$, $^{115}In^{14}N^+$, and $^{113}Cd^{16}O^+$, memory effects and tailing from ^{127}I are the main obstacles for the determination of ^{129}I. For ICP-MS techniques, detection limits of 2.5 μBq·g^{-1} ^{129}I or ^{129}I/^{127}I ratios of 10^{-7}−10^{-8}, respectively, have been reported.[110,130,131] However, triple quadrupole ICP-MS with an octopole reaction system (oxygen as a reaction gas) have been applied successfully for the detection of Fukushima-derived ^{129}I in soil.[130,131] The highest ^{129}I activity concentration (154 mBq·kg^{-1}) was found in soil from Ohkuma town, approximately 5 km from Fukushima Daiichi, with a ^{129}I/^{127}I ratio of 51.2×10^{-8}.[130]

In addition to the above example, only relatively few environmental studies on ^{129}I from Fukushima were published so far. A study of soil contamination around the Fukushima Daiichi NPP (distance 3.6−59 km) found a surface deposition between 15.6 and 6060 mBq/m^2.[124] Iodine-129 concentrations in Japanese rainwater immediately after the accident increased by approximately 4 orders of magnitude when compared with the pre-Fukushima levels. Concentrations decreased with an effective half-life of 29 days. Since physical decay of ^{129}I is negligible, this reflects the sole environmental dispersion and washout from the atmosphere. In a European study,[6] short-lived ^{131}I ($T_{1/2}$ = 8.02 days) exhibited an effective half-life of approximately half of the physical half-life. In any case, Xu et al.[125] monitored several peaks in the ^{129}I concentration in rainwater in the months following the accident, which is thought to be the result of re-emission of deposited ^{129}I from Fukushima to the atmosphere. After each event, concentrations decreased again as expected.

Recent studies by Krausova et al.[112] on ^{129}I confirm the outstanding applicability of animal thyroids as biomonitors for radioiodine that has been shown for ^{131}I, in many earlier studies (see ref 73 and references therein). For future studies on the fate of ^{129}I in the marine environment, fish thyroids or seaweed may be regarded as suitable media.[132]

Concentrations of ^{129}I in near-shore surface seawater of the Pacific were approximately 3 orders of magnitude above the pre-Fukushima background,[128] which will be a significant tracer signal for studies of oceanic mixing processes.[26] Povinec et al.[26] showed that the ^{129}I levels (or the ^{129}I/^{137}Cs ratio, respectively) at all stations of their study was influenced by the Fukushima accident up to a depth of at least 200 m. Estimates of the amount of ^{129}I discharged directly to the sea vary between 2.35 GBq (or 0.35 kg)[114] and 7 GBq.[26] Povinec et al.[26] further estimate that 4.6 GBq of ^{129}I was released to the atmosphere and deposited in the Pacific Ocean. The resulting ^{129}I activity concentration in surface seawater (30–600 km off the coast) was monitored to vary between 0.01 and 0.8 μBq/L. Iodine-129 was found to exist in mainly inorganic form in Pacific seawater: It is mainly iodide with an I^-/IO_3^- ratio of 8.7 in surface water (<20 m) and about 2–3 in subsurface water (>50 m). However, stable ^{127}I was found to be present predominately in iodate form with a relatively constant ratio of 0.2.[114] It appears that it takes a much longer time for ^{129}I with its "nuclear history" to reach equilibrium with the oxidation states of natural ^{127}I.

ACTINIDES

The actinides comprise the 5f-block elements actinium (atomic number 89) through lawrencium (atomic number 103). Elements with higher atomic numbers than uranium (92) are predominantly anthropogenic. Actinides are technically categorized in the "major actinides" (uranium, plutonium) and "minor actinides" (neptunium, americium, curium, berkelium, californium, einsteinium, and fermium). Many nuclides of the actinides are α-emitters, some of which exhibit a relatively high specific activity (depending on the respective half-life). Their presence in the environment gives rise to health concerns based on the resulting high radiotoxicity of these radionuclides. In their recent paper, Zheng et al.[133] summarized the challenges of Pu monitoring after the Fukushima accident. In the following, some recent developments and questions shall be shortly summarized.

Environmentally relevant actinides, primarily the plutonium isotopes, are produced through neutron capture(s) in ^{238}U. Plutonium-239 is produced in the nuclear reaction ^{238}U(n,γ)^{239}U, followed by β^- decay of the ^{239}U ($T_{1/2}$ = 23.5 m) to ^{239}Np ($T_{1/2}$ = 2.4 days) and subsequent β^- decay to ^{239}Pu. Further neutron captures yield ^{240}Pu and ^{241}Pu, the latter of which is a β^- emitter that decays to ^{241}Am. Sum activities of $^{239+240}$Pu can be determined by α-spectrometry (or LSC), however, due to their very similar α-particle energies, radioanalytical methods can usually not be used to distinguish the isotopic ratios between ^{239}Pu and ^{240}Pu. Due to the fallout of atmospheric nuclear weapons tests, Pu has become a ubiquitous element in nature. Any "fresh" contamination hence must be distinguished from the "old" background. This requires determination of the isotopic ratio ^{240}Pu/^{239}Pu by mass spectrometry. Alternatively, the atom ratios ^{241}Pu/^{239}Pu or ^{238}Pu/$^{239+240}$Pu, respectively, can help identifying a source, because the production of ^{238}Pu, ^{240}Pu and ^{241}Pu is a function of burn-up or burning age.[134] The determination of the most characteristic ^{240}Pu/^{239}Pu ratio requires ultrasensitive methods such as accelerator mass spectrometry[135] as well as extensive chemical purification and pretreatment.[136] The ratio is 0.18–0.2 for weapons fallout and approximately 0.4–0.6 for reactor plutonium. Other sources such as Chernobyl or the discharges from Windscale/Sellafield or the Mayak reprocessing plant contributed to the global environmental inventory of plutonium to a minor extent.[137]

Due to their low volatility, discharge of actinides from Fukushima was expected to be low.[21] This assumption was confirmed for Europe, for example, by Lujaniene et al.,[138] who found atmospheric actinides after the Fukushima nuclear accident at a level 4 orders of magnitude lower than after Chernobyl and concluded that Fukushima was a negligible source of plutonium at least in remote locations such as Lithuania.

A few studies from Japan investigated actinides in the environment,[9,21,139−141] however, so far only two studies provided solid, mass spectrometric isotopic evidence for the release of reactor plutonium from the damaged Fukushima reactors.[135,142] Nevertheless, plutonium and minor actinides are among the understudied pollutants after the Fukushima nuclear accident.

Zheng et al.[142] found only low activity concentrations of ^{239,240}Pu, with values ranging between 0.019 ± 0.003 and 1.400 ± 0.023 Bq/kg, most of them carrying the signature of global fallout. However, for three samples, they could attribute most of the plutonium to the Fukushima nuclear accident. For the soil sample from J-Village (Figure 4), Zheng et al. calculated the contribution from "old" fallout plutonium to the overall ^{239,240}Pu activity to 13%. According to this study, the preliminary estimations of the total releases of ^{239,240}Pu from Fukushima were in the range of 1.0×10^9 to 2.4×10^9 Bq,[142] or approximately 2×10^{-5} % of the core inventory.[133] Taken into account that Fukushima's total plutonium inventory was 3.5 times higher than Chernobyl's, it is remarkable that the plutonium releases from the Fukushima NPP were estimated 4 orders of magnitude lower than from Chernobyl.[142] However, based on their findings of a ^{241}Pu/^{239,240}Pu activity ratio of >100 in case of Fukushima (compared with 83 ± 5 from the

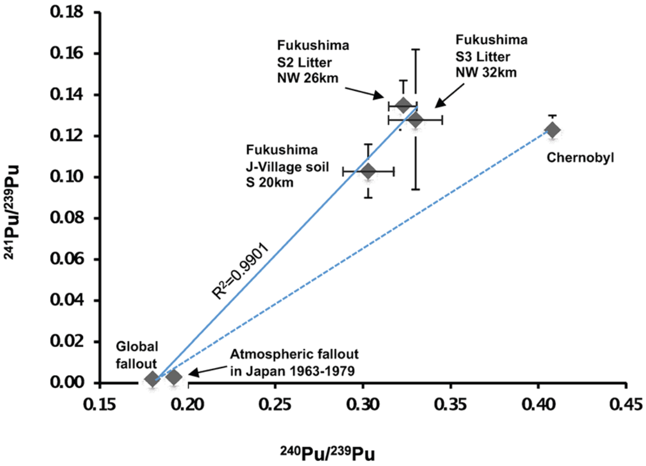

Figure 4. Mixing plot of ^{241}Pu/^{239}Pu atom ratio vs ^{240}Pu/^{239}Pu atom ratio for samples collected in the 20–30 km zones of Fukushima prefecture, Japan, and a comparison of isotopic composition with those of the Chernobyl accident and the global fallout sources. Taken from Zheng et al.[142] Reproduced as licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 Unported License.

Chernobyl accident), the authors emphasize the need for a long-term dose assessment of ^{241}Pu and ^{241}Am, which has a high radiotoxicity. The cause for this observation may be releases from Fukushima's reactor No. 3 that was partly operated with relatively plutonium-rich mixed oxide fuel.

Kirchner et al.[134] hypothesized that the release of plutonium could have been a consequence of the hydrogen explosions and a resulting liberation and release of fuel fragments. Indications for a particulate release of Pu from Fukushima were presented in a recent paper.[135] In that study, most samples contained the ^{240}Pu/^{239}Pu signature of fallout Pu, but there was least one vegetation sample whose isotope ratio (0.381 ± 0.046) evidenced reactor plutonium in the environment ($^{239+240}$Pu activity concentration 0.49 Bq/kg). Another sample was suspected to carry the isotopic signature of reactor plutonium, however, with higher uncertainty. Plutonium content and isotope ratios differed considerably even for very close sampling locations, for example, the soil and the plants growing on it. As already predicted by Kirchner et al.,[134] this strong localization might indicate a particulate Pu release. Although the sum Pu activity concentrations in the plant material were so low, they would not have exceeded the regulatory limit for Pu in food,[19] releases of particulate Pu raises much concern because it is of high radiological risk if incorporated.

One understudied topic is actinides in seawater and other environmental waters. A part of that contaminated cooling water and groundwater found its way back into the Pacific Ocean, giving rise to environmental concerns. In two studies by the Zheng group[136,139] marine sediments from 30 km off the Fukushima NPP were investigated with special focus on plutonium. However, the activity concentrations of the relevant nuclides as well as the ^{240}Pu/^{239}Pu atomic ratios were comparable with the background due to global fallout. As predicted by numerical modeling,[143] the results suggest a negligible contribution of the Fukushima nuclear accident to the plutonium contamination levels of marine sediments outside a 30 km radius around the plant, although the number of measurements is not yet sufficient to allow for an ultimate assessment. Moreover, information on the distribution of dissolved actinides is still limited in scientific literature (see below) and needs to be addressed in future works accordingly.

Other actinides are also still severely understudied.[133] Immediately after the accident, γ-spectrometric detections of short-lived ^{239}Np in hot spots in Japan were published.[9] Spectral overlap of the most intense peak of ^{239}Np at 106 keV with the fission product ^{129m}Te, however, made follow-up studies necessary, which indeed detected low concentrations of reactor plutonium (see above).[135]

One of the few studies dedicated to actinides in environmental waters was published by Sakaguchi et al.[141] The authors studied river water, paddy field water, and ocean water for actinides, in particular plutonium and uranium isotopes including the predominantly anthropogenic ^{236}U, which is a suitable tracer for environmental and geochemical processes.[144−146] In addition to the radiotoxicity (which depends on the half-life of the respective U isotope), U is also a poisonous element. However, ^{236}U it is rather of academic and scientific interest than of health concern. No reactor-derived uranium (enriched ^{235}U) could be found in vegetables from Chiba and Ibaraki in April/May 2011.[147] Uranium-236 is mainly produced via $^{235}\mathrm{U}(\mathrm{n_{th}},\gamma)^{236}\mathrm{U}$ and, especially in nuclear weapons, $^{238}\mathrm{U}(\mathrm{n},3\mathrm{n})^{236}\mathrm{U}$. Unfortunately, the background for the ^{236}U/^{238}U ratio is not known for Japanese river waters that would allow for the assessment of the Fukushima nuclear accident.[141] Austrian river water,[145] for comparison, showed much higher values for this ratio (possibly due to the Chernobyl accident), which implies that the releases from Fukushima were at least relatively small. The authors of ref 141 could not draw ultimate conclusions with respect to plutonium in river water due to large measurement uncertainties in that one sample, but the value obtained was only slightly higher than a background from 1990. Samples of ocean water also only reflected global fallout via its ^{240}Pu/^{239}Pu ratio.

For a short discussion of the "orphan" radionuclides ^{103}Ru and ^{106}Ru as well as ^{36}Cl, the reader is referred to the SI.[37,98,106]

In summary, the above examples illustrate the variety of scientific challenges, the multitude of target nuclides that call for monitoring and further investigation. Unfortunately, some for some radionuclides, important information can no longer be gathered because of the radionuclides' relatively short half-lives, for example, the radioxenon isotopes ^{131m}Xe, ^{133m}Xe, ^{133}Xe, and ^{135}Xe, as well as ^{103}Ru, ^{35}S or ^{89}Sr. In other cases, especially ^{3}H and ^{85}Kr but also ^{90}Sr and ^{99}Tc, the distinction between Fukushima's contribution and the background (caused by the fallout from nuclear weapon tests, NFRP releases or the Chernobyl accident) causes a problem. Any early activity concentration gradient of ^{3}H and ^{85}Kr caused by the Fukushima releases has probably been erased by dilution and migration processes in the environment. Without ^{89}Sr as an indicator of a "fresh" release, it will be difficult to assess the contribution of Fukushima-^{90}Sr in the ^{90}Sr background. The environmental processes of other radionuclides such as ^{129}I or the actinides will be easier to follow using characteristic isotopic ratios such as ^{129}I/^{127}I or ^{240}Pu/^{239}Pu. Some of the "forgotten" radionuclides, for example, ^{14}C, ^{36}Cl, ^{129}I or ^{236}U are more of academic interest because of their applicability as environmental tracer nuclides. Other radionuclides such as ^{90}Sr and the shorter-lived actinides (Pu, Am) are of great radiological concern (especially if in particulate form) and hence need to be monitored for radiation protection purposes. Last but not least, the above studies and problems also exemplify the urgent need for comprehensive and published data on the background of potentially relevant radionuclides in the environment, so that in case of any future accident, the "fresh" components can be distinguished from the background.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information contains (a) Time evolution of ^{35}S activity measured in SO_2 gas and sulfate aerosol collected at Scripps Institution of Oceanography (SIO), La Jolla, CA (Figure S1). (b) Diagram of ^{129}I sources and inventory in the environment (Figure S2). (c) Discussion of ^{103}Ru and ^{106}Ru as well as ^{36}Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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