Radioanalytical Investigations of Water Samples from the Vicinity of the Nuclear Power Plants “Chernobyl” and “Fukushima Daiichi”

Radioanalytische Untersuchungen von Wasserproben aus der Umgebung der Kernkraftwerke „Tschernobyl“ und „Fukushima Daiichi“

Von der Fakultät für Mathematik und Physik

Der Gottfried Wilhelm Leibniz Universität Hannover

zur Erlangung des Grades

Doktorin der Naturwissenschaften

- Dr. rer. nat. -

genehmigte Dissertation von

M.Sc. **Rebecca Querfeld**

geboren am 12. Juli 1990 in Hildesheim

2021

Referent: Prof. Dr. Georg Steinhauser
Institut für Radioökologie und Strahlenschutz
Gottfried Wilhelm Leibniz Universität Hannover

Korreferent: Prof. Dr. Clemens Walther
Institut für Radioökologie und Strahlenschutz
Gottfried Wilhelm Leibniz Universität Hannover

Korreferent: Prof. Dr. Carla Vogt
Institut für Analytische Chemie
Technische Universität Bergakademie Freiberg

Tag der Promotion: 28.05.2021

One never noticed

what has been done;

one can only see

what remains to be done.

- Marie Curie -

Abstract

Nuclear accidents can release large amounts of radioactivity that affects not only the vicinity of the nuclear power plant (NPP), but can be detected in large parts of the world. This work targets the effects of the largest nuclear accidents, the Chernobyl nuclear accident on April 26, 1986, and the Fukushima accident on March 11, 2011. The importance for radioecology is to understand the behavior and dispersion of radionuclides in the environment. To achieve a comprehensive understanding, the environmental fate of the radionuclides needs to be studied intensively for several years.

In this work, the fission products ^{90}Sr, ^{129}I, and ^{137}Cs and reactor nuclides ^{3}H, and ^{134}Cs were analyzed in the compartment water from the immediate vicinity of the Chernobyl and Fukushima NPPs, and the methods were adapted for these measurements. Both, radioanalytical and mass spectrometrical methods were used, such as liquid scintillation counting, gamma spectrometry via high-purity germanium detector, and accelerator mass spectrometry. The optimized methods were subsequently applied to natural water samples from the Chernobyl exclusion zone with large sample volumes. Further adaptations were made for small sample volumes of Fukushima surface water samples, which were sampled only a month after the accident. Finally, both drinking water as well as a variety of surface water samples from sites of the Tokyo 2020 Olympic Games were tested for their radionuclide content to assess potential risks to athletes and visitors.

In the Chernobyl water samples, activities of ^{90}Sr and ^{137}Cs were still easily detectable even after more than 30 years later. The activities ranged from 0.6 - 4.1 Bq/kg for ^{90}Sr and 0.06 - 8 Bq/kg for ^{137}Cs. With increasing distance from the NPP, a decrease in activities was observed.

In the Fukushima surface water samples, taken one month after the accident, high levels of contamination could be determined. In particular, the tritium activity concentration of a puddle sample near the Fukushima NPP showed the highest reported concentration so far of 184 ± 2 Bq/L. Comparison of the puddle sample with water from a close proximity rice paddy showed ratios of 1 % for radiocesium, 12 % for ^{129}I, and about 40 % for ^{3}H and ^{90}Sr. The cause of the decreased activity concentration of the radionuclides are different: for cesium and iodine this is the result of adsorption onto natural minerals and organic matter respectively, whereas the differences in the concentration of ^{3}H and ^{90}Sr are mainly caused by dilution.

Analysis of potable water samples from Japan revealed no radiological concerns for a two week stay in Japan as athlete or visitor of the Olympic Games (< 3 µSv). It was found that the main contributor to internal dose is inhalation of na4tural radioactive radon (27 µSv). Air dose rate measurements were conducted at all Olympic Games venues to determine the radiological hazards of external dose. By means of this investigation, it could be exemplified by concrete measurements that Japan generally has low air dose rates.

Keywords: Radioecology, Chernobyl, Fukushima Daiichi, Olympic Games Tokyo 2020

Contents

List of Abbreviations

ALPS	Advanced Liquid Processing System
AMS	Accelerator Mass Spectrometry
ChNPP	Chernobyl Nuclear Power Plant
CTBT	Comprehensive Nuclear-Test-Ban Treaty
EBR-I	Experimental Breeder Reactor I
FDNPP	Fukushima Daiichi Nuclear Power Plant
GE Mark	General Electric Boiling Water Reactor inside a Mark containment
HPGE	High-Purity Germanium
HTO	Tritium containing Water
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-QQQ-MS	Inductively Coupled Plasma-Triple Quadrupole-Mass Spectrometry
INES	International Nuclear and Radiological Event Scale
LoD	Limit of Detection
LoQ	Limit of Quantification
LSC	Liquid Scintillation Counting
NPP	Nuclear Power Plant
PTBT	Partial Test Ban Treaty
RBMK	Reaktor Bolschoi Moschtschnosti Kanalny
TEPCO	Tokyo Electric Power Company
TU	Tritium Unit

1 Introduction

This PhD thesis is a cumulative thesis and includes three publications. The introducing chapters provide background and context for these publications, including theoretical background information and insight from current literature. The focus of this thesis lies on the optimization of different (radio-)analytical treatments for radionuclides and on the application on water samples from Chernobyl and Fukushima. The overreaching objective of the thesis is to provide a scientific basis for the risk assessment for participants of the 2021 Tokyo Olympic Summer Games.

D1 R. Querfeld, W. Schulz, J. Neubohn, G. Steinhauser; Antropogenic radionuclides in water samples from the Chernobyl exclusion zone. *J Radioanal Nucl Chem* **318**, 423-428 (2018). https://doi.org/10.1007/s10967-018-6030-y

D2 R. Querfeld, A.-E. Pasi, K. Shozugawa, C. Vockenhuber, H.-A. Synal, P. Steier, G. Steinhauser; Radionuclides in surface waters around the damaged Fukushima Daiichi NPP one month after the accident: Evidence of significant tritium release into the environment. *Sci Total Environ* **689**, 451-456 (2019). https://doi.org/10.1016/j.scitotenv.2019.06.362

D3 R. Querfeld, M. Hori, A. Weller, D. Degering, K. Shozugawa, G. Steinhauser; Radioactive Games? Radiation Hazard Assessment of the Tokyo Olympic Summer Games. *Environ Sci Technol* **54 (18)**, 11414-11423 (2020). https://doi.org/10.1021/acs.est.0c02754

2 Theory

2.1 The History of Nuclear Energy

The history of nuclear energy began with the discovery of uranium in 1789 by Martin Klaproth, a German scientist. Around 100 years later, in 1895, Wilhelm Roentgen discovered ionizing radiation by passing an electric current through an evacuated glass tube and producing continuous X-rays. A year later, Henry Becquerel noticed that pitchblende caused a photographic plate to darken, even though there was no other light source present. He discovered that his observation could be explained by beta radiation (electrons) and alpha particles (helium nuclei). Marie and Pierre Curie were the ones to name this phenomenon “radioactivity”. Subsequently, they isolated polonium and radium from the pitchblende in 1898. Paul Ulrich Villard discovered gamma rays, which proved to show similar characteristics like X-rays, as a third type of radiation from pitchblende in 1900. The term γ-radiation was introduced by Ernest Rutherford, who chose it in 1903 in continuation of the terms α- and β-radiation that were introduced in 1899. In 1902, Ernest Rutherford concluded that radioactivity, as a spontaneous event emitting an alpha or beta particle from the nucleus, creates a different element. In 1909, Rutherford discovered that the mass of atoms is concentrated in their centers, thus discovering the atomic nucleus. In 1919, in order to receive a complete understanding of the atom, he fired alpha particles from a radium source into nitrogen and observed a nuclear reaction of the type $^{14}N(\alpha,p)^{17}O$. Following this discovery, he theorizes the existence of a neutral particle in the nucleus called ‘neutron’ in 1920. Based on the results of Irene Joliot-Curie, the daughter of Marie and Pierre Curie, which stated that - what she believed - gamma radiation was being able to knock protons out of parafin, James Chadwick conducted experiments on the topic and found Rutherford's neutrons in 1932, proving their existence. [1]

With the discovery of neutrons, many researchers started irradiation experiments with various elements and nuclides. In 1938, Otto Hahn and Fritz Strassman conducted probably the most important of these experiments by bombarding neutrons onto a uranium target. By that, they found that the “activation product”, in explicably, was a barium radioisotope. It was Lise Meitner and Otto Robert Frisch who identified this phenomenon as ‘splitting of the atom’ and named it nuclear fission [2]. One year later, in 1939, Leó Szillárd and Enrico Fermi performed neutron multiplication studies and recognized nuclear fission as a potential way to induce a chain reaction. With this discovery, Szillárd together with Eugene Paul Wigner and Edward Teller determined that the chain reaction induces multiple nuclear fission reactions. The fission reactions are followed by a release of incredible amounts of energy. They realized the potential use of nuclear reactions as form of weapons. During the same year, they convinced Albert

Einstein, a famous scientist at this time, to sign a letter warning President Roosevelt of the possibility of German nuclear weapons. Afterwards, Roosevelt authorized a study on uranium, leading to the formation of the Advisory Committee on Uranium, which started with research of a nuclear weapon. In 1942, at the University of Chicago, Fermi successfully created the first controlled nuclear chain reaction. By successfully performing this experiment, the so-called Manhattan Project was able to grow quickly in size and speed. Two types of nuclear bombs were invented simultaneously, one working with enriched uranium, and the other one made of plutonium. Enormous efforts were expended to obtain the incredibly high amounts of uranium and plutonium needed: Three large-scale processing sites were built. The first one was located in Oak Ridge, the second one in Hanford, and the last in Los Alamos. In Oak Ridge, the first gram-quantities of plutonium for study were produced, even though its main task was uranium enrichment. In Hanford, the reactors were used for plutonium production. Also plutonium extraction chemistry plants have been built. The results of production and enrichment processes converged in Los Alamos, where the development of weapon technology took place. Both elements proved successful for nuclear bomb production. However, despite the higher risks and uncertainty regarding its design, the plutonium implosion device was preferred and successfully tested at the Trinity site in New Mexico in July 1945. In August 6 and 9, 1945, “Little Boy” and “Fat Man” were dropped on Hiroshima and Nagasaki, resulting in the complete destruction of the two cities. 250,000 people died in the explosions. Six days later, Japan surrendered unconditionally, ending World War II [3].

In August 5, 1963, the governments of the Soviet Union, the United Kingdom and the United States signed the Partial Test Ban Treaty (PTBT) before it was opened for signature by other countries. The ‘Treaty Banning Nuclear Weapon Tests in the Atmosphere, in Outer Space and Under Water’ prohibited all test detonations of nuclear weapons except those conducted underground. Three centuries later, on September 10, 1996, PTBT has been modified and is known as the ‘Comprehensive Nuclear-Test-Ban Treaty’ (CTBT), which was adopted by the United Nations General Assembly and signed by 184 states. The CTBT bans all nuclear tests, for both civilian and military purposes, in all environments. [4]

After World War II and the revelation of the destructive power of nuclear fission, the first civilian experimental liquid metal-cooled reactor, called EBR-I, was attached to a generator in 1951, producing the first nuclear generated electricity in Idaho, USA. Admiral Rickover pushed to use reactors to power submarines. The USS Nautilus launched in 1954 as the first nuclear-powered submarine. Soon after, the Soviet Union opened the first non-military, electricity-producing reactor. Many nuclear reactors were built to provide an efficient and relatively cheap supply of electricity through the 1960s and 1970s. With uranium readily available, electricity produced by nuclear power plants is economically favored and emission-free with a very low mining and transportation footprint. In addition, plutonium from nuclear disarmament efforts is frequently used for civilian purposes. With this perspective, different types of reactors were developed in various countries over the years of the second half of the 20th century for cheap and plentiful electricity production. [5]

The use of nuclear energy led to several nuclear power plant accidents, leading to a release of radionuclides. In the following chapters, the worst nuclear accidents in history – Chernobyl and Fukushima – are briefly introduced.

2.2 The Chernobyl Nuclear Accident

The Chernobyl nuclear accident (April 26, 1986) was the most significant nuclear accident in history [6, 7]. It was classified as an impact 7 event (Major accident) of the International Nuclear and Radiological Event Scale (INES).

The accident occurred during a safety test and was caused by a cascade of operating errors. In addition, the reactor type itself promoted the failure. The Chernobyl reactor number 4 was a RBMK-1000 reactor (Russian: реактор большой мощности канальный, РБМК; reaktor bolshoy moshnosti kanalnyy, "high-power channel-type reactor"): It is a graphite-moderated nuclear power reactor designed and built by the Soviet Union, using low enriched (2 % ^{235}U) uranium dioxide fuel. It has a unique design, instead of a large steel pressure vessel surrounding the entire core, each fuel assembly is enclosed in an individual 8 cm diameter pipe (called “channel”) which allows the flow of cooling water around the fuel. The RBMK is an early Generation II reactor and the oldest commercial reactor design still in wide operation [8]. Important aspects of the RBMK reactor design contributed to the 1986 Chernobyl disaster: the 4.5 m graphite displacer ends of the control rods, the active removal of decay heat, the positive void coefficient properties and instability at low power levels [9]. The Chernobyl RBMK experienced a very large reactivity excursion, leading to a steam and hydrogen explosion, a large fire and subsequent meltdown. The released radioactivity spread over a huge part of Europe. After the Chernobyl accident, some of the flaws in the design of RBMK-1000 reactors were corrected and several reactors have since been operating without any serious incidents for over 30 years [9]. To date, 10 RBMK reactors are still operating in Russia [9]. The last of these reactors will be decommissioned in 2050 [9].

The reactor was built for production of electricity and weapons grade plutonium and started its operation time in 1984. The accident-causing test was scheduled as a safety test to check if the coasting turbines after shutdown could be sufficient to supply enough electricity for the cooling water pumps until the emergency generators have started up, in the event of a power failure and shutdown of the reactor. The test began at 13:05 on April 25, 1986 with the power reduction at 50 % and shut down of the emergency cooling system. At 14:00 the test was interrupted, because the City of Kiev expressed the demand for more electricity, and even after raising the power level, the operation crew kept the emergency system shut off. At 23:10 the test was continued, but with a different operation crew due to a change of work shifts and the power of the reactor should be reduced to 25 % of its normal operation power. At 00:28 (April 26, 1986), the power dropped to a level of 1 % and usually an RBMK type reactor had to be shut down completely whenever the power of a reactor drops below 20 %. Yet the crew decided on continuation of the protocol and performed another attempt to increase the power by removing more control rods. At 00:32, the reactor reached a power level of 7 % and parts of the safety systems were still shut down. Only 4 (of 8) cooling-pumps were operating at this time. Around 20 minutes later, after closing the turbine fast-acting valves, the temperature of the coolant and the pressure in the vessel increased dramatically. The shift leader wanted to induce an emergency shutdown of the reactor by reinserting the control rods, but by performing this action the opposite effect was induced: because of the graphite spacers, the neutrons were better moderated, the power increased to even greater extent, and by that also the temperature. A series of explosions occurred, the top of the reactor containment vessel, as well as the rooftop of the reactor-building were blasted away during this event. The surrounding air flow into the reactor caused the graphite to start burning and the flames spread over a large area. Around 05:00, the fires outside of the reactor building were extinguished, but it was not possible to cool and/or stop the burning graphite inside of the reactor [8].

On April 27, 1986, the remaining three reactors located on the Chernobyl site shut down and the evacuation of the population of Pripyat started. With helicopters, different materials (lead, clay, sand, dolomite, and boron carbide) were thrown into the reactor, but the temperature continued to increase [10]. It took ten more days (May 6, 1986) to extinguish the burning reactor by pumping nitrogen into the reactor [11].

On April 28, 1986, without any European country knowing about this accident, a contamination alarm at the nuclear power plant Forsmark in Sweden indicated an unusually high, yet inexplicable release of radioactivity into the atmosphere. Due to the change shifts, the crew members coming from outside were found to be contaminated. After a complete check of their measurement systems, Forsmark concluded they were not the source of contamination. The Chernobyl accident was first announced officially by a Soviet news agency on April 29, 1986. In the following days, the radioactive plume reached great parts of Western Europe and due to rainfall, the radioactivity was washed out and deposited, which caused large contaminated areas in Europe. After several days, on May 14, Michail Gorbachev, the later president of Soviet Union, announced the accident to the population via television [11].

Throughout the following months in 1986, debris from the site was removed and a sarcophagus was built (and finished in November), to cover the damaged reactor. The remaining three reactors started to operate again [10, 11].

A total of 5300 PBq of mainly volatile radionuclides (nuclides of I, Cs, and Te) were released into the environment, as well as other radionuclides, as for example radiostrontium and actinides (in the form of nuclear fuel particles, often referred as "hot particles") [12]. These particles were and can still be found in soil samples up to a distance of 100 km from Chernobyl nuclear power plant (ChNPP) [13]. When hot particles are deposited in the environment, weathering processes take place and radionuclides are subsequently mobilized [14, 15].

The radioecological effects and the radiological impact on the waterbodies in the vicinity of the ChNPP have been studied thoroughly in the years after the accident [16]. However, since previous studies proved a great variability of the ecological half-lives of many relevant radionuclides in natural aquatic ecosystems, the current status of activity levels in the waters remains an interesting topic of scientific investigation. Mirzoyeva et al. determined the ecological half-lives (T_{eco}) of ^{90}Sr in components of the Dnieper River basin and found considerable variability for aquatic organisms (T_{eco} = 4-24 y) [17]. Their findings were in a good agreement with Pröhl et al., who found similar values for water in Ukrainian rivers and freshwater reservoirs (T_{eco} = 6-24 y) for ^{90}Sr [18]. For ^{137}Cs, multiple ecological half-lives are given, reflecting various environmental processes: 2-7 y (for rapid wash-off from the watershed) and 8-73 y (increasing fixation of radionuclides), respectively [18–20].

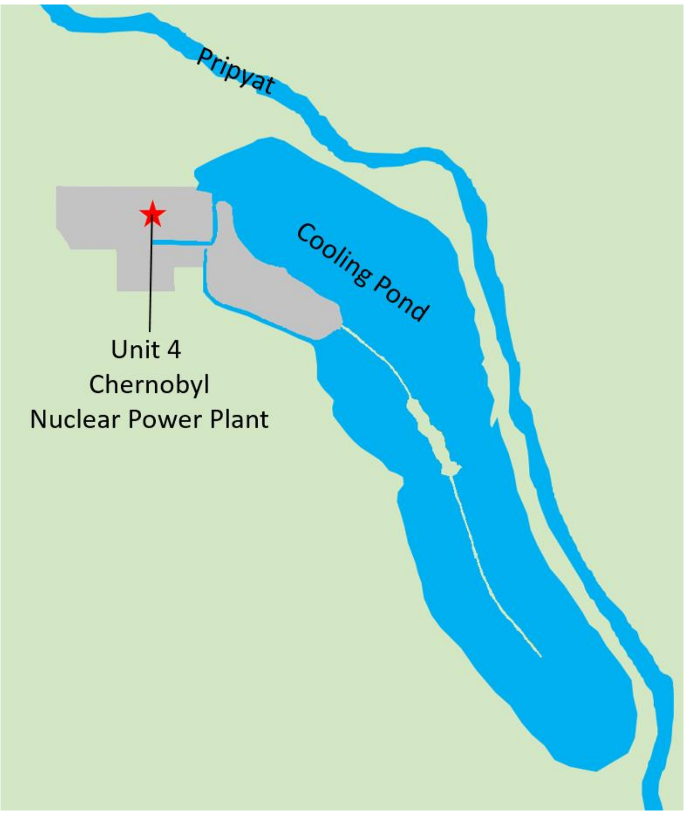

Figure 1 Overview of the area around the Chernobyl nuclear power plant with the channels, the cooling pond and the Pripyat river.

The cooling pond of the ChNPP is one of the major water bodies adjacent to the site (see Figure 1) that were heavily contaminated. The cooling pond was designed for the purpose of cooling all four units at ChNPP. The water level has been adjusted at 110.7 m above sea level, which exceeded the low water stage of the Pripyat River by 7 m. Because of a high head pressure between the pond and the river, combined with the high water-permeability of the dam material, leakage through the dam resulted. To compensate the losses from leakage and evaporation, the water level was maintained using a pumping station, serving the purpose of refilling the pond with water from the Pripyat River. After the permanent shutdown of the power plant in 2000 [21], the pumping station was shut down in May 2014. As a result, the water level has been decreasing continuously and had lowered 5 m by the end of 2017 [22].

Before the accident, from 1976 to April 1986, the cooling pond contamination was associated with the operation of the ChNPP. The main source of contamination in the first 2-3 years after the start-up of the ChNPP was non-reusable water discharged into the pond. The total annual release of activity of fission products was 37-370 GBq (excluding tritium). Cesium-137 accounted for 10% of the total activity and the input of other sources, flow of fission products and corrosion products with service water, deposition of aerosol emissions on the water surface, was an order of magnitude smaller. In the following years, the input from the global fallout was higher than the discharges of radionuclides and aerosol emissions from the ChNPP. Two additional radioactive releases to the cooling pond occurred in 1981 and 1982: A leak and a radiation related incident. Open literature does not give any information about the scale or characteristics of these events [22].

The contamination of the cooling pond during the accident in 1986 occurred in two ways. The first included the deposition of radioactive particles (hot particles) from the damaged reactor fuel onto the surface of the cooling pond. The second was the discharge of highly radioactive water through the outlet channel from the reactor emergency cooling system and the water used to extinguish the fire. A significant increase of dissolved ^{90}Sr was observed between 1987 and 1988 due to chemical alterations and corrosion processes of the hot particles [23]. The weathering and corrosion process of these particles is closely linked to their chemical composition and prevailing chemical nature of the environment. According to their composition, Kashparov et al. [15] categorized three groups of hot particles formed during the ChNPP accident. The first group contains fuel particles (UO_2) that originated from the mechanical fragmentation through the explosions [24], which are chemically relatively stable. The second group consists of oxidized fuel particles (UO_{2+x}) that formed during the graphite fires. These particles exhibit high dissolution rates because the UO_2 core is surrounded by a layer of

U_2O_5/U_3O_8 [24]. The third group is chemically rather inert and exhibits low dissolution rates because these are fuel particles embedded into a zirconium matrix (ZrU_xO_y) that originated through annealing of UO_2 fuel with zirconium materials inside the molten reactor core. However, most of the hot particles sank to the benthic division of the cooling pond and have been stored in a chemically stable state due to the lack of oxygen in the anoxic ground [23]. Due to the decreasing water level of the cooling pond, the hot particles become exposed to atmospheric oxygen and chemical alterations and weathering have started. While the flooded hot particles are likely to survive 100 years and more, the actually exposed particles will decompose within 15-25 years [25]. As a result, the newly exposed particles are causing a further contamination of the cooling pond and the surrounding area [26].

2.3 The Fukushima Nuclear Accident

The Fukushima nuclear accident occurred after a strong earthquake followed by a tsunami on March 11, 2011. After Chernobyl, it was the second nuclear accident classified as an impact 7 event on the INES scale.

First commissioned in 1970, the Fukushima Daiichi nuclear power plant (FDNPP) consisted of six boiling water reactors. These light water reactors drove electrical generators with a combined power of 4.7 GW, making Fukushima Daiichi one of the 15 largest nuclear power stations in the world. Fukushima was the first nuclear plant to be designed, constructed, and run in conjunction with General Electric and Tokyo Electric Power Company (TEPCO). The blocks 1-5 are of type GE Mark I while reactor block 6 is of type GE Mark II. In most cases uranium dioxide was used as fuel, although mixed oxide fuel rods were used in block 3. In all blocks, the reactor core is located in the reactor pressure vessel. The reactor pressure vessel is located in the pressure chamber. For this type of reactor, the containment consists of the pressure chamber and an annular condensation chamber. In case of an incident, pressure can be released from the reactor pressure vessel into the condensation chamber by steam release via safety and relief valves, thus allowing the pressure in the reactor pressure vessel to be regulated. The condensation chamber is partially filled with water as coolant, which also has to be cooled, as it is heated by the steam. A steady power supply must be available during operation, but also in case of a shutdown to ensure cooling by electrically operated pumps. For this reason, emergency diesel generators and batteries are installed [27].

On March 11, 2011 at 14:46 local time, Japan faced the most powerful earthquake in its history since the seismological recordings started in 1900. The earthquake had a magnitude of 9.0 and its epicenter was about 130 km offshore of the eastern coast of Honshu Island [28]. The event that triggered the accident in the TEPCO FDNPP was a tsunami resulting from the powerful earthquake. The tsunami waves had a run-up height up to 40 m and travelled about 10 km inland [29]. At the time of the earthquake, three blocks were in operation (blocks 1, 2, 3) and three were shut down for service (blocks 4, 5, 6) [27]. The earthquake caused destruction in the vicinity of the power plant, which resulted in the failure of the external power supply of the power plant. As a result, the emergency diesel generators took over the power supply and blocks 1 to 3 were quickly shut down. However, the tsunami destroyed the emergency power supply of the power plant a short time later. This resulted in the loss of cooling of the reactors, temperature, and pressure inside the reactors and a fraction of the fission products became volatile and migrated out of the fuel material into a gas phase [30]. At the time when the reactor cores overheated, the gaseous elements were released to the reactor pressure vessel. Volatile elements, iodine, tellurium, cesium and noble gases were released first [30].

The first major release of radionuclides occurred shortly after the accident began on March 12. The release followed a hydrogen explosion in Unit 1. The radioactive plume moved along the Japanese coast in a northeasterly direction and eventually turned toward the Pacific Ocean. The plume was detected as an increase in the continuously monitored gamma dose rate at Minamisoma, located about 25 km north of the FDNPP. This release caused a dry deposition of radionuclides along the east coast of Miyagi Prefecture, but appeared to have little to no impact on residents in these areas [31].

The second major release was caused by controlled venting on March 13 and an uncontrolled hydrogen explosion on March 14 in Unit 3. During that time, fortunately, the wind was blowing towards the Pacific Ocean and no elevated dose rates were detectable either in the Fukushima Prefecture or on Honshu Island [31].

In the next two days the weather conditions changed, causing the radioactive plume from another controlled venting on the morning of March 15, and an explosion inside Unit 2. The highest dose rate since the beginning of the accident was measured near the main gate. The radioactive plume followed complex travel patterns, depending on the prevailing weather conditions. It moved first southwards and then north-west. Light precipitation caused wet deposition west and south-west of the accident site [32, 33]. Due to precipitation, the radioactive material deposited on land was mostly distributed north-west of the power plant at a distance of 40 km [7].

It was approximated that due to the westerly wind, about 70-80% of the radionuclides released in the Fukushima accident were deposited in the Pacific Ocean. Activity concentrations in the Pacific Ocean measured 30 km off-shore from the power plant on March 23 were 77 Bq/L for ^{131}I and 134 Bq/L for ^{137}Cs [34]. The sea on the east coast of Japan was also contaminated by direct discharges of radioactive water. A total of about 4 PBq of ^{137}Cs and 7 GBq of ^{129}I [35] were discharged directly into the Pacific Ocean during the accident, with more being released later on [34].

The total amounts released in the atmosphere for the most significant radionuclides of ^{131}I and ^{137}Cs are estimated to be 160 PBq and 15 PBq, respectively [36]. The total amount of radioactivity (excluding noble gases) released to the atmosphere from Fukushima is estimated to be around 520 PBq [7]. In addition to the highly volatile radionuclides, small amounts of low volatile nuclides of the elements strontium, plutonium and uranium were released [7].

As mentioned earlier, the amount of ^{131}I released was an order of magnitude higher than that of ^{137}Cs. Most of the ^{131}I results are estimates derived from AMS measurements of ^{129}I. The known isotopic ratio of ^{131}I/^{129}I was used to retrospectively calculate the activity of ^{131}I, since all ^{131}I decayed about 80 days after the accident. The highest activity concentration measured for ^{131}I was 187 MBq/m^2. The activity was corrected to the corresponding date, March 12. The highest activity concentration for ^{137}Cs was 15.5 MBq/m^2, again an order of magnitude lower than for iodine [30].

The evacuation of the people living around the NPP took place in multiple steps. First, the evacuation order was issued within a 3 km radius of FDNPP and the order to stay indoors was issued within a 10 km radius at 21:23 on March 11, 2011. One day later, the evacuation order was issued within a 10 km radius (05:44) and later that day (18:25) within a 20 km radius [37]. 76,000 people lived within this area, and more than 97 % of residents were evacuated by March 15 when the highest amount of radioactive plume was released from FDNPP [38, 39]. It was later decided to additionally evacuate areas where the annual cumulative radiation dose was expected to exceed 20 mSv/year. Figure 2 shows a map of the evacuation zones on April 22, 2011 planned by the Fukushima Prefectoral Government. Overall, 164,865 citizens were evacuated from 13 municipalities surrounding the NPP in May, 2011 [37, 40–42].

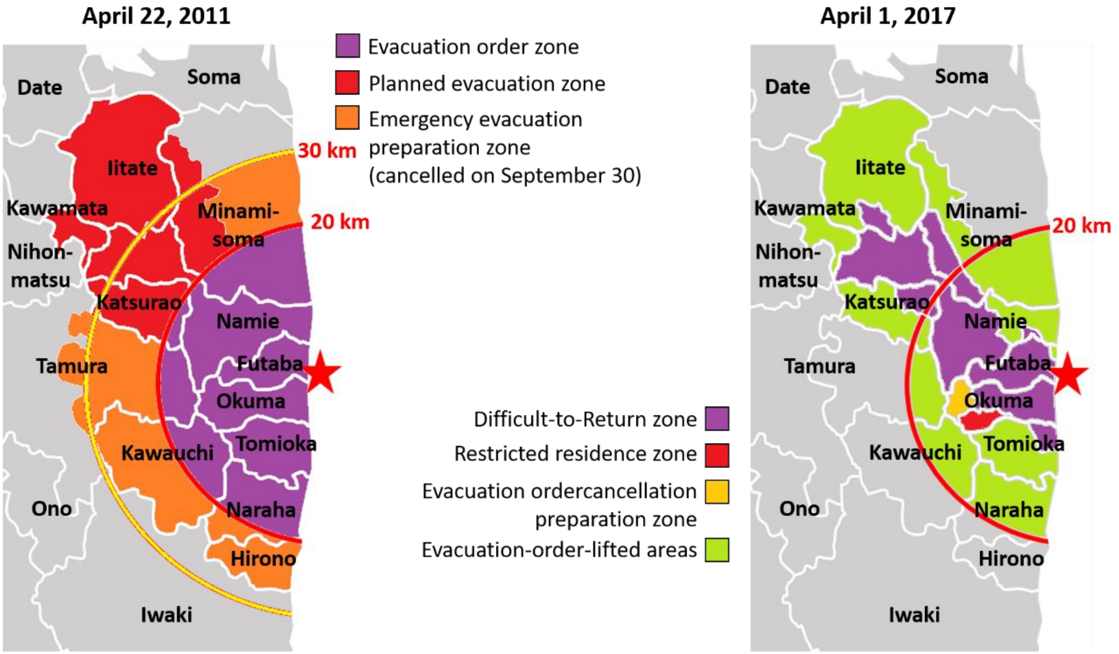

Figure 2 Evacuation map of Fukushima from April 22, 2011 and April 1, 2017.

The lifting of each evacuation order started in 2012 step-by-step. On April 1, 2017, the evacuation designated zones (371 km^2) occupy 2.7 % of the areas of Fukushima Prefecture (13,783 km^2) [37]. The number of evacuees is still at 43,214 as of December, 2018 [37]. The reconstruction and revitalization in the 'Difficult-to-Return' zones are showing steady progress with remediation and construction underway [37].

After the accident, many efforts have been made to stop the release of more radionuclides and to decommission the FDNPP, which will probably take at least 30-40 years. At the FDNPP, a large amount of contaminated water has been continuously generated over the last 10 years. The treatment of this water is one of the major problems facing the decommissioning efforts. Two main sources are producing this contaminated water: The continuous cooling of the inside of the reactors and groundwater flowing into the buildings, which is mixed with the contaminated water [43]. To treat this continuously increasing amount of contaminated water, many facilities were developed and constructed at the FDNPP. A steel seaside impermeable wall was installed in 2015 to stop the flow of contaminated groundwater to the sea. Another landside-impermeable wall (frozen soil wall) was installed around the outside of the buildings. After confirming that the radioactive concentration (including tritium) is below the regulatory limit of 1500 Bq/L [44], the subdrain water is discharged right into the sea. Because of these measures, the amount of contaminated water flowing to the sea has been decreased from about 540 m^3/day (May 2014) [45] to less than 200 m^3/day today [43].

Three systems are installed at FDNPP to process the collected contaminated water. First, the water flows through a cesium adsorption system, which removes a major part of the cesium and strontium isotopes. Two different zeolite-based systems are being used: KURIOS (using chabazite) and SARRY (using crystalline silico-titanate) [46]. Then it is sent to a desalination system, which uses a reverse osmosis membrane. After this step, the permeated water is recycled as cooling water for the reactors. The remaining water was stored until the Advanced Liquid Processing System (ALPS) started its operation in 2013. This system contains several adsorption units and is optimized to remove more than 62 different contaminants [43]. Despite all this effort, small amounts of contaminants and tritium remain in the water, which is stored as so called 'tritiated water' in tanks on the FDNPP site [43]. Tritium is a low energy beta emitter is relatively harmless, and has the lowest dose coefficient for those radioactive isotopes reported in the tanks [47]. The total amount of tritium stored in these tanks is reported to be around 0.86 PBq [48]. On December 11, 2021, the capacity of tritiated water tanks of 1,370,000 m^3 will be reached [49]. As of December 17, 2020, the total amount of stored treated water from 1,240,237 m^3 was reported [49]. The space for water tank constructions at FDNPP has nearly reached its limit [45]. TEPCO and the Japanese government are considering the release of tritiated water into the Pacific Ocean, which has been widely discussed by scientists and the media [43, 45, 50].

2.4 Radionuclides of Interest

In this chapter, some background information on the nuclides of interest will be provided. These nuclides are tritium (^{3}H), strontium-90 (^{90}Sr), iodine-129 (^{129}I), cesium-134 (^{134}Cs) and cesium-137 (^{137}Cs). All of them are β^--emitters and are produced in a reactor by fission or neutron activation. Some of these nuclides are of greater importance in the context of environmental monitoring than other radioactive isotopes. All of them were released during the accidents of Chernobyl and Fukushima.

2.4.1 Radiocesium

Cesium isotopes were among the most significant radionuclides released during both the Chernobyl and especially the Fukushima nuclear accident. Cesium is an alkali metal and has several radioactive isotopes in addition to one stable isotope, ^{133}Cs. The main focus after the Fukushima accident was on the two radioactive isotopes, ^{134}Cs and ^{137}Cs, with half-lives of 2.1 and 30.1 years, respectively. Both cesium isotopes decay to barium by beta decay. The decay schemes of both cesium isotopes are presented in Figure 3 and Figure 4. Cesium is a very volatile element because of its low boiling point at 671 °C [51]. This explains why cesium was one of the main elements released from the Fukushima power plant.

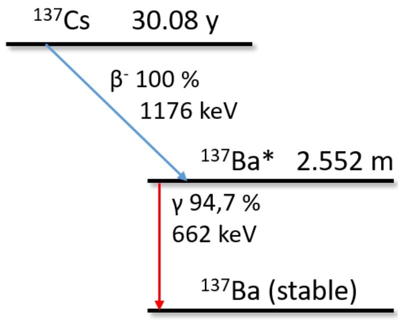

Figure 3 Decay scheme of ^{137}Cs

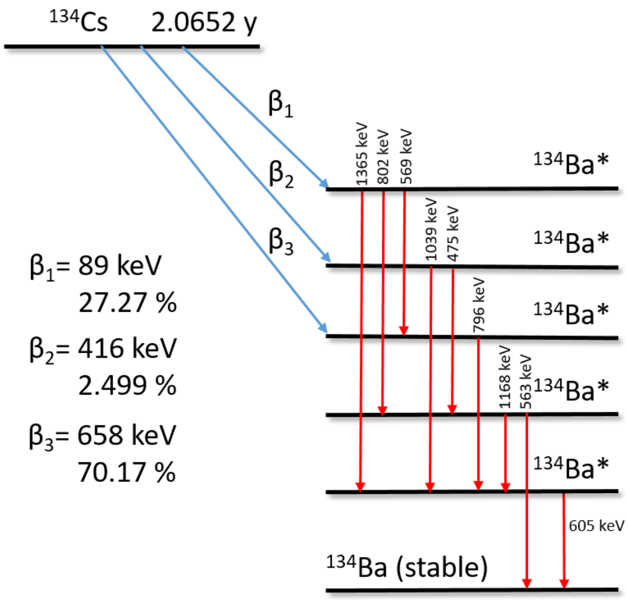

Figure 4 Simplified decay scheme of ^{134}Cs

Cesium-137 is a fission product of uranium and plutonium, with a high fission yield of 6.2 % (^{235}U) and 6.6 % (^{239}Pu), while ^{134}Cs is produced by neutron activation from stable ^{133}Cs [52]. Large amounts of ^{134}Cs and ^{137}Cs (8.3 - 50 and 7 - 20 PBq respectively) were released from FDNPP [30], which show a characteristic isotopic fingerprint of the Fukushima accident. The ^{134}Cs/^{137}Cs activity ratios were found to be about 0.9-1.1 in the Fukushima releases [53], showing that both isotopes of cesium were released in almost equal amounts. The cesium isotope releases from the Chernobyl accident resulted in a ^{134}Cs/^{137}Cs ratio of about 0.6 [7]. With known isotope ratios, it is possible to distinguish releases between different nuclear events [54]. For example, if a site is contaminated from multiple nuclear events, the ratios can be used to calculate the fractions and determine how much activity comes from each event. This may be particularly relevant for ^{137}Cs due to its long half-life, as it is present in the environment for hundreds of years after release, and there is a possibility that a site may be contaminated with ^{137}Cs due to several different nuclear events. In the case of the Fukushima accident, isotope ratios were used to determine releases from various reactor units and waste storage tanks [55]. A distinction of the four reactors involved in the Fukushima nuclear accident solely by ^{134}Cs/^{137}Cs activity ratios, however, is much more challenging.

Cesium also has radiological significance because it resembles potassium in biological systems. Both elements are alkali metals, which allows cesium to accumulate in human and animal tissues, causing a radiation dose with a biological half-life of 110 days . After the Fukushima accident, one of the major concerns was the effect of cesium in agriculture and stock farming [56].

2.4.2 Radiostrontium

Strontium is an alkaline earth metal and therefore occurs in the +II oxidation state. Due to its boiling point of 1384 °C [51], it is classified as a medium volatile element. Strontium has three main radioactive isotopes ^{90}Sr, ^{89}Sr and ^{85}Sr, two of which are beta-emitting radionuclides (^{90}Sr, ^{89}Sr), and ^{85}Sr decays by electron capture. The beta-emitting strontium isotopes are formed as fission products, and in radioanalytical chemistry ^{85}Sr is often used as radioactive tracer [52]. Strontium-85 is typically produced by the nuclear reaction ^{85}Rb(p,n)^{85}Sr in a cyclotron [57]. The high radiotoxicity of radiostrontium is of high concern for the public safety. It is characteristically a chemical homologue to calcium, which causes strontium to be highly relevant from a radioecological point of view. As they are both alkaline earth metals, strontium can accumulate in bones and by constant, long-term irradiation enhances the probability of causing leukemia or skeletal cancer [58]. The biological half-life of ^{90}Sr in higher organisms ranges from 80 days in exchangeable compartments up to years in bone tissue as strontium substitutes calcium in calcium hydroxylapatite (the mineral matrix in bones) [59]. The decay scheme of ^{90}Sr is presented in Figure 5. Strontium-90 decays to ^{90}Y, which adds to the radiotoxicity of strontium because ^{90}Y has a fairly short half-life (64 hours [60]) and high maximum beta energy of 2.27 MeV.

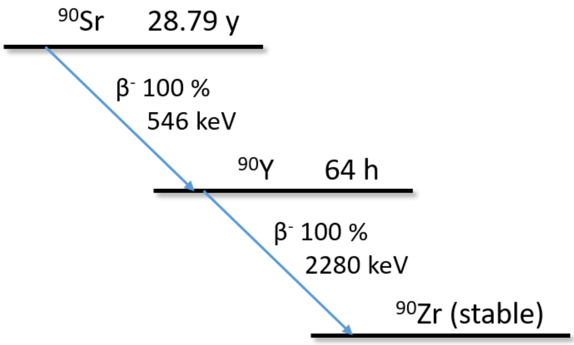

Figure 5 Decay scheme of ^{90}Sr to ^{90}Y and ^{90}Zr

An estimated total of 600 PBq ^{90}Sr has been released in the course of atmospheric nuclear explosions of the 20th century [61]. Studies on the anthropogenic release of strontium into the environment show that emissions from the FDNPP accident were relatively low, as most strontium remained in the (molten) core. The atmospheric releases of different strontium isotopes have been estimated to be around 0.1 PBq for ^{90}Sr and 2 PBq for ^{89}Sr. These released activities correspond to about 0.03% of the total radiostrontium inventory in the reactor units [35].

The greatest focus concerning FDNPP releases is on ^{90}Sr, due to its high fission yield of 5.8 % (^{235}U) and long-term radiological relevance. Since ^{90}Sr is a pure beta emitter, it is usually directly measured by liquid scintillation counting, LSC, but a gas ionization detector can also be used. The daughter nuclide of ^{90}Sr, ^{90}Y can also be used for the determination of ^{90}Sr activity, by measurement with Cherenkov counting after an ^{90}Y ingrowth period of approximately

2-3 weeks. Due to its short half-life (50 d), ^{89}Sr decayed shortly after the FDNPP accident and for that reason did not raise concern in long-term safety assessment.

Not many studies exist about strontium releases from FDNPP. This might be due to the fact that measurement of strontium is not as straightforward as other, mostly gamma-emitting, radionuclides [62]. Strontium-90 requires separation from other radionuclides before it can be measured and the measurement is highly time consuming if the ^{90}Y ingrowth technique is used.

Although little radiostrontium was released into the atmosphere, accidental and possibly intentional discharges of the reactor cooling waters caused contamination in the Pacific Ocean. Therefore, the activity concentration of radiostrontium in seawater has been studied thoroughly after the Fukushima accident. Measured activity concentrations in a previous study ranged from 0.8 to 85 Bq/m^3 and 19-265 Bq/m^3 for ^{90}Sr and ^{89}Sr, respectively [63]. Because of the short half-life of ^{89}Sr, all detectable activity in these studies could be assigned to the Fukushima event, since every possible source of previous contamination of ^{89}Sr had been decayed prior to the Fukushima releases. By contrast, the ^{90}Sr results have to be compared to background levels, since traces from previous nuclear events can be found. Studies on inland samples generally have very low activity concentrations, with a maximum of around 1 Bq/g (up to 4 orders of magnitude lower then ^{137}Cs concentration in the same sample). Due to the low volatility of strontium, atmospheric releases are significantly lower than those of cesium or iodine isotopes [62].

Strontium isotopes can also be used to determine the source of nuclear contamination. Isotopic ratios can be calculated using either strontium isotopes only, e.g. ^{89}Sr/^{90}Sr, or the ratio of strontium and cesium (^{90}Sr/^{137}Cs) can be used. Based on these radionuclide ratios, it is possible to determine the source or even to estimate the activity of the particular nuclide if the ratio and activity of the other nuclides are known. This is part of nuclear forensics. The ^{89}Sr/^{90}Sr ratio in samples from the Pacific Ocean collected after the Fukushima accident ranged from 1.8 to 4.3 [63]. The ^{90}Sr/^{137}Cs ratio in the seawater samples was about 0.02 and could be used to estimate the released activity of ^{90}Sr because the activity of ^{137}Cs is well known. Using the ^{90}Sr/^{137}Cs isotope ratio, the calculated amount of ^{90}Sr released to the Pacific Ocean ranges from 90 to 900 TBq [35].

2.4.3 Tritium

Hydrogen has three naturally occurring isotopes, two of which are stable (^{2}H, ^{1}H) and the third is the radioactive tritium (^{3}H) [52]. Tritium is a soft beta emitter with a maximum beta energy of 18.6 keV [60] and a relatively long half-life of 12.3 years. Tritium is produced naturally by cosmic ray interactions with nitrogen and, in particular, by the reaction between neutrons and nitrogen in the upper atmosphere ($^{14}N(n,^{3}H)^{12}C$) [58].

Typically, tritium occurs in nature as tritiated water, HTO, but a small amount can also be bound in hydrogen gas, HT. Tritium can also replace hydrogen atoms in organic molecules. In the environment, tritium is incorporated into the hydrogen cycle and rapidly diluted. The biological half-life of tritium is 12 days, which is relatively short [64]. Combining these properties with the low beta energy it emits during decay, it can be summarized that tritium does not pose major radiation protection concerns. Tritium decays to stable ^{3}He, as presented in its decay scheme in Figure 6.

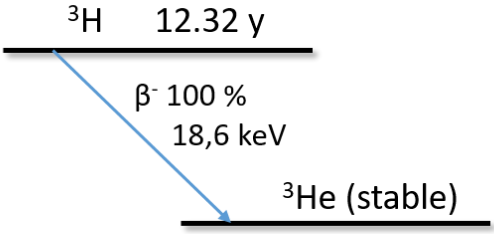

Figure 6 Decay scheme of ^{3}H

Anthropogenic tritium was released into the atmosphere in large quantities during the nuclear testing era, especially thermonuclear (fusion) tests in 1952-1963. The production of this anthropogenic bomb-related tritium, is based on the reaction of lithium with neutrons in [$^{6}Li(n,\alpha)^{3}H$] [52]. Tritium can also be produced as a ternary fission product with a fission yield of 0.01 %, or in other neutron activation reactions including reactions with boron [$^{10}B(n,2\alpha)^{3}H$] or helium [$^{3}He(n,p)^{3}H$] [52].

In publications, the concentration of tritium is generally presented as tritium units (TU), which describes the ratio of tritium to hydrogen in rain water before the nuclear age. One tritium unit has 1 tritium atom for 10^{18} hydrogen atoms ($^{3}H/^{1}H= 10^{-18}$) [52]. When expressed as activity, 1 tritium unit equals 0.118 Bq/L [58].

Tritium levels have been monitored for decades, and there have been two peak concentrations over the years. In the Northern Hemisphere, the first peak concentration of tritium was about 10,000 TU at the time of the thermonuclear tests. The second peak of anthropogenic tritium releases was caused by the Chernobyl accident in 1986. At Japan, tritium levels have been monitored since 1961, and have been around 10 TU since the 1980s. As a background level of tritium before the accident, precipitation samples collected in Tsubuka, Japan, in 2010 showed tritium levels of 6 TU. The tritium concentration within the first precipitation, 170 km from the

FDNPP, was 160 TU [65]. Until this thesis, the highest measured tritium activity concentration of 1342 TU was measured in a precipitation sample 10 days after the accident at a distance of 25 km from the NPP [66]. In the present thesis, we found the highest tritium activity concentration of 1560 ± 17 TU (decay corrected to the accident) in a puddle sample, collected on April 11, 2011, approximately 1.5 km from the FDNPP site [D2].

2.4.4 Radioiodine

Iodine is an element of the halogen group and is a non-metal and can adopt oxidation states ranging from –I to +VII. Iodine has one stable isotope, ^{127}I and several radioactive isotopes, of which ^{131}I and ^{129}I are the most significant when studying the Fukushima accident. In Fukushima, ^{131}I was one of the most significant fission products released among cesium isotopes -134 and -137. Iodine-131 has a short half-life of 8 days, whereas ^{129}I has a half-life of $1.57 \cdot 10^{7}$ years. Iodine-129 decays to stable xenon by beta decay and the decay scheme is presented in Figure 7. The maximum beta energy of ^{129}I is 154 keV. It is estimated that the largest released activity of a single radionuclide, 150-160 PBq, was from ^{131}I released from Fukushima, if noble gases are excluded. For the long-lived iodine isotope ^{129}I, the amount of released activity is estimated to total about 8 GBq. Iodine was released predominantly in the atmosphere, but the greatest impact was to the Pacific Ocean, not only by deposition from the atmosphere but also by direct release from contaminated cooling water [67].

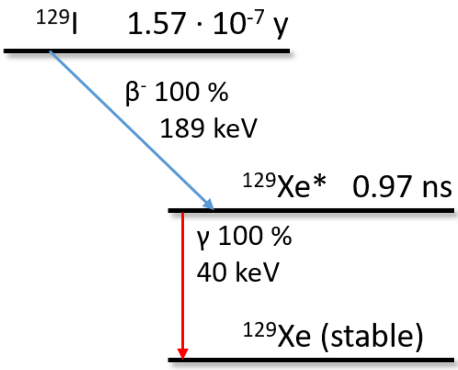

Figure 7 Decay scheme of ^{129}I

Iodine-131 is radiologically considered to be one of the most harmful radionuclides released from the FDNPP, as it exhibited a high activity immediately after the accident. Iodine is known to have a high affinity to the thyroid. Thus, having a high probability of causing thyroid cancer, especially in children. Iodine-129 is of little radiological concern compared with than ^{131}I, but it is an important oceanographic and ecological tracer and serves as a sensitive fingerprint of nuclear pollution in the environment [68]. Furthermore, when estimating the impact and dosimetry of ^{131}I after the Fukushima accident, ^{129}I is also very important nuclide. Because of the identical chemical behavior of different iodine isotopes, ^{129}I can still be used retrospectively as an environmental analog for short-lived ^{131}I, which decayed within few weeks after the accident. The information provided by the ^{129}I measurements can be used to reconstruct the levels and distribution of the short-lived ^{131}I [67]. In order to reconstruct the ^{131}I contents, the ratio of iodine isotopes, ^{129}I/^{131}I, is applied. The ^{129}I/^{131}I isotope ratio measured after the accident was about 16 in precipitation and 32 in soil samples. The ratio in soil samples is decay corrected to March 15, 2011, and the value in precipitation is an average of the period March 3-31, 2011 [68, 69]. In comparison, the ^{129}I/^{131}I ratios measured in rainwater after the Chernobyl accident ranged from 16 to 35 [70]. Based on the results of those studies, the Fukushima and Chernobyl radioiodine ratios are comparable.

Not only the ratios of iodine isotopes can be calculated, but also, in general, the activity ratios of different radioisotopes such as $^{129}I/^{137}Cs$ and $^{131}I/^{137}Cs$. The $^{129}I/^{137}Cs$ activity ratio measured after the Fukushima accident averaged $1.1 \cdot 10^{-6}$ in aerosol samples [71], during the same ratio measured after the Chernobyl accident was $2.75 \cdot 10^{-7}$ [72]. In air samples, the value after the Fukushima accident for $^{131}I/^{137}Cs$ averaged 32 collected within 80 km of the FDNPP. In samples with greater distance, the $^{131}I/^{137}Cs$ ratio was higher. The values of $^{131}I/^{137}Cs$ in samples collected at a distance of 2000-12,000 km ranged from 63 to 77. The values increase with distance due to the transport phase of the radionuclides. After release, ^{137}Cs is bound to aerosol particles, while ^{131}I is transported either in aerosol particles or in the gas phase. During transport, the aerosol particles containing the radionuclides, in this case ^{137}Cs and partially ^{131}I, are efficiently deposited by rain or gravity, while the nuclides in the gas phase, ^{131}I, remain longer in the atmosphere [71].

3 Methods

3.1 Samples

The water samples for this thesis were collected during three sampling campaigns:

- Chernobyl surface waters including cooling pond water, from 2017 [D1]
- Fukushima surface water from the vicinity of the FDNPP sampled 1 month after the accident [D2]
- Potable and surface water from venues in Japan of the Tokyo 2020 Olympic Games [D3]

The sampling of Chernobyl surface water from the exclusion zone occurred on May 16 and 17, 2017. Ten water samples were taken directly from the shore, after removing floating matter (e.g., algae or pollen) from the surface. Figure 1 in [D1] shows a map of the sampling sites and detailed sampling location are given in Table 2 [D1]. Different types of surface water were collected widely around the entire area around the power plant and Chernobyl City: Tap water from Chernobyl City, rainwater collected from the rooftop of a car, water of the cooling pond, water from the channel which leads into the cooling pond, puddle water at the checkpoint, water from the Ush river and from the Pripyat River Bay, water of ponds near the street to Chernobyl city, and water from a swamp. The sample volume was 1 L each except the rainwater sample, which was 600 mL. The samples were stored, untreated, in PET bottles in a refrigerator until further sample preparation.

The sampling of Fukushima surface water samples was performed on April 10, 2011. The exact locations and sample types are presented in Table S1 [D2] and the sample collection locations are also shown in Figure S1 [D2]. There were three different types of samples; puddle, paddy water and seawater samples. Puddles in this study refer to a water sample that is collected from cracks in an asphalt based road, paddy water refers to rice paddy field and there was one seawater sample collected from surface of the Pacific Ocean very close to the shore. All samples had been filtered with 0.45 µm membrane filters prior to any sample preparation. The samples were stored in plastic vials (PP) that were sealed in plastic bags to avoid any leakage. The vials were kept in a refrigerator until further sample preparation. The sample volumes vary between 40 and 100 mL.

The Olympic water samples include two types: Potable water (tap water and bottled water) as well as surface water and tap water. A total of 12 potable water samples in PET bottles were bought in supermarkets. The content of the bottled water was produced in the prefectures Hokkaido, Fukushima, Chiba, Tokyo, Kanagawa (2 independent samples), Ishikawa, Hyogo, Shimane, Hiroshima, Fukuoka, and Kumamoto. In addition, 4 surface water samples were taken on February 14 and 19, 2018, to address concerns of athletes getting into contact with these surface waters. They were taken from the venues of the Windsurfing competition (Tsurigasaki Surfing Beach, Chiba), Sailing (Enoshima Yacht Harbour, Kanagawa), Triathlon Swimming (Odaiba Marine Park, Tokyo) and Canoe Slalom (Kasai Canoe Slalom Course, Tokyo) and one tap water sample from the Cycling Track (Izu Velodrome, Shizuoka). All sampling prefectures and venues are shown in Figure 2 [D3]. The sample volume was 1 L each and the samples were stored, untreated, in a refrigerator in PET bottles until further sample preparation.

3.2 Sample Preparation and Method Optimization

This thesis consists of three parts: The method optimization for each nuclide of interest, especially for ^{90}Sr with respect to the Chernobyl water samples; utilization of these methods for the Fukushima water samples where only small volumes were available; and lastly, confirming that these methods are suitable for low-level measurements with low detection limits for the Olympic water samples.

The initial step was to measure the air dose rates of the wrapping surface of the water samples with a contamination monitor (Berthold Technologies, LB 124 SCINT). These air dose rates are the first indicator of activity in these samples. All samples were prepared by means of the same treatment sequence: First the samples were acidified and filtered, following a gamma measurement to determine ^{137}Cs activity, then the preparation for ^{90}Sr, ^{3}H, and in the case of the Fukushima samples for ^{129}I.

Prior to any measurements, the water samples from the Chernobyl exclusion zone and from venues in Japan of the Olympic games 2020 were acidified with 1 mL nitric acid (VWR Chemicals, 69 %, p.a.) to 1 L solution and filtered through a 2-4 µm Whatmann^{TM} filter paper. In addition, for some of the measurements a defined volume was filtered through a 0.45 µm syringe filter (VWR, PP-membrane), which will be described in the respective radionuclide section. The Fukushima surface samples were first filtered through a 0.45 syringe filter and later acidified (or alkalized for iodine sample preparation). The exact sample treatment of the different campaigns is given in the publications [D1, D2, D3].

3.2.1 Radiocesium

Cesium did not need any special separation or sample preparation, because the characteristic gamma energies of both cesium isotopes were used for determination (605 keV and 795 keV for ^{134}Cs, 662 keV for ^{137}Cs). The only preparation for cesium isotope measurements included filling the water samples into a defined geometry. In this thesis, Marinelli beakers in different sizes 500 – 1500 mL (Chernobyl water and Olympic water) and 50 mL centrifuge tubes (Fukushima water) were used. Efficiency calibrations were done with the same geometry before measurement. The calibration solution included known activities of different energy radionuclides and by measuring the counts and knowing the initial activity, the efficiency of the high-purity germanium detector at a defined energy could be determined. The main focus of the gamma measurements was to determine the activities of cesium isotopes ^{134}Cs and ^{137}Cs.

The samples from Chernobyl and Fukushima were measured with the software GENIE2K on a high-purity germanium detector. The measurement times ranged from 1 to 6 days, depending on each sample activity. Every sample was measured until the uncertainty for ^{137}Cs peak was 10 % or less. The Olympic samples were measured in Dresden, Germany, in a low-level underground laboratory called “Felsenkeller”.

3.2.2 Radiostrontium

The strontium separation was performed with the extraction chromatography resin, ‘SR Resin’, from Triskem. Together with Weller et al., we tested these resins at different conditions [73]. One test included the long-term storage of unloaded SR resins at different temperatures, another tested the storage of ^{85}Sr loaded resins under highly acidic conditions and also under a combination of acidic and complexing agent conditions. Finally, the reusability of the resin material was investigated [73].

One part of this thesis was to evaluate the process on the basis of its recovery determination using stable strontium, which is readily applied with the addition of the carrier solution, and which process is able to perform the recovery calculation with ^{85}Sr. For samples which can be estimated to have rather low-level activities, the recovery determination procedure using stable strontium and measurement via ICP-AES have been proven favorable. This is especially applicable to the Olympic water samples, which were expected to contain ^{90}Sr activities from none to barely above LoD. Chernobyl sample material that has been characterized beforehand, has likewise been evaluated via stable Sr carrier recovery calculations to test this method. As the Fukushima surface water samples were expected to show higher activities, ^{85}Sr addition was chosen for recovery determination.

Strontium extraction chromatography

The strontium-selective part of the resin is the crown ether 4,4’(5’)-di-t-butylcyclohexano-18-crown-6, which has an inner diameter of the crown fitting perfectly to the ionic radius of a strontium cation coordinated by two nitrate anions. One percent of the crown ether is diluted in 1-octanol and the resulting organic solution is embedded into an inert chromatographic stationary phase. The particle size of the chromatographic stationary phase was 50 - 100 µm [74].

The strontium ion is loaded on the resin with 8 M nitric acid (highest equilibrium constant k of 90) and eluted with 0.025 M nitric acid (k less than 1). For this reason, an easy separation of strontium from calcium is possible because of calcium’s low affinity towards the stationary phase. The barium retention is relatively high on the SR resin, but has maximal affinity at 3 M nitric acid, in which case a resin loading with 8 M results in washing the Ba off the column. Furthermore, tetravalent actinides show significant retention on the Sr column. Through addition of oxalic acid as a competitive complexing agent, the tetravalent actinides are washed from the column. Lead has an even higher affinity to the resin than strontium and, moreover, has natural occurring radioisotopes ^{210}Pb and ^{212}Pb.

Interferences from sodium or calcium with concentration lower than 0.5 M are not significant, but a calcium mass above 320 mg shows an influence on the chemical yield. Moreover, concentrations of higher than 0.1 M potassium show a similar decrease of the chemical yield. In this case, prior oxalate precipitation is recommended. The maximal capacity of one SR resin is 21 mg for a 2 mL column, it is recommended to work at 10-20 % of the maximum capacity. It was also found that the particle size used has influence on the elution band. A smaller particle size distribution results in narrower elution band but slower flow rates [74, 75].

3.2.3 Tritium

Tritium with its low beta energy of 18 keV is preferably measured via LSC. Tritium activity concentration of natural waters (precipitation, groundwater, surface waters) has recently reached a level too low to be directly measured by low-level liquid scintillation (LSC) techniques. In order to measure tritium in environmental water samples, an enrichment of tritium containing water (HTO) in H_2O is necessary. In this thesis, two different methods for tritium enrichment were applied: distillation and electrolysis.

Distillation

A tritium enrichment via distillation process lies in the physical basis that the rates of escaping atoms and molecules from a liquid surface to a gaseous phase are generally inversely proportional to the square roots of their masses (Graham's Law) [76]. Multistage distillation techniques are necessary for satisfactory results, because the fractionation factor of HTO in H_2O is rather small [77]. The setup and the procedure are both straightforward and inexpensive, as most equipment is commonly available in every chemical laboratory. The major disadvantages of distillation as an enrichment process are the relatively long times required for enrichment, the poor reproducibility, and the modest enrichment factors achieved [78]. The degree of separation also decreases significantly with increasing temperature; at 100 °C, the separation factor is only about 1.036 [78]. Optimal fractionation of tritium relative to water is achieved at the same distillation times at a pressure of about 130 to 160 mbar (at which water boils at 52-55 °C) [79]. Distillation of water samples represents a purification process that is particularly useful when water samples are contaminated with organic matter, interfering chemicals or radionuclides [80].

The used equipment setup consisted of basic distillation glassware. The focus was on removal of the beta emitting radionuclides present in the solution and concentration of tritiated water. Hold-back carriers were included into the procedure: By addition of sodium carbonate, sodium iodide and sodium sulphite, volatile radionuclides can be retained. Most radionuclides in water samples can barely be vaporized. However, some nuclides can be released if the hold-back carriers are not used. An example of a vaporizable, interfering radionuclide is ^{14}C, which is most likely to be released as carbon dioxide during distillation, but can be retained by sodium carbonate. Another example is iodine (e.g. ^{129}I and ^{131}I), which readily vaporizes as I_2, but it is reduced to non-vaporazible iodide by sodium sulphite.

To ensure that no HTO was in the glassware at the beginning of the experiment, all glass equipment and teflon sealing was dried in an oven at 105 °C beforehand. The distillation was performed under vacuum to further enhance the process. The maximum temperature in the distillation apparatus ranged between 61 to 76 °C. The samples were distilled until dry with care taken to prevent splashing of the residue.

Electrolysis

The tritium activity concentration can be increased to a measurable level by electrolytic enrichment. During electrolytic enrichment of tritium, water is decomposed into its individual components, hydrogen and oxygen. Due to the isotope effect, the compound HTO has a lower reaction and migration rate than H_2O. Even though isotopes of one element show the same chemical behavior, isotope effects can occur due to the noticeable mass differences. Whenever a vectored force has an effect on different isotopes, as for example when a centrifugal force is applied, a mass fractionation can take place. This mass fractionation happens to be unaffected by the chemical properties of the element itself. For hydrogen and tritium, the mass difference is a factor of three, giving a relatively high probability of isotope effects to occur. These effects have to be considered when working with tritiated water. For isotopes with masses larger than carbon, the isotope effect can be neglected. By means of the isotope effect, HTO can be separated from H_2O via electrophilic enrichment. The larger the initial water volume, the larger the enrichment factor, i.e., the ratio of the final to the initial tritium activity concentration of a sample increases. Common tritium enrichment factors range from about 3 [81] to 18 [82] for 250 mL initial water volume, from 18 [83] to 28 [82] for 500 mL initial water volume, and can reach 75 or even 175 for 1 L or 2 L initial water volume [84]. With the setup used in this work, an enrichment factor of 13 (reduction of 200 mL to approx. 15 mL) was achieved. During this process, gases are produced and ventilation should be applied. When hydrogen concentration in the surrounding air reaches a critical level (4 – 77 volume % H_2), uncontrollable oxyhydrogen reactions can take place [85].

3.2.4 Radioiodine

Due to its long half-life of 15.7 Ma and the low β- and γ-energies, direct radiometric measurements of ^{129}I are only possible with comparatively high concentrations. In order to circumvent this issue, accelerator mass spectrometry (AMS) was chosen as the analytical method for ^{129}I determination. The mode of operation is based on multiple separations of the analyte from isobaric interferences of the sample matrix. By application of this technique, extremely low LoDs are achieved, which makes this method ideally suited for ^{129}I determination.

For AMS measurements, the iodine must be extracted from the water samples, precipitated as silver iodide, and pressed into specialized AMS targets. The method used in this work for extraction and preparation of silver iodide targets for AMS measurement is a variant of the method performed by Hou et al. [86].

Different volumes are needed to prepare water samples for AMS measurements according to the expected $^{129}I/^{127}I$ ratios. Only a few milliliters (5 - 10 mL) are needed for samples from the immediate vicinity of the reprocessing plants (ratio of ca. 10^{-6}), while up to 1 L is necessary for lower ratios, for example in precipitation and surface waters. For the samples prepared in this work, volumes of 1 - 38 mL were applied and mixed with 50 µL of the Woodward iodine-added carrier. Woodward iodine is ^{127}I of high isotopic purity ($^{129}I/^{127}I$ isotopic ratio of 10^{-14}), which can be obtained from special geological deposits, usually sealed from the atmosphere. Due to the very low ^{129}I content, Woodward iodine is suitable for "dilution" of seawater samples highly concentrated in ^{129}I for sensitive AMS. The challenging part of the ^{129}I sample preparation for the measurement is in the identification of suitable activity levels for the AMS. On the one hand, contamination of the AMS facility has to be avoided, which is why too high activities are impractical. On the other hand, if too high dilutions are applied and ^{129}I levels appear to be near the LoD, high uncertainties of the measurement results will be unavoidable. The exact treatment is described in [D3]. The concentration of stable iodine ^{127}I in the initial samples was measured via ICP-MS and each result was used for calculation of ^{129}I activity concentration by means of the corresponding $^{129}I/^{127}I$ ratio.

Accelerator mass spectrometry

Negatively charged ions are ablated from the surface of the samples precipitated as silver iodide (AgI) by a Cs sputter source, accelerated and sent through the first mass separator. Only ions with the set mass-to-charge ratio (m/z = 129) are able to pass. The decisive step occurs in the +3 MV Tandem Accelerator, since the gas used there and the "stripper coil" cause the introduced iodine to lose electrons, leaving it with a +4 charge. Interfering ions, which are on the same isobar, yet chemically different from iodine, do not show a +4 charge after this step. In this way the most interfering xenon isotope ^{129}Xe can be removed from the measurement. The subsequent mass analyzers separate again according to the defined m/z ratio. It is thereby possible to achieve detection limits for ^{129}I/^{127}I ratios in the order of 10^{-14} [87].

4 Conclusion and Outlook

In this thesis, modern radioanalytical and mass spectrometry techniques were used and partly optimized for the relatively long-lived radionuclides ^{3}H, ^{90}Sr, ^{129}I and $^{(134)+137}$Cs in environmental water samples. The behavior and durability of commonly used SR resin for separation of radiostrontium under several possible sample preparation steps were investigated. Afterwards, surface water samples from Chernobyl and Fukushima were analyzed for their radioactive content by optimization of methods for small volume samples. The applied methods were then validated for their detection limits with low-level potable water samples.

For radiostrontium measurements, the yield tracer ^{85}Sr does show slight increases of the count rate of ^{90}Sr in LSC measurements increasing the detection limits. For ultra-low-level analyses, the use of stable strontium was proven to be sufficient and its benefits regarding the analytical procedure were highlighted. The concentrations of interfering cations (e.g. Ca^{2+}, Ba^{2+}, Pb^{2+}) and the overloading of strontium can be controlled prior to the extraction with the first aliquot (for example with ICP-AES). Therefore, it can be evaluated if there is a necessity for an increased amount of SR resin needed to avoid a breakthrough of the Sr due to excessive loading of the resin. After extraction, another aliquot can be used to determine the recovery rate. In this thesis, the application of this method showed recovery rates between 72 and 95 % [D1].

Nearly all water samples from Chernobyl exclusion zone exhibited detectable activities of ^{90}Sr and ^{137}Cs, even after more than 30 years (approx. one half-life of these isotopes after the accident in 1986) [D1]. It was found that neither the rainwater sample from the Kopachi village did exceed the detection limit of ^{90}Sr (LoD = 0.07 Bq/kg), nor the puddle water sample near the checkpoint to the Chernobyl exclusion zone, nor tap water from a laboratory in Chernobyl city, nor water from the Ush river contain detectable amounts of ^{90}Sr or ^{137}Cs. The other samples of this study contain detectable amounts of 0.6 – 4.1 Bq/kg for ^{90}Sr and 0.06 – 8 Bq/kg for ^{137}Cs. Two significant observations have been made: The aqueous environment in the southern region of the ChNPP is characterized by low contamination levels and the ^{90}Sr/^{137}Cs ratio seemingly tending to increase with distance from the source.

The Fukushima surface water samples have a high scientific value due to the timing of the sampling only one month after the nuclear accident [D2]. Four of those samples exhibited tritium in detectable concentrations of 5 – 184 Bq/L. One puddle water sample, collected approximately 1.5 km from the FDNPP site, showed the highest tritium activity concentration reported in scientific literature of 184 ± 2 Bq/L, the highest concentration until that date was at 160 Bq/L in precipitation at a distance of 25 km 10 days after the accident. Strontium-90 was detected in all samples, but only the puddle water sample exceeded the limit of quantification (LoQ = 1 Bq/L). The Pacific Ocean water sample investigated in this study showed a higher tritium concentration compared to other seawater samples from different sampling campaigns at a later stage after the accident, including non-coastal areas. The ^{134}Cs/^{137}Cs ratio of 1.1 ± 0.3 indicates that virtually the entirety of radiocesium in this sample is Fukushima-derived. Activities of long-lived ^{129}I were determined and used to retrospectively assess the contamination levels with highly radiotoxic, short-lived ^{131}I. Since the storage of the samples between sampling and analyzing was not optimal, the calculated activity concentrations of ^{131}I should be regarded as the minimum concentrations. The puddle samples exhibited high ^{131}I concentrations of ≥ 300 Bq/L, the one from close proximity almost 5 kBq/L, and is in line with the highest ^{131}I activity concentration reported for rainwater. In addition, the activity concentration of the seawater sample of 88 ± 2 Bq/L is in a good agreement with other studies. The comparison of a puddle and a paddy sample from the same location gave information about the radioecological characteristics of the analyzed fission products. The ratios given by the tritium activity concentration of those samples showed the isotope dilution effect from precipitation (puddle sample) and stagnant water (rice paddy sample). The deviation from this ratio for other nuclides may reflect adsorption to minerals (cesium) or organic matter (iodine).

Potable water and surface water samples from Olympic sites in Japan for Tokyo 2020 have been analyzed for a radiological hazard assessment for internal and external exposures [D3]. In addition, air dose rates at all Olympic sites were measured for assessments of the external exposure. An extensive literature review helped provide information on internal exposure from radon inhalation in Japan and was compared to countries where other Olympic Games have taken place. Strontium-90 could not be detected in any of those samples with a detection limit of 70 mBq/L. The tritium activity in a potable water sample from Fukushima prefecture was below the pre-accident background. The potable water sample from Chiba exceeded the ^{137}Cs activity above the detection limit with 3.1 ± 0.7 mBq/L. However, the radiocesium level is far below the regulatory limit of 10 Bq/kg. It could be shown that the effective dose for a two-week stay in Japan can predominantly be attributed to the flights to and from Japan and internal dose by inhalation of natural radioactive ^{222}Rn and its progeny.

For further investigation on this topic, the Fukushima surface water samples should be measured for their ^{135}Cs/^{137}Cs-ratio, especially for environmental nuclear forensics studies. By means of determination of isotopic ratios, these samples may lead to more information about the process of the Fukushima accident. An additional recommendation for future studies is to adopt in-situ measurements for radiostrontium via liquid extraction chromatography coupled with ICP-QQQ-MS system as a rapid radiostrontium measurement system. Usage of such a coupled system provides greater enhancement of consistent repetition of measurements, as well as the possibility to reach even lower limits of detection. Optimization and continuous advancements regarding the chemical sample preparation are the most important targets to aim for in radioanalytical science.

5 References

1. Minder W (1981) Geschichte der Radioaktivität. Springer, Berlin, Heidelberg, New York

2. Mayer-Kuckuk T (2002) Kernphysik, 7., überarbeitete und erweiterte Auflage. Teubner Studienbücher Physik. Vieweg+Teubner Verlag, Wiesbaden

3. Mania H (2013) Kettenreaktion: Die Geschichte der Atombombe, 2. Aufl. Rowohlt, Reinbek bei Hamburg

4. Corden PS, Zartman IW, Melamud M et al. (2014) Historical context and steps to implement the CTBT. In: Meerts P, Melamud M, Zartman IW (eds) Banning the Bang or the Bomb? Negotiating the Nuclear Test Ban Regime. Cambridge University Press, Cambridge, pp 17–31

5. Neles JM, Pistner C (2012) Kernenergie: Eine Technik für die Zukunft? Technik im Fokus. Springer Berlin Heidelberg; Imprint; Springer, Berlin, Heidelberg

6. Beresford NA, Fesenko S, Konoplev A et al. (2016) Thirty years after the Chernobyl accident: What lessons have we learnt? J Environ Radioact 157:77–89. https://doi.org/10.1016/j.jenvrad.2016.02.003

7. Steinhauser G, Brandl A, Johnson TE (2014) Comparison of the Chernobyl and Fukushima nuclear accidents: A review of the environmental impacts. Sci Total Environ 470-471:800–817. https://doi.org/10.1016/j.scitotenv.2013.10.029

8. Chernobyl | Chernobyl Accident | Chernobyl Disaster - World Nuclear Association. https://www.world-nuclear.org/information-library/safety-and-security/safety-of-plants/chernobyl-accident.aspx. Accessed 14 Nov 2020

9. RBMK Reactors | reactor bolshoy moshchnosty kanalny | Positive void coefficient - World Nuclear Association. https://www.world-nuclear.org/information-library/nuclear-fuel-cycle/nuclear-power-reactors/appendices/rbmk-reactors.aspx. Accessed 14 Nov 2020

10. Czakainski M (ed) (2007) Der Reaktorunfall in Tschernobyl: Unfallursachen, Unfallfolgen und deren Bewältigung, Sicherung und Entsorgung des Kernkraftwerks Tschernobyl, 4. Aufl. Informationskreis KernEnergie, Bonn

11. Kerner A, Stück R, Weiß F-P (2011) Der Unfall on Tschernobyl 1986. Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Garching bei München, Köln, Sonderdruck in atw, Ausgabe 2/2011

12. Scientific Committee on the Effekts of Atomic Radiation (2000) Sources and effects of ionizing radiation. United Nations, New York

13. Kashparov VA, Lundin SM, Zvarich SI et al. (2003) Soil Contamination with Fuel Component of Chernobyl Radioactive Fallout. Radiochemistry 45:173–183. https://doi.org/10.1023/A:1023897612740

14. Salbu B, Kashparov V, Lind OC et al. (2018) Challenges associated with the behaviour of radioactive particles in the environment. J Environ Radioact 186:101–115. https://doi.org/10.1016/j.jenvrad.2017.09.001

15. Kashparov V, Yoschenko V, Levchuk S et al. (2012) Radionuclide migration in the experimental polygon of the Red Forest waste site in the Chernobyl zone – Part 1: Characterization of the waste trench, fuel particle transformation processes in soils, biogenic fluxes and effects on biota. Applied Geochemistry 27:1348–1358. https://doi.org/10.1016/j.apgeochem.2011.11.004

16. Kryshev II (1995) Radioactive contamination of aquatic ecosystems following the Chernobyl accident. J Environ Radioact 27:207–219. https://doi.org/10.1016/0265-931X(94)00042-U

17. Mirzoyeva NY, Egorov VN, Polikarpov GG (2013) Distribution and migration of ^{90}Sr in components of the Dnieper River basin and the Black Sea ecosystems after the Chernobyl NPP accident. J Environ Radioact 125:27–35. https://doi.org/10.1016/j.jenvrad.2013.02.011

18. Pröhl G, Ehlken S, Fiedler I et al. (2006) Ecological half-lives of ^{90}Sr and ^{137}Cs in terrestrial and aquatic ecosystems. J Environ Radioact 91:41–72. https://doi.org/10.1016/j.jenvrad.2006.08.004

19. Smith JT, Fesenko SV, Howard BJ et al. (1999) Temporal Change in Fallout ^{137}Cs in Terrestrial and Aquatic Systems: A Whole Ecosystem Approach. Environ Sci Technol 33:49–54. https://doi.org/10.1021/es980670t

20. Smith JT, Comans R, Elder DG (1999) Radiocaesium removal from European lakes and reservoirs: Key processes determined from 16 Chernobyl-contaminated lakes. Water Research 33:3762–3774. https://doi.org/10.1016/S0043-1354(99)00087-1

21. (2006) Environmental consequences of the Chernobyl accident and their remediation: Twenty years of experience ; report. Radiological assessment reports series, vol 1239. Internat. Atomic Energy Agency, Vienna

22. Kanivets V, Laptev G, Konoplev A et al. (2020) Distribution and Dynamics of Radionuclides in the Chernobyl Cooling Pond. In: Kalmykov SN, Kato K, Konoplev A (eds) Behavior of Radionuclides in the Environment II. Springer Singapore, Singapore, pp 349–405

23. Bugai DA, Waters RD, Dzhepo SP et al. (1997) The cooling pond of the Chernobyl Nuclear Power Plant: A groundwater remediation case history. Water Resour Res 33:677–688. https://doi.org/10.1029/96WR03963

24. Salbu B, Krekling T, Lind OC et al. (2001) High energy X-ray microscopy for characterisation of fuel particles. Nucl Instrum Methods Phys Res 467-468:1249–1252. https://doi.org/10.1016/S0168-9002(01)00641-6

25. Bulgakov A, Konoplev A, Smith J et al. (2009) Fuel particles in the Chernobyl cooling pond: Current state and prediction for remediation options. J Environ Radioact 100:329–332. https://doi.org/10.1016/j.jenvrad.2008.12.012

26. Steinhauser G (2018) Anthropogenic radioactive particles in the environment. J Radioanal Nucl Chem, Articles 318:1629–1639. https://doi.org/10.1007/s10967-018-6268-4

27. Band S (ed) (2013) Fukushima Daiichi: 11 März 2011 : Unfallablauf : Radiologische Folgen, 2nd edn. Stellungnahmen zu Kernenergiefragen, GRS-S-53. Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Köln

28. Thielen H (2012) The Fukushima Daiichi nuclear accident - an overview. Health Phys 103:169–174. https://doi.org/10.1097/HP.0b013e31825b57ec

29. Hamada N, Ogino H (2012) Food safety regulations: what we learned from the Fukushima nuclear accident. J Environ Radioact 111:83–99. https://doi.org/10.1016/j.jenvrad.2011.08.008

30. IAEA (2015) The Fukushima Daiichi accident. International Atomic Energy Agency, Vienna

31. Mathieu A, Korsakissok I, Quelo D et al. (2012) Atmospheric Dispersion and Deposition of Radionuclides from the Fukushima Daiichi Nuclear Power Plant Accident. Elements 8:195–200. https://doi.org/10.2113/gselements.8.3.195

32. IAEA International Peer Review of Japan's Mid-and-Long-Term Roadmap Towards the Decommissioning of TEPCO's Fukushima Daiichi Nuclear Power Station. https://www.iaea.org/newscenter/pressreleases/iaea-team-completes-fourth-review-of-japans-plans-to-decommission-fukushima-daiichi. Accessed December 2018

33. Kinoshita N, Sueki K, Sasa K et al. (2011) Assessment of individual radionuclide distributions from the Fukushima nuclear accident covering central-east Japan. Proc Natl Acad Sci U S A 108:19526–19529. https://doi.org/10.1073/pnas.1111724108

34. Yoshida N, Kanda J (2012) Geochemistry. Tracking the Fukushima radionuclides. Science 336:1115–1116. https://doi.org/10.1126/science.1219493

35. Povinec PP, Aoyama M, Biddulph D et al. (2013) Cesium, iodine and tritium in NW Pacific waters - a comparison of the Fukushima impact with global fallout. Biogeosciences 10:5481–5496. https://doi.org/10.5194/bg-10-5481-2013

36. Hirose K (2012) 2011 Fukushima Dai-ichi nuclear power plant accident: summary of regional radioactive deposition monitoring results. J Environ Radioact 111:13–17. https://doi.org/10.1016/j.jenvrad.2011.09.003

37. Fukushima Prefectural Government (2021) Transition of evacuation designated zones. https://www.pref.fukushima.lg.jp/site/portal-english/en03-08.html. Accessed 26 Jan 2021

38. Hayano RS, Adachi R (2013) Estimation of the total population moving into and out of the 20 km evacuation zone during the Fukushima NPP accident as calculated using "Auto-GPS" mobile phone data. Proc Jpn Acad Ser B Phys Biol Sci 89:196–199. https://doi.org/10.2183/pjab.89.196

39. Hasegawa A, Ohira T, Maeda M et al. (2016) Emergency Responses and Health Consequences after the Fukushima Accident; Evacuation and Relocation. Clin Oncol (R Coll Radiol) 28:237–244. https://doi.org/10.1016/j.clon.2016.01.002

40. Hasegawa J, Hidaka H, Kuriyama S et al. (2015) Change in and long-term investigation of neurootologic disorders in disaster-stricken Fukushima prefecture: retrospective cohort

study before and after the Great East Japan Earthquake. PLoS ONE 10:e0122631. https://doi.org/10.1371/journal.pone.0122631

41. Morita T, Ando M, Ohtsu Y (2019) Mass evacuation and increases in long-term care benefits: Lessons from the Fukushima nuclear disaster. PLoS ONE 14:e0218835. https://doi.org/10.1371/journal.pone.0218835

42. Murakami M, Takebayashi Y, Ono K et al. (2020) The decision to return home and wellbeing after the Fukushima disaster. International Journal of Disaster Risk Reduction 47:101538. https://doi.org/10.1016/j.ijdrr.2020.101538

43. Buesseler KO (2020) Opening the floodgates at Fukushima. Science 369:621–622. https://doi.org/10.1126/science.abc1507

44. Shozugawa K, Hori M, Johnson TE et al. (2020) Landside tritium leakage over through years from Fukushima Dai-ichi nuclear plant and relationship between countermeasures and contaminated water. Sci Rep 10:19925. https://doi.org/10.1038/s41598-020-76964-9

45. Yamanishi T, Kakiuchi H, Tauchi H et al. (2020) Discussions on Tritiated Water Treatment for Fukushima Daiichi Nuclear Power Station. Fusion Science and Technology 76:430–438. https://doi.org/10.1080/15361055.2020.1716454

46. Triplett M (2015) Cesium Removal and storage - Update on Fukushima Daiichi Status. https://www.hanford.gov/files.cfm/Attachment_6_Cs_Presentation_PNNL.pdf. Accessed 10 Feb 2021

47. Eckerman K, Harrison J, Menzel H-G (2012) Compendium of dose coefficients based on ICRP Publication 60. ICRP publication, vol 119. Elsevier, Oxford, UK

48. TEPCO Electric Power Company Holding, Inc. (2020) TEPCO Draft Study Responding to the Subcommittee Report on Handling ALPS Treated Water. https://www.tepco.co.jp/en/decommission/progress/watertreatment/images/200324.pdf. Accessed 27 Jan 2021

49. Treated Water Portal Site | Tokyo Electric Power Company Holdings, Incorporated (2021) Treated Water Portal Site | Tokyo Electric Power Company Holdings, Incorporated. https://www4.tepco.co.jp/en/decommission/progress/watertreatment/index-e.html. Accessed 27 Jan 2021

50. BBC (2020) Fukushima: Japan 'to release contaminated water into sea'. BBC News

51. Binnewies M, Finze M, Jäckel M et al. (2016) Allgemeine und Anorganische Chemie, 3., vollständig überarbeitete Auflage. Springer Spektrum, Berlin

52. Lehto J, Hou X (2011) Chemistry and analysis of radionuclides: Laboratory techniques and methodology. Wiley-VCH-Verl., Weinheim

53. Merz S, Steinhauser G, Hamada N (2013) Anthropogenic radionuclides in Japanese food: Environmental and legal implications. Environ Sci Technol 47:1248–1256. https://doi.org/10.1021/es3037498

54. Friese JI, Kephart RF, Lucas DD (2013) Comparison of radionuclide ratios in atmospheric nuclear explosions and nuclear releases from Chernobyl and Fukushima seen in gamma ray spectrometry. J Radioanal Nucl Chem 296:899–903. https://doi.org/10.1007/s10967-012-2213-0

55. Komori M, Shozugawa K, Nogawa N et al. (2013) Evaluation of Radioactive Contamination Caused by Each Plant of Fukushima Daiichi Nuclear Power Station Using ^{134}Cs/^{137}Cs Activity Ratio as an Index. Bunseki Kagaku 62:475–483. https://doi.org/10.2116/bunsekikagaku.62.475

56. Yasunari TJ, Stohl A, Hayano RS et al. (2011) Cesium-137 deposition and contamination of Japanese soils due to the Fukushima nuclear accident. Proc Natl Acad Sci U S A 108:19530–19534. https://doi.org/10.1073/pnas.1112058108

57. Mansel A, Gruhne S, Franke K et al. (2014) Production of ^{85}Sr at a 18MeV-cyclotron and purification for geochemical investigations. Appl Radiat Isot 92:22–24. https://doi.org/10.1016/j.apradiso.2014.06.001

58. Steinhauser G (2014) Fukushima's forgotten radionuclides: A review of the understudied radioactive emissions. Environ Sci Technol 48:4649–4663. https://doi.org/10.1021/es405654c

59. Shagina NB, Tolstykh EI, Degteva MO et al. (2015) Age and gender specific biokinetic model for strontium in humans. J Radiol Prot 35:87–127. https://doi.org/10.1088/0952-4746/35/1/87

60. Lederer CM, Shirley VS, Browne E (1978) Table of isotopes, 7. ed. Wiley, New York

61. Povinec PP, Liong Wee Kwong L, Kaizer J et al. (2017) Impact of the Fukushima accident on tritium, radiocarbon and radiocesium levels in seawater of the western North Pacific Ocean: A comparison with pre-Fukushima situation. J Environ Radioact 166:56–66. https://doi.org/10.1016/j.jenvrad.2016.02.027

62. Steinhauser G, Schauer V, Shozugawa K (2013) Concentration of Strontium-90 at Selected Hot Spots in Japan. PLoS ONE 8:e57760. https://doi.org/10.1371/journal.pone.0057760

63. Casacuberta N, Masqué P, Garcia-Orellana J et al. (2013) ^{90}Sr and ^{89}Sr in seawater off Japan as a consequence of the Fukushima Dai-ichi nuclear accident. Biogeosciences 10:3649–3659. https://doi.org/10.5194/bg-10-3649-2013

64. Weaver CL, Harward ED, Peterson HT (1969) Tritium in the environment from nuclear powerplants. Public Health Rep 84:363–371

65. Matsumoto T, Maruoka T, Shimoda G et al. (2013) Tritium in Japanese precipitation following the March 2011 Fukushima Daiichi Nuclear Plant accident. Sci Total Environ 445-446:365–370. https://doi.org/10.1016/j.scitotenv.2012.12.069

66. Kashiwaya K, Muto Y, Kubo T et al. (2017) Spatial variations of tritium concentrations in groundwater collected in the southern coastal region of Fukushima, Japan, after the nuclear accident. Sci Rep 7:12578. https://doi.org/10.1038/s41598-017-12840-3

67. Hou X, Povinec PP, Zhang L et al. (2013) Iodine-129 in seawater offshore Fukushima: Distribution, inorganic speciation, sources, and budget. Environ Sci Technol 47:3091–3098. https://doi.org/10.1021/es304460k

68. Miyake Y, Matsuzaki H, Fujiwara T et al. (2012) Isotopic ratio of radioactive iodine (^{129}I/^{131}I) released from Fukushima Daiichi NPP accident. Geochem J 46:327–333. https://doi.org/10.2343/geochemj.2.0210

69. Xu S, Freeman SPHT, Hou X et al. (2013) Iodine isotopes in precipitation: Temporal responses to ^{129}I emissions from the fukushima nuclear accident. Environ Sci Technol 47:10851–10859. https://doi.org/10.1021/es401527q

70. Michel R, Handl J, Ernst T et al. (2005) Iodine-129 in soils from Northern Ukraine and the retrospective dosimetry of the iodine-131 exposure after the Chernobyl accident. Sci Total Environ 340:35–55. https://doi.org/10.1016/j.scitotenv.2004.08.006

71. Xu S, Zhang L, Freeman SPHT et al. (2015) Speciation of radiocesium and radioiodine in aerosols from Tsukuba after the Fukushima nuclear accident. Environ Sci Technol 49:1017–1024. https://doi.org/10.1021/es504431w

72. Mironov V, Kudrjashov V, Yiou F et al. (2002) Use of ^{129}I and ^{137}Cs in soils for the estimation of ^{131}I deposition in Belarus as a result of the Chernobyl accident. J Environ Radioact 59:293–307. https://doi.org/10.1016/S0265-931X(01)00080-7

73. Weller A, Querfeld R, Köhler F et al. (2019) Aspects of quality assurance and performance of strontium-selective resins under non-routine conditions: old resins, delayed elution. Journal of Radioanalytical and Nuclear Chemistry, Articles 320:467–474. https://doi.org/10.1007/s10967-019-06484-y

74. Alvarez A, Navarro N, Salvador S (1995) New method for ^{90}Sr determination in liquid samples. Journal of Radioanalytical and Nuclear Chemistry, Articles 191:315–322. https://doi.org/10.1007/BF02038227

75. Horwitz EP, Dietz ML, Chiarizia R (1992) The application of novel extraction chromatographic materials to the characterization of radioactive waste solutions. J Radioanal Nucl Chem 161:575–583. https://doi.org/10.1007/BF02040504

76. Binnewies M (2011) Allgemeine und Anorganische Chemie, 2. Aufl. Spektrum Akademischer Verlag, Heidelberg, Neckar

77. Verhagen, B. Th., Sellschop, J. P. F. (1965) Enrichment of Low-Level Tritium by Thermal Diffusion for Hydrological Applications. Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1964:398–405

78. Jacobs DG (1968) Sources of tritium and its behavior upon release to the environment

79. Zel'venskii, Y. D., Nikolaev, D. A., Tatarinski, V. S., Sbalygin, V. A. (1965) Concentration of Water Samples for the Determination of the Tritium Content. SovietAtomic Energy 18:466–472

80. L'Annunziata MF (ed) (2012) Handbook of radioactivity analysis, 3. ed. Elsevier, Amsterdam

81. Janković MM, Todorović DJ, Todorović NA et al. (2012) Natural radionuclides in drinking waters in Serbia. Appl Radiat Isot 70:2703–2710. https://doi.org/10.1016/j.apradiso.2012.08.013

82. Groning M, Auer R, Brummer D et al. (2009) Increasing the performance of tritium analysis by electrolytic enrichment. Isotopes Environ Health Stud 45:118–125. https://doi.org/10.1080/10256010902872042

83. Baresic, J., Krajcar Bronic, I., Horvatincic, N., Obelic, B., Sironic, A., Kozar-Logar, J. (2011) Tritium Activity Measurement of Water Samples Using Liquid Scintillation Counter and Electrolytical Enrichment. Proceedings of the 8th Symposium of Croatian Radiation Protection Association:461–467

84. Morgenstern U, Taylor CB (2009) Ultra low-level tritium measurement using electrolytic enrichment and LSC. Isotopes Environ Health Stud 45:96–117. https://doi.org/10.1080/10256010902931194

85. Jander G, Blasius E (1995) Einführung in das anorganisch-chemische Praktikum: (einschliesslich der quantitativen Analyse) ; mit 61 Tabellen, 14., neu bearb. Aufl. Hirzel, Stuttgart, Leipzig

86. Hou X, Hansen V, Aldahan A et al. (2009) A review on speciation of iodine-129 in the environmental and biological samples. Anal Chim Acta 632:181–196. https://doi.org/10.1016/j.aca.2008.11.013

87. Walther C, Wendt K (2020) Radioisotope mass spectrometry. In: L'Annunziata MF (ed) Handbook of radioactivity analysis, Fourth edition. Academic Press, London, United Kingdom, pp 861–898

6 Publications and own contributions

6.1 Publication 1:

Antropogenic radionuclides in water samples from the Chernobyl exclusion zone

R. Querfeld, W. Schulz, J. Neubohn, G. Steinhauser

Journal of Radioanalytical and Nuclear Chemistry **318**, 423-428 (2018)

https://doi.org/10.1007/s10967-018-6030-y

Authors contributions:

R.Q. and G.S. designed research

W.S. and G.S. performed sampling

R.Q. and J.N. performed research

R.Q. and G.S. wrote manuscript

6.2 Publication 2:

Radionuclides in surface waters around the damaged Fukushima Daiichi NPP one month after the accident: Evidence of significant tritium release into the environment

R. Querfeld, A.-E. Pasi, K. Shozugawa, C. Vockenhuber, H.-A. Synal, P. Steier, G. Steinhauser

Sci Total Environ **689**, 451-456 (2019)

https://doi.org/10.1016/j.scitotenv.2019.06.362

Authors contributions:

R.Q. and A.-E.P. contributed equally to the study

R.Q., A.-E.P. and G.S. designed research

K.S. performed sampling

R.Q., A.-E.P., C.V., H.-A.S. and P.S. performed research

R.Q. and G.S. wrote manuscript

6.3 Publication 3:

Radioactive Games? Radiation Hazard Assessment of the Tokyo Olympic Summer Games

R. Querfeld, M. Hori, A. Weller, D. Degering, K. Shozugawa, G. Steinhauser

Environmental Science and Technology **54 (18)**, 11414-11423 (2020)
https://doi.org/10.1021/acs.est.0c02754

Authors contributions:

R.Q. and G.S. designed research

M.H., K.S. and G.S. performed sampling and air dose measurements

R.Q., A.W., and D.D., performed research

R.Q. and G.S. wrote manuscript

7 Curriculum vitae

Persönliche Daten:

Name	Rebecca Querfeld (geb. Roberg)
Geboren	am 12. Juli 1990 in Hildesheim

Ausbildung:

02.2017-05.2021	Promotion am Institut für Radioökologie und Strahlenschutz, Arbeitskreis Steinhauser (LUH), zu dem Thema „Radioanalytische und chemisch analytische Untersuchungen von Wasserproben aus der Umgebung der Kernkraftwerke Tschernobyl und Fukushima Daiichi“
10.2014 - 12.2016	Studiengang: M. Sc. Analytik (LUH)
	Masterarbeit zu dem Thema „Herstellung und Charakterisierung eines ^{7}Be-Tracers aus Regenwasser“
10.2010 - 09.2014	Studiengang: B. Sc. Chemie (LUH)
	Bachelorarbeit zu dem Thema „Präparation und Charakterisierung von silberhaltigen Polymerschichten“
06.2010	Allgemeine Hochschulreife, Gymnasium Sarstedt

Berufliche Erfahrung:

Seit 06.2020	Wissenschaftliche Referentin bei der Bundesgesellschaft für Endlagerung mbH, Abteilung Technik Endlagersicherheit: Sicherheitstechnische Planung und Begleitung des Betriebes und der Rückholungsphase für die Schachtanlage Asse II, Ermittlung und Bewertung der Strahlenexposition für die Bevölkerung in der Umgebung eines Endlagers, Planung von Charakterisierungsmessungen für die Rückholung
02.2017 - 04.2020	Wissenschaftliche Mitarbeiterin am Institut für Radioökologie und Strahlenschutz: Betreuung von Studierenden- und Strahlenschutzpraktika, Wartung und Kontrolle verschiedener Messsysteme: ICP-OES: Thermo Scientific iCAP 6200 duo, ICP-QQQ-MS: Agilent 8900, LSC: Hidex 300 SL; Organisation und Durchführung verschiedener Veranstaltungen: NEXT-Konferenz, Fachverband Strahlenschutz Jahrestagung 2017, LSC Anwendertreffen 2018
03.2015 - 04.2015 & 05.2014 - 09.2014	HiWi am Institut für Anorganische Chemie, Arbeitskreis Vogt (LUH): Praktikumsbetreuung, Untersuchung der Freisetzung von Wolfram durch die Verwendung von „Wolframspritzen“

Wissenschaftliche Publikationen:

D. Zok, T. Blenke, S. Reinhard, S. Sprott, F. Kegler, L. Syrbe, R. Querfeld, Y. Takagai, V. Drozdov, I. Chyzhevskyi, S. Kirieiev, B. Schmidt, W. Adlassnig, G. Wallner, S. Dubchak, G. Steinhauser (2021): Determination of Characteristic vs. Anomalous ^{135}Cs/^{137}Cs Isotopic Ratios in Radioactively Contaminated Environmental Samples, *Environmental Science and Technology,* Volume 55, Issue 8, pp. 4984-4991, https://doi.org/10.1021/acs.est.1c00180

R. Querfeld, M. Hori, A. Weller, D. Degering, K. Shozugawa, G. Steinhauser (2020): Radioactive Games? Radiation Hazard Assessment of the Tokyo Olympic Summer Games. *Environmental Science and Technology*, Volume 54, Issue 18, pp. 11414-11423, https://doi.org/10.1021/acs.est.0c02754

R. Querfeld, A.-E. Pasi, K. Shozugawa, C. Vockenhuber, H.-A. Synal, P. Steier, G. Steinhauser (2019): Radionuclides in surface waters around the damaged Fukushima Daiichi NPP one month after the accident: Evidence of significant tritium release into the environment, *Science of The Total Environment,* Volume 689, pp 451-456, https://doi.org/10.1016/j.scitotenv.2019.06.362

O. Masson, G. Steinhauser, D. Zok, O. Saunier, H. Angelov, D. Babić, V. Bečková, J. Bieringer, M. Bruggeman, C.I. Burbidge, S. Conil, A. Dalheimer, L.-E. De Geer, A. de Vismes Ott, K. Eleftheriadis, S. Estier, H. Fischer, M.G. Garavaglia, C. Gasco Leonarte, K. Gorzkiewicz, D. Hainz, I. Hoffman, M. Hýža, K. Isajenko, T. Karhunen, J. Kastlander, C. Katzlberger, R. Kierepko, G.-J. Knetsch, J. Kövendiné Kónyi, M. Lecomte, J.W. Mietelski, P. Min, B. Møller, S.P. Nielsen, J. Nikolic, L. Nikolovska, I. Penev, B. Petrinec, P.P. Povinec, R. Querfeld, O. Raimondi, D. Ransby, W. Ringer, O. Romanenko, R. Rusconi, P.R.J. Saey, V. Samsonov, B. Šilobritienė, E. Simion, C. Söderström, M. Šoštarić, T. Steinkopff, P. Steinmann, I. Sýkora, L. Tabachnyi, D. Todorovic, E. Tomankiewicz, J. Tschiersch, R. Tsibranski, M. Tzortzis, K. Ungar, A. Vidic, A. Weller, H. Wershofen, P. Zagyvai, T. Zalewska, D. Zapata García, and B. Zorko (2019): Airborne concentrations and chemical considerations of radioactive ruthenium from an undeclared major nuclear release in 2017, *Proceedings of the National Academy of Sciences*, Volume 116, Issue 34, pp 16750-16759, https://doi.org/10.1073/pnas.1907571116

A. Weller, R. Querfeld, F. Köhler, G. Steinhauser (2019): Aspects of quality assurance and performance of strontium-selective resins under non-routine conditions: old resins, delayed elution. *Journal of Radioanalytical and Nuclear Chemistry*, Volume 320, pp 467–474, https://doi.org/10.1007/s10967-019-06484-y

C. Tiessen, D. Bemmerer, G. Rugel, R. Querfeld, A. Scharf, G. Steinhauser, S. Merchel (2019): Accelerator mass spectrometry (AMS) for beryllium-7 measurements in smallest rainwater samples. *Journal of Radioanalytical and Nuclear Chemistry*, Volume 319, pp 965-973, https://doi.org/10.1007/s10967-018-6371-6

R. Querfeld, W. Schulz, J. Neubohn, G. Steinhauser (2018): Antropogenic radionuclides in water samples from the Chernobyl exclusion zone, *Journal of Radioanalytical and Nuclear Chemistry,* Volume 318, Issue 1, pp 423-428, https://doi.org/10.1007/s10967-018-6030-y

R. Querfeld, S. Merchel, G. Steinhauser (2017): Low-cost production of a ^{7}Be tracer from rainwater and purification: preliminary results, *Journal of Radioanalytical and Nuclear Chemistry*, Volume 314, Issue 1, pp 521–527, https://doi.org/10.1007/s10967-017-5433-5

R. Querfeld, M.R. Tanha, L. Heyer, F. Renz, G. Guggenberger, F. Brandstätter, L. Ferrière, C. Koeberl, G. Steinhauser (2017): On the occurrence and origin of anthropogenic radionuclides found in a fragment of the Chelyabinsk (LL5) meteorite, *Meteoritics and Planetary Science*, Volume 52, Issue 6, pp 1244-1250, https://doi.org/10.1111/maps.12855

Konferenzbeiträge:

R. Querfeld, D. Zok, L. Grüger, G. Steinhauser (2019): Determination of ^{135}Cs/^{137}Cs-ratios via ICP-QQQ-MS: Tests with ^{137}Cs and sample pretreatment. *Jahrestagung Nuklearchemie*, GDCh, Dresden, Deutschland, 25.-27. September 2019

R. Querfeld, K. Shozugawa, M. Hori, D. Degering, G. Steinhauser (2019): Assessment of radiation hazards for athletes or visitors of the Tokyo 2020 Olympic Games. *2nd International Conference on Radioanalytical and Nuclear Chemistry, (JRNC-RANC),* Budapest, Ungarn, 5.-10. Mai 2019

R. Querfeld, L. Grüger, D. Zok, G. Steinhauser (2019): ^{135}Cs/^{137}Cs- Verhältnisse bestimmen via ICP-QQQ-MS: Vorversuche mit ^{137}Cs. *SAAGAS 27*, München, Deutschland, 24.-27. Februar 2019

R. Querfeld, K. Shozugawa, M. Hori, G. Steinhauser (2019): Radioanalytical investigations of surface water samples from Fukushima. *SAAGAS 27*, München, Deutschland, 24.-27. Februar 2019

R. Querfeld, A.-E. Pasi, G. Steinhauser (2018): Determination of tritium and strontium-90 in water samples from Fukushima. *LSC Anwendertreffen*, Hannover, Deutschland, 11.-12. September 2018

R. Querfeld, K. Shozugawa, M. Hori, D. Degering, G. Steinhauser (2018): Radioanalytical Investigations of Water Samples from Fukushima. *Methods and Applications of Radioanalytical Chemistry, (MARC XI)*, Kona, USA, 8.-13. April 2018

R. Querfeld, G. Steinhauser (2017): Herstellung und Charakterisierung eines Beryllium-7 Tracers aus Regenwasser, *SAAGAS 26*, Wien, Österreich, 20.-22. Februar 2017

8 Danksagung

Mein besonderer Dank gilt meinem Doktorvater, Georg Steinhauser, der mich bei all den verschiedenen Studien dieser Promotion unterstützt und angeleitet hat. Außerdem möchte ich mich bei ihm und Clemens Walther für die Möglichkeit bedanken, die Promotion am IRS durchzuführen und meine Ergebnisse auf mehreren Konferenzen zu präsentieren. Frau Carla Vogt möchte ich für die Übernahme des zweiten Korreferats und meiner Zeit in ihrem Arbeitskreis während meiner Bachelor und Master Zeit danken.

Furthermore, I would like to thank Katsumi Shozugawa and Mayumi Hori for their time and great commitment in collecting countless water samples from Fukushima and all over Japan and, of course, for all air dose rate measurements.

Mein Dank geht ebenfalls an die Kollegen der ETH Zürich, der TU Wien und dem VKTA, Christof Vockenhuber, Hans-Arno Synal, Peter Steier sowie Detlev Degering, ohne deren Messungen meine Arbeit unvollständig gewesen wäre.

Einer Person kann ich gar nicht genug danken, denn ohne ihre von Zeit zu Zeit aufmunternden Worte, wäre ich wohl heute nicht da, wo ich bin. Liebe Anica Weller ich danke dir für die gemeinsame Zeit, die wir bereits seit dem Bachelorstudium miteinander verbracht haben, für die gute Freundschaft die sich in dieser Zeit entwickelt hat und sich in einer mehrjährigen Büropartnerschaft nur intensiviert hat. Du warst immer meine liebste Mitbewohnerin auf allen gemeinsamen Dienstreisen und Gedanken an das romantische Dinner in Bremerhaven werden mich immer zum Lächeln bringen!

Besonderer Dank geht ebenfalls an Fabian Köhler und Martin Weiß, mit denen ich besonders während der Promotion viel Zeit verbracht habe und die mir ebenfalls kontinuierlich mit Rat und Tat durch die Höhen und Tiefen dieser Arbeit halfen.

Der Therapiezimmer-Gemeinschaft bestehend aus Annika Wunnenberg, Sandra Reinhard und Anica bin ebenfalls für all die Gespräche, die wir im Laufe der Zeit geführt haben, zu Dank verpflichtet und den außer-universitären Unternehmungen, die wir in der Zeit unternommen haben, ich hoffe, dass wir auch zukünftig die Zeit finden werden!

Mein besonderer Dank geht an Stefan Bister, der mir während der Laborarbeit immer mit Rat und Tat zur Seite stand und mir viele praktische Tipps zum Strahlenschutz beibrachte. Er hatte stets eine helfende Hand, sei es für die Planung und Optimierung neuer Versuchsansätze oder beim Besorgen von verschiedenen Labormaterialien. Die gemeinsamen Stunden im Labor während der Praktika und den Laborputzen werden mir stets ein Lächeln ins Gesicht zaubern.

Des Weiteren gilt mein Dank Hilal Alemdar-Aydin, Gabriele Erb-Bunnenberg, Sebastian Büchner, Rüdiger Sachse, Karl-Heinz Iwannek, Michael Täschner und Ralf Groffmann, die in Labor-, Technik- und IT-Fragen seit Beginn meines Forschungspraktikums stets hilfreich waren und jedes benötigte Gerät wieder zum Laufen bekommen haben. Natürlich möchte ich Beate Riebe und Monika Gorny an dieser Stelle nicht vergessen, vielen Dank für all die Gespräche und Unterstützungen!

Ich bedanke mich bei Frank Koepke, Nurije Elezi, Younes und Michael Senft, die in der Werkstatt immer hilfsbereit waren und den legendären Bratwurst-Freitag organisiert haben. Ich werde den gut gefüllten Gefrierschrank der Werkstatt vermissen.

Als hohe erste Vorsitzende der Liquidatoren bleibt es mit unabdingbar, mich bei Peter Brozynski und Wolfgang Schulz für die zahlreichen Trainingseinheiten mit unseren Liquidatoren zu bedanken. Ich hoffe ihr findet eine würdige Vertretung, die bereit ist, ebenfalls so viele Spenden für das Team einzutreiben und euch mit Fan-Gesängen anzutreiben.

Es gibt noch so viele weitere Menschen am IRS, denen ich danken möchte, zum einen der Bürogemeinschaft mit Manuel Raiwa, Kevin Stiewe und Tobias Kampmeier, ich denke, wir hatten viele lustige Stunden zusammen. Zum anderen der (un)regelmäßigen Kaffeerunde bestehend aus Hauke Bosco, Claudia Furnier, Paul Hanemann, Mohammad Tanha, Erik Pönitz, Nanne Schumann, Daniel Heine, Vivien und Simon Pottgießer, Marcus Mandel und [please insert your name here] es tut mir leid, dass ich mir zuletzt zu wenig Zeit für euch genommen habe, auch wir hatten zahlreiche lustige Momente, sowie Ideen und Konzepte, die wir unbedingt weiterführen sollten. Außerdem allen anderen, die ich an dieser Stelle vergessen haben sollte, namentlich zu erwähnen … Mit vielen von Euch habe ich sowohl den Kaffee als auch all die anderen tollen regelmäßigen Momente wie den Burger-Dienstag, den Pasta-Mittwoch und die gelegentlichen Dönerstage gerne verbracht, diese Zeiten werde ich vermissen. Besonders die Trash-Filmabende oder Spielerunden mit dem einen oder anderen Feierabendbierchen sollten fortgeführt werden.

Auch dem restlichen Arbeitskreis von #gutaussehend gilt mein Dank, besonders Dorian Zok und Tobias Blenke. Die vielen Stunden im Labor waren äußerst amüsierend.

Natürlich möchte ich auch Julia Stadler und Felix Stäger nicht vergessen, euch bin ich dankbar, dass ihr sowohl unser Büro als auch die Pflege von Karlo übernommen habt, den schmusigsten Kater der Welt, der es versteht, mit seinem Schnurren alle Wunden wieder zu heilen.

Bedanken möchte ich mich auch bei einigen Studenten, die teils erheblich zu meiner Arbeit beigetragen haben. Anna-Elina Pasi, Lena Grüger und Luisa Syrbe auch ihr seid Teil dieser Arbeit und ich habe immer gerne mit euch zusammengearbeitet.

Meinen Begleitern während des Studiums Lailah Helmich, Sina Baruth, Vanessa Harms und Julia Schubert gilt ebenfalls mein Dank, ich hoffe, wir führen die vielen Stammtisch-Runden fort.

Ein tausendfacher Dank geht an meine Familie, meinen Ehemann und meine Freunde, die mich und meine Arbeit seit dem Beginn meines Bachelorstudiums im Jahr 2010 immer unterstützt haben.

Zusammenfassend kann ich nur betonen:

IRS das geilste Institut der Welt, deeer Welt, deeeeeeer Weeeeeeeeeeeeeelt!

9 Eigenständigkeitserklärung

Hiermit erkläre ich,

1. - die geltenden Regeln der gemeinsamen Ordnung für die Promotion Doktor der Naturwissenschaften (Dr. rer. nat.) an der Gottfried Wilhelm Leibniz Universität Hannover zu kennen und eingehalten zu haben, sowie mit einer Prüfung nach den Bestimmungen der Promotionsordnung einverstanden zu sein.

2. - dass die vorliegende Dissertation von mir selbstständig verfasst wurde, wobei keine Textabschnitte von Dritten oder eigene Prüfungsarbeiten ohne Kennzeichnung übernommen wurden. Alle benutzten Hilfsmittel und Quellen wurden in der Arbeit angegeben.

3. - Dritten, weder unmittelbar noch mittelbar, geldwerte Leistungen für Vermittlungstätigkeiten oder die inhaltliche Ausarbeitung der Dissertation erbracht zu haben.

4. - die Dissertation noch nicht als Prüfungsarbeit für eine andere Prüfung eingereicht zu haben.

5. - weder die Gleiche, noch eine in wesentlichen Teilen ähnliche, noch eine andere Abhandlung dieser Arbeit bei einer anderen Fakultät oder bei einer anderen Hochschule als Dissertation eingereicht zu haben.

6. - dass ich damit einverstanden bin, dass die Dissertation einer Überprüfung der Einhaltung allgemein geltender wissenschaftlicher Standards unterzogen wird.