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possible age determination of modern wood samples“

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2 Abstract

The accuracy of radiocarbon (^{14}C) dating for modern wood samples, particularly those from the mid-20th century onward, has been compromised due to anthropogenic fossil fuel emissions, which have altered the natural levels of ^{14}C in the atmosphere. As a result, there is a growing need for supplementary methods to improve the precision of age determination for these samples.

The suitability of ^{90}Sr and ^{129}I as supplementary methods for the age determination of wood samples, particularly in the context of modern dendrochronological analyses, is investigated. Building on established radiocarbon dating techniques, these radionuclides are considered as potential indicators for differentiating between materials from before and after the era of nuclear weapons testing. The main objective of the work was to analyze the migration of ^{90}Sr and ^{129}I in tree rings and evaluate the applicability of these isotopes as dating methods.

Techniques such as Accelerator Mass Spectrometry (AMS) and Ion-Laser Interaction Mass Spectrometry (ILIAMS) were used for the measurements, both conducted at the Vienna Environmental Research Accelerator (VERA). These high-precision methods enable the detection of trace amounts of radionuclides in the samples. AMS was used to measure ^{129}I and ^{14}C , while ILIAMS was employed for measuring ^{90}Sr . The chemical sample preparation also played a crucial role in isolating the analytes for measurement and minimizing unwanted interferences.

Contrary to initial assumptions that ^{90}Sr remains fixed in the heartwood after deposition, it migrates within the xylem of the trees. This migration complicates the use of ^{90}Sr as a reliable marker for dendrochronological studies, as significant amounts of ^{90}Sr were detected in tree rings formed long before the nuclear era. This suggests decades-long movement of the isotope.

Similarly, ^{129}I , while exhibiting lower mobility, also shows fluctuations in concentrations. This indicates uneven uptake and storage of the isotope, influenced by varying environmental factors. Additionally, problems were encountered when measuring ^{129}I in the wood matrix, as the applied chemical method presented challenges. These difficulties hindered the precise determination of ^{129}I and resulted in inconsistent findings.

While the isotopes ^{90}Sr and ^{129}I may have potential for age determination of samples formed before the nuclear testing era, they are not recommended for samples from or near the nuclear testing period. The migration of these isotopes, the variability of their concentrations in different trees, and the difficulties in the preparation chemistry of ^{129}I for AMS measurement, highlight the challenges of using these radionuclides for precise age determination of wood samples.

3 Zusammenfassung

Die Genauigkeit der Radiokarbondatierung (^{14}C) für moderne Holzproben, insbesondere solche aus der Mitte des 20. Jahrhunderts, wurde durch anthropogene fossile Brennstoffemissionen beeinträchtigt, die die natürlichen ^{14}C -Werte in der Atmosphäre verändert haben. Daher besteht ein zunehmender Bedarf an ergänzenden Methoden, um die Präzision der Altersbestimmung dieser Proben zu verbessern.

Die Eignung von ^{90}Sr und ^{129}I als ergänzende Methoden zur Altersbestimmung von Holzproben, insbesondere im Zusammenhang mit modernen dendrochronologischen Analysen, wird untersucht. Aufbauend auf etablierten Radiokohlenstoffdatierungstechniken (^{14}C) werden diese Radionuklide als potenzielle Indikatoren zur Unterscheidung von Materialien vor und nach der Ära der Kernwaffentests betrachtet. Hauptziel der Arbeit war es, die Migration von ^{90}Sr und ^{129}I in Baumringen zu analysieren und die Anwendbarkeit dieser Isotope als Datierungsmethoden zu bewerten.

Techniken wie die Beschleuniger-Massenspektrometrie (AMS) und die Ionen-Laser-Interaktions-Massenspektrometrie (ILIAMS) wurden für die Messungen verwendet, die beide am Vienna Environmental Research Accelerator (VERA) durchgeführt wurden. Diese hoch- präzisen Methoden ermöglichen den Nachweis von Spuren Mengen von Radionukliden in den Proben. AMS wurde zur Messung von ^{129}I und ^{14}C verwendet, während ILIAMS zur Messung von ^{90}Sr eingesetzt wurde. Auch die chemische Probenvorbereitung spielte eine entscheidende Rolle bei der Isolierung der Analyten zur Messung und der Minimierung unerwünschter Störungen.

Entgegen der anfänglichen Annahme, dass ^{90}Sr nach der Ablagerung im Kernholz fixiert bleibt, migriert es innerhalb des Xylems der Bäume. Diese Migration erschwert die Verwendung von ^{90}Sr als verlässlichen Marker für dendrochronologische Studien, da erhebliche Mengen von ^{90}Sr in Baumringen nachgewiesen wurden, die lange vor der nuklearen Ära gebildet wurden. Dies deutet auf eine jahrzehntelange Bewegung des Isotops hin.

Ebenso zeigt ^{129}I , obwohl es eine geringere Mobilität aufweist, Schwankungen in den Konzentrationen. Dies weist auf eine ungleichmäßige Aufnahme und Speicherung des Isotops hin, die durch unterschiedliche Umweltfaktoren beeinflusst wird. Zusätzlich traten bei der Messung von ^{129}I in der Holzmatrix Probleme auf, da die angewandte chemische Methode Herausforderungen darstellte. Diese Schwierigkeiten behinderten die präzise Bestimmung von ^{129}I und führten zu inkonsistenten Ergebnissen.

Obwohl ^{90}Sr und ^{129}I Potenzial für die Altersbestimmung von Proben haben, die vor der Ära der Kernwaffentests entstanden sind, werden sie nicht für Proben aus oder nahe der Kernwaffen-Testperiode empfohlen. Die Migration dieser Isotope, die Variabilität ihrer Konzentrationen in verschiedenen Bäumen und die Schwierigkeiten bei der Vorbereitung der Chemie von ^{129}I für AMS verdeutlichen die Herausforderungen bei der Verwendung

3 Zusammenfassung

dieser Radionuklide zur präzisen Altersbestimmung von Holzproben.

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4 Introduction

"Carbon is a remarkable element: together with hydrogen, it is a component of all organic compounds and is fundamental to life."

(Sheridan Bowman, 1990, p.9, [1])

Radiocarbon (^{14}C) is continuously produced in the upper atmosphere by neutrons from cosmic rays interacting with nitrogen atoms. These radiocarbon atoms then bind to oxygen atoms, forming CO_2 , which circulates through the biosphere and becomes incorporated into living organisms. When an organism dies, it stops the uptake of carbon, and the radiocarbon it accumulated also decays with a half-life of 5730 years. Very old materials, such as fossil fuels, no longer contain radiocarbon because it has all decayed since their time of death.

When dating material with the radiocarbon method, the $^{14}\text{C}/^{12}\text{C}$ ratio in a sample is usually measured with conventional Accelerator Mass Spectrometry (AMS) and the age of a sample is determined through its proportion of present modern carbon. A diverse range of scientific fields rely on radiocarbon analysis, such as archaeological dating and forensic tissue characterization. The concentration of ^{14}C in a sample, directly after its death, is proportional to the amount of ^{14}C present in the atmosphere. ^{14}C is naturally produced by cosmic rays at a relatively constant rate, which makes precise age dating possible for older samples [1].

However, starting in 1890 with industrialization and the nuclear age, the carbon concentration in the atmosphere has been greatly changed by human influence. The nuclear weapon tests in particular increased the atmospheric ^{14}C concentration in the 1950s to around twice the pre-nuclear value, which can be seen in the year of 1963 in Fig. 4.1. $F^{14}\text{C}$ being the fraction of modern ^{14}C in the atmosphere in the northern hemisphere, which corresponds to ~ 1.0 in pre nuclear times. Fossil fuel emissions in the past have injected carbon dioxide lacking ^{14}C into the atmosphere due to the absence of ^{14}C in fossil fuels [2]. This phenomenon was first suggested by Hans E. Suess in 1955 [3] and was called the Suess effect. The anthropogenic emission of large amounts of ^{12}C into the atmosphere has disrupted the $^{14}\text{C}/^{12}\text{C}$ ratio, affecting radiocarbon dating accuracy, as the altered ratio no longer reflects the true age of organic samples.

H. Graven (2015) [5] used a model to simulate the $\Delta^{14}\text{CO}_2$ over the years since the beginning of the nuclear age. A simple carbon cycle model including the ocean, biosphere and atmosphere as components is used to describe the CO_2 reservoirs. Representative Concentration Pathways (RCPs) are used to describe possible dynamics of carbon in the atmosphere. Using historical data recorded until the year 2005 and the described model

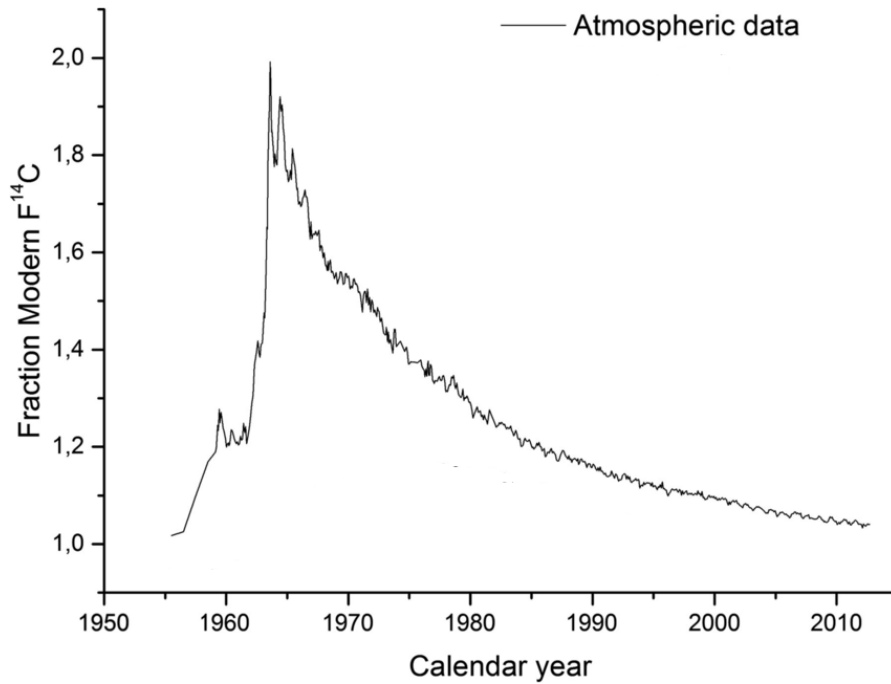


Figure 4.1: ^{14}C Bomb-peak shown as Fraction Modern, $F^{14}\text{C}$ in the atmosphere in the northern hemisphere, $F^{14}\text{C}$ being ~ 1.0 in pre nuclear times, corresponding to the natural $^{14}\text{C}/^{12}\text{C}$ in the atmosphere, taken from Lång et al. 2016 [4].

for futuristic scenarios, predictions of the $^{14}\text{C}/\text{C}$ ratio in atmospheric CO_2 ($\Delta^{14}\text{CO}_2$) can be seen in Fig 4.2 [5]. The different curves show RCP scenarios, where RCP2.6 stands for the case of low fossil fuel emission in the future, where $\Delta^{14}\text{CO}_2$ remains nearly constant at around -15‰ and RCP8.0 stands for the case of drastically rising fossil fuel emissions, with $\Delta^{14}\text{CO}_2$ reaching -250‰ in 2100.

By continuous injection of fossil CO_2 , containing only stable ^{12}C and ^{13}C , newly formed organic material shows an apparent aging effect. The samples resemble material with decreased ^{14}C levels due to radioactive decay. Should the fossil fuel emissions further reach a value of over ten PgC y^{-1} in 2050 as seen in Fig 4.2, by 2050, fresh organic samples could possess the same $^{14}\text{C}/^{12}\text{C}$ ratio as those from 1050, potentially turning them indistinguishable via radiocarbon dating. This phenomenon threatens the viability of current ^{14}C applications and may significantly impact various fields [5].

The search for a complimentary radionuclide that can give information about the formation time of a sample is the aim of this master's thesis. The primary focus is to determine whether a sample originates before or after the period of nuclear bomb testing. Commonly, organic material that needs to be ^{14}C age-determined includes wood, bone material, charcoal, or textiles. In this thesis, wood, specifically tree rings, is used as the testing material.

Using dendrochronological analysis, the specific formation year of a tree ring can be

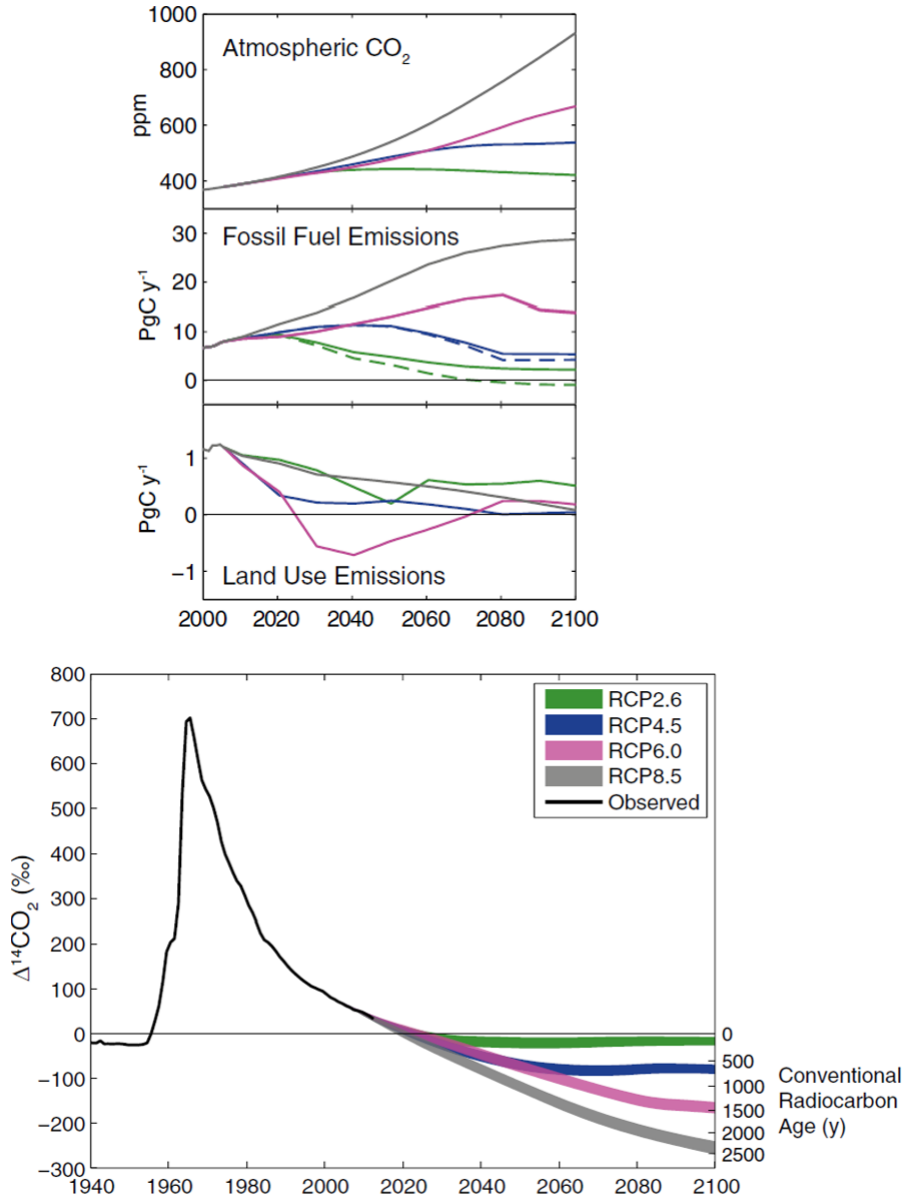


Figure 4.2: CO₂ emissions and $\Delta^{14}\text{CO}_2$ in the atmosphere over time for different RCP scenarios. *Left:* *Upper* plot describes the atmospheric CO₂ concentrations in ppm, *Middle* plot describes fossil fuel emissions in Petagram Carbon per year [PgC y⁻¹], *Lower* plot describes the land use emissions in Petagram Carbon per year PgC y⁻¹. *Right:* Change of $\Delta^{14}\text{CO}_2$ in the atmosphere, observed until 2005 and modeled for different RCP scenarios from 2005-2100. RCP2.5 projects a change in $\Delta^{14}\text{CO}_2$ to -15‰, RCP4.5 to -80‰, RCP6 to -150‰, and RCP8.5 to -250‰ by the year 2100, taken from [5].

4 Introduction

determined. Measuring isotopes in tree rings provides information on whether the concentrations of the analyzed isotope, mirror the atmospheric fallout deposition and other emissions from nuclear events.

Accelerator Mass Spectrometry (AMS) is the preferred, and often the only, method for analyzing several key radioisotopes. However, the degree of procedural establishment varies across different isotopes. While ^{14}C is routinely measured in dozens of laboratories worldwide, almost on a quasi-commercial scale [6], ^{129}I was analyzed in 12 facilities in 2021 [7]. The measurement of ^{90}Sr has been tried out in less than ten facilities [8] with AMS and is a new development at VERA. In this work, we chose to conduct exploratory measurements on the well-established ^{129}I and the emerging AMS isotope ^{90}Sr .

Chapter 5 provides a brief overview of tree physiology and reviews previous literature on dendrochronological analysis of radioisotopes in tree rings. ^{129}I and ^{90}Sr have previously been investigated and suggested for further analysis. The elementary properties of the isotopes and their global abundance are described in chapter 6 and chapter 7. Chapter 8 describes the applied chemical treatment and isotope measurement techniques that were used for this thesis. Finally chapter 9 analyzes the results of the experiments carried out.

5 Environmental tree samples and dendrochronology

"(...),dendrochronology is the precise and reliable assignment of the year of formation of tree rings.(...).Dendrochemistry is a subdiscipline of dendrochronology that analyzes and interprets the woodchemistry of precisely dated tree rings."
(Balouet et al. 2009, [9])

For dendrochemical analysis, understanding the uptake and transport of isotopes is essential. This process is influenced by the overall nutrient uptake of trees, which can vary significantly between different species.

Therefore, to understand the factors influencing nutrient transport in trees, the principles of dendrochronology, and why different trees exhibit varying concentrations and storage locations for nutrients, it is essential to dive into the microstructure of trees. This includes examining their cellular makeup and the primary differences among various tree species. Familiarity with key terminologies related to tree biology is crucial for comprehending scientific literature on trees and nutrient analysis.

The following chapter provides an overview of the main components of trees and their functions. This foundation will help identify which trees and tree parts are suitable for dendrochemical analysis using AMS and how their unique structures impact nutrient transport and storage.

5.1 Introduction to main tree components

Figure 5.1 shows the structure of a tree trunk. The bark can be seen on the outside, consisting of layers of periderm and the secondary phloem. The phloem is responsible for the transport of nutrients. Between the secondary xylem is a layer of vascular cambium. [10] The vascular cambium is responsible for the formation of the xylem and the phloem. Dead phloem cells build the bark of the tree [11]. The secondary xylem consists of the so-called heartwood and the sapwood. Heartwood is dead xylem material consisting of dead cells and is the central support of the tree. The trunk part of the wood where its cell system is still alive is called the sapwood. It is characterized by its function of sap flow, transporting nutrients from the roots to the inner part of the tree and the metabolic storage and synthesis. A layer of xylem, which always grows seasonally, forms a tree ring. Therefore, a tree ring corresponds to the growth of the tree in one year [10]. However, in

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some tree species, such as palm trees or mesquites, this seasonal ring formation does not occur [12].

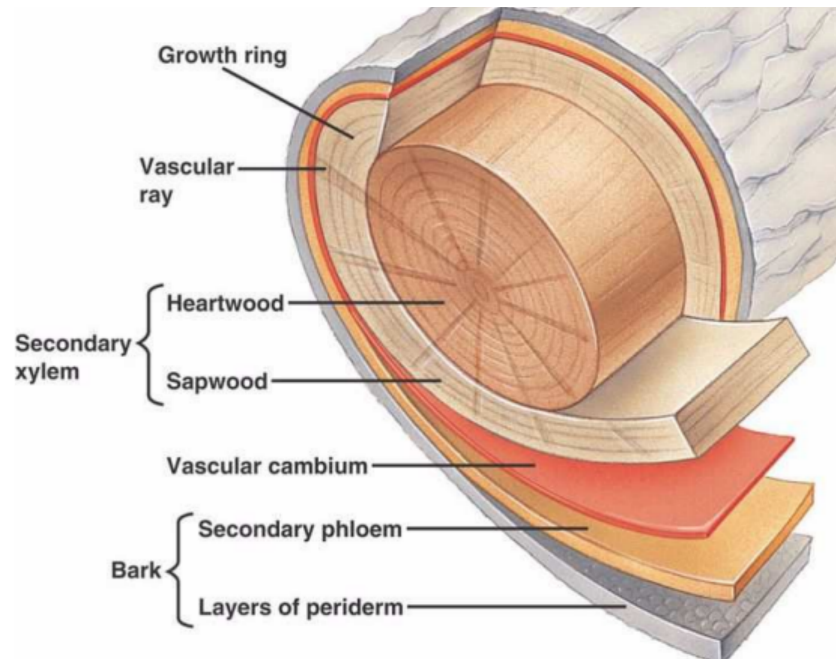


Figure 5.1: Structure of wood taken and modified from [13]

5.1.1 Angio- and gymnosperms physiology

Describing tree species, one has to differentiate between angio- and gymnosperms. Angiosperms are called hardwoods, gymnosperms are called softwoods. Angiosperms are deciduous trees with broad leaves that change color. Examples of these trees are species such as oaks, birches, beeches or ash trees. Hardwoods usually have a more complex cell structure with a great number of cell types, which vary among themselves [13]. Gymnosperms are in most cases evergreen conifers which have scaly leaves and cones with seeds. Examples of gymnosperms are spruces, larches and pines. In contrast to hardwood, softwoods do not have a large variation in cell types and have a simpler structure. The biggest difference between the two tree species is that hardwoods consist of so-called vessel element cells, which softwoods lack. Both tree species have the so-called parenchyma cells, which are alive even in advanced growth [13].

5.1.2 Microscopic structure of softwoods and hardwoods and nutrient transport

Softwoods

Softwoods are characterized by a simpler anatomical structure than hardwoods and are predominantly made up of axial tracheids which account for over 90% of the wood's volume. These tracheids, elongated and narrow and usually 2-6 mm long, not only facilitate mechanical support and water conduction within the wood but also feature small pits that allow for the transfer of water and nutrients between neighbouring cells. The structure of these rows, which radiate outward, showcases changes in the thickness of the wall from the earlywood to the latewood within each growth ring. Water moves between them through bordered pits where their ends meet. A picture of a row of tracheid cells of a Colorado fir (*Abies concolor*) can be seen in Fig. 5.2a. While this arrangement is crucial for the tree's functioning, it does not transport water as efficiently as the vessel elements in hardwoods [13].

Additionally, softwoods may contain axial parenchyma and specialized structures such as resin canals, although these are less common and contribute minimally to the wood's volume. Resin canals, surrounded by parenchyma cells that produce resin, are more prominent in certain species like pine and Douglas-fir and are visible in cross-sectional views. Ray parenchyma cells in softwoods are responsible for the lateral transport of biochemicals, forming narrow, brick-like structures within the rays that can vary in visibility and are critical for species identification [13]. A picture of a microscopic radial cross section of a spruce (*Picea abies*) showing parenchyma cells can be seen in Fig. 5.2b.

Hardwoods

Hardwoods exhibit a more complex structure compared to softwoods, featuring a variety of cell types and arrangements that facilitate water conduction and mechanical support. The axial system of hardwoods contains diverse fibrous elements, variously sized and arranged

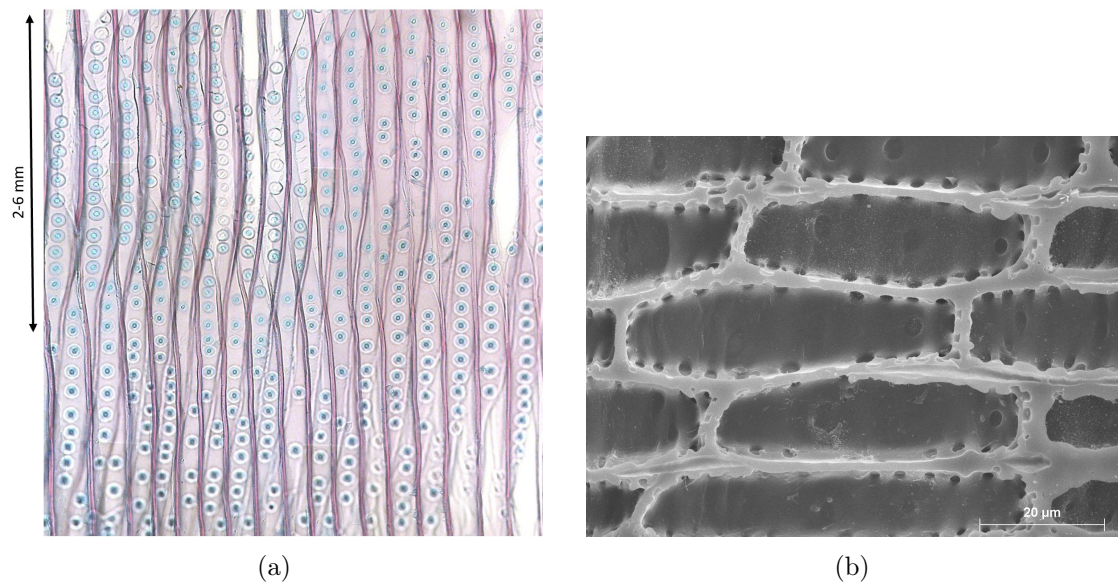


Figure 5.2: Principal cell types in a coniferous tree: (a) Microscopic view of a thin section of *Abies concolor* (Colorado Fir) tracheid cells from horticulture in Schwaz, Tyrol, taken and modified from [14]; (b) Axial parenchyma cells in a wood ray of *Picea abies*, taken from [15].

vessel elements, and abundant axial parenchyma, which distinguish them significantly from the mostly tracheid-based structure of softwoods. Additionally, hardwoods have specialized water-conducting cells known as vessel elements that are stacked to form vessels with perforation plates at the ends, and their radial system consists of rays made up of ray parenchyma cells, showing a greater variety in size and shape. [13]

5.1.3 Chemical composition of wood

Wood primarily consists of carbon, hydrogen, and oxygen, with carbon being the most prevalent element, as highlighted by its average composition of 49% by dry weight. Minor elements like nitrogen are present in small amounts, and inorganic residues known as ash constitute about 0.1% after combustion. The main organic compounds in wood are cellulose, which makes up nearly half of the weight in both hardwoods and softwoods, along with varying levels of hemicellulose and lignin, which differ across different types and species of wood [10].

5.1.4 Nutrient uptake by trees

There are two main path ways for nutrient uptake by trees:

Root uptake: Nutrient uptake via the roots begins with absorption by root epidermis and hairs through specialized transport proteins. The uptake depends strongly on the

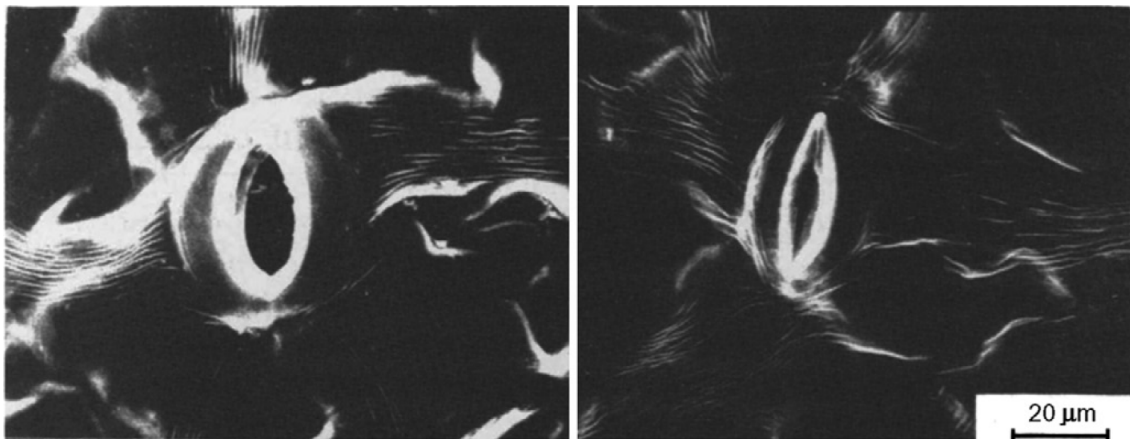


Figure 5.3: Electron analyser image of open (left) and closed (right) Stomata, taken and modified from [17].

root structure and size as well as the soil quality [16]. Subsequently, they are selectively loaded into the sapwood, the living portion of the xylem. This process involves complex interactions between different cellular and tissue structures, ensuring efficient and selective nutrient uptake and transport. Once in the sapwood, nutrients are transported upwards, distributed to various parts of the tree based on their chemical characteristics and specific functional roles within the tree [17].

Foliar uptake through the leaves: Stomata are tiny openings on the surface of leaves that allow gaseous substances like CO_2 or SO_2 to enter the leaf. At the same time, these openings help minimize the loss of water from the leaf through a process called transpiration. They help with photosynthesis and hydration, as well as nutrient uptake from the atmosphere. Nutrients taken up through foliar absorption are transported into the xylem via the phloem, which results in a faster incorporation of elements into the xylem, comparing to root uptake. However it may happen, that nutrients are taken up by stomata, but their transport is not supported by the phloem, which makes them accumulate in the leaves. This is the case for calcium [18]. An image of an open and closed stomata can be seen in Fig. 5.3 [17].

A simplified sketch of the two uptake mechanisms as well as their pathways into the outer xylem are shown in Fig. 5.4.

To understand the way of nutrient uptake, it is crucial to know, which essential elements a tree consists of. The elemental composition of one specific tree cannot give information on the importance of the elements it needs for survival, because the composition strongly depends on its environmental surroundings. Through depriving plants of certain elements, studies were able to show that trees consist of **macro- and micronutrients**. While macronutrients are necessary in larger amounts for the tree survival and are essential

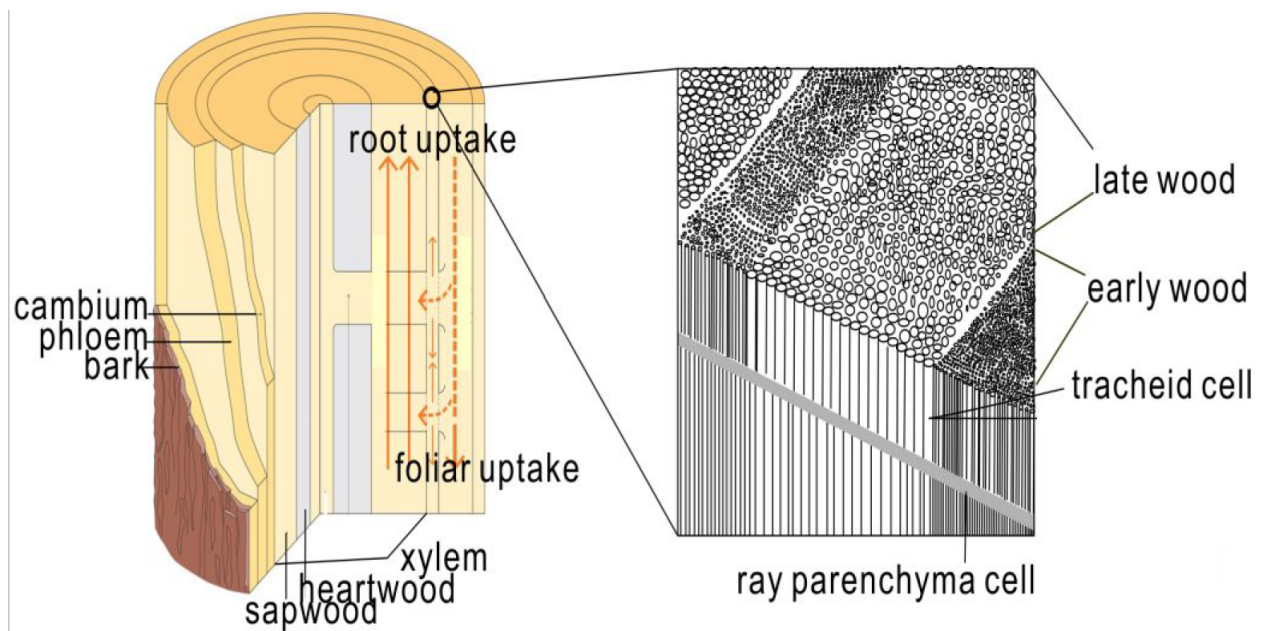


Figure 5.4: Schematic view of foliar and root uptake of nutrients and the pathways for their incorporation into the xylem, taken and modified from [19].

components of larger molecules such as proteins, micronutrients are necessary for enzyme function, but in much less concentrations. Lastly there are elements that are found in trees, which are not necessary for the trees survival but absorbed because of their higher abundance in the environment, the so called **trace elements**.

The 14 major elemental components of a tree can be classified into *four groups*:

The *first group* consists of carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S), being the main components of biological compounds such as amino and nucleic acids, proteins and enzymes.

The *second group*, consisting of phosphorus (P), silicon (Si) and boron (B) are bound by hydroxyl groups through esterification processes.

The first and second group belong to the group of macronutrients which are the building stones of the tree cells and essential for the trees survival.

The *third group* contains potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), manganese (Mn) and chlorine (Cl), which are elements mainly taken up as ions from the soil and are responsible for various general functions inside of the tree. Calcium, as an example is responsible for the formation of oxalates and pectins, which are components of the plant's cell walls and stabilize the trees xylem.

The *fourth group* contains iron (Fe), manganese (Mn), zinc (Zn) and copper (Cu). Their task is to create chelate compounds, which is one of the tasks of the elements of the third group. However, these elements are found in smaller quantities in the environment and therefore also in tree tissue, which explains their categorisation into the fourth group.

5.1 Introduction to main tree components

The third and fourth group belong to the group of micronutrients which play an essential role in the development and the nutrient exchange of the tree. A table of the essential micro and macro nutrients groups for trees and their uptake pathways, functions and occurrences can be seen in Tab. 5.1 whose content was taken and adapted from Marschner et al. (2012) [17].

Table 5.1: Macronutrient and micronutrient uptake in trees, taken from [17].

Nutrient	Uptake
Macronutrients	
Group 1: C, O, H, N, S	HCO_3^- , H_2O , O_2 , N_2 , SO_4^{2-} , SO_2 as ions from the soil or as gases like SO_x , NO_x , CO_2 for S, N, and C through stomata from the atmosphere
Group 2: P, Si, B	Phosphates, boric acid or borate, silicic acid from soil uptake
Micronutrients	
Group 3: K, Na, Ca, Mg, Mn	As ions from the soil solution
Group 4: Fe, Mn, Zn, Cu	As ions or chelates from soil solution

5.2 Dendrochemistry

"Plants are living organisms; they do not passively record environmental changes, and observed chemical trends in tree rings are the result of complex physiological interactions between the individual and the surrounding environment."

(Binda et al. (2021), [16])

There are several factors that have to be considered when performing a dendrochemical analysis. The reliability of using individual radioisotopes as proxies has been a subject of discussion since the inception of dendrochemistry [16].

The uptake mechanism of the tree has to be taken into account: Tree's main uptakes come from the roots and leaves. Considering the root uptake, one has to look at the soil quality and the root length of the chosen tree. Both factors can lead to a delayed uptake of the analyzed elements, therefore possibly reacting delayed to environmental changes. The stomatal element uptake leads to a direct incorporation of environmental circumstances into the tree rings. For a dendrochemical analysis in regard to the concentration of radioisotopes in the atmosphere, a fast incorporation into the xylem is aspired. An example of immediate accumulation in the xylem of atmospheric mercury into the xylem has been observed in a larch by Peckham et al. (2019) [16].

Next, the mobility of nutrients in the xylem has to be considered. Given the significant differences among trees, as described in previous chapters, it is crucial to carefully select the appropriate tree type for analysis. Compared to hardwoods, softwoods have a xylem composed of a simpler cell structure. Hardwoods possess a complex cellular system, including vessel elements that allow for more extensive radial exchange of nutrients and water between cells. While there are some deciduous trees that primarily consist of tracheid cells, so called ring porous trees, they are significantly in the minority. In contrast, softwoods primarily rely on tracheid cells to transport nutrients vertically from the roots upward. The only cells that facilitate limited radial exchange in softwoods are the parenchyma cells. Consequently, the mobility of elements between xylem cells is significantly more restricted in coniferous trees than in deciduous trees. Translocation of the researched element through the xylem would destroy any signal or pattern of the environmental changes [16]. One key aspect that remains debated is the duration of heartwood formation, which plays a crucial role in the radial transport of nutrients within a tree. When heartwood forms, the parenchyma cells responsible for nutrient transport, particularly in the radial direction, die off, effectively halting this transport. However, the timeline for heartwood formation varies significantly between tree species, and no consensus has been reached on the exact duration. While some studies suggest that heartwood formation may take as little as one year in certain species, others argue that it could take up to ten years in others. If heartwood formation is prolonged, radial nutrient transport can continue for several years, especially if the analyzed element is not immediately incorporated into the cell wall. This extended transport period

can compromise the dendrochemical signal, potentially distorting the accuracy of age determinations based on isotopic analysis [20].

Other than the tree properties, the chemico-physical features of the analyzed element have to be taken into account. These are for example solubility, charge-to-ionic radius ratio or lipophilic properties. Various analysis, regarding different elements have been conducted in the past. Lead, magnesium, sodium, potassium and calcium have been analyzed and while magnesium, lead and calcium showed low mobility within the tree rings sodium and potassium show high mobility [16].

Another important factor that has to be considered is the fractionation factor, which is corrected for in various radioisotope appliances like $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$. When considering the uptake of isotopes by trees, it is important to note that isotopes are selected differently due to their varying masses, even though chemically, they would have the same characteristics. For example, trees are more likely to absorb ^{12}C than ^{13}C . Without correcting for this, the ratio of isotopes would be inaccurate. Therefore, a fractionation factor must be applied to account for this natural preference [21].

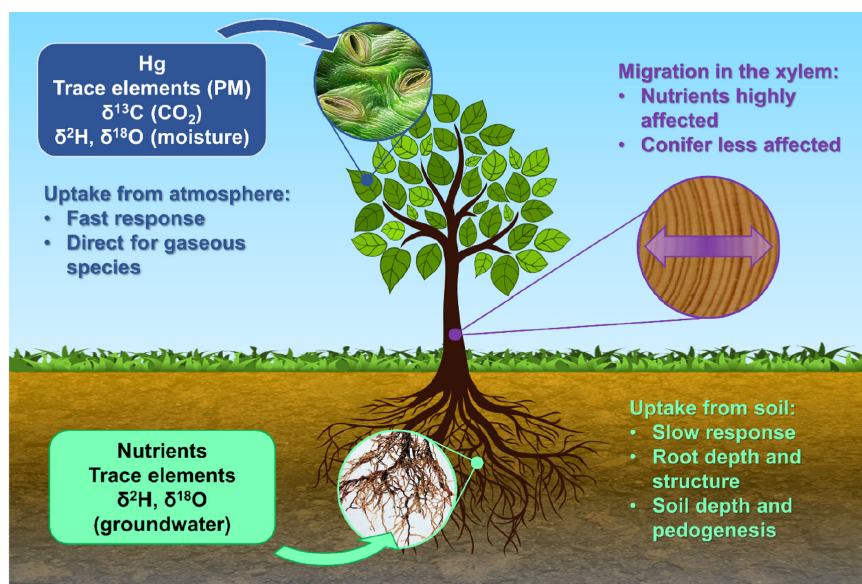


Figure 5.5: Uptake mechanisms, incorporation and dendrochemical characteristics of elements in trees, taken from [16].

Previous literature on radioisotopes in tree rings is analyzed in the following sections.

5.2.1 ^{137}Cs

Several studies have investigated the presence of ^{137}Cs in tree rings [22, 23, 24, 25, 26]. Barci-Funel et al. (1995) [25] and Kohno et al. (1988) [22] both focused specifically on

5 Environmental tree samples and dendrochronology

coniferous trees for their analyses. Barci-Funel et al. (1995) [25] used gamma spectrometry with high-purity germanium (HPGe) detectors, while Kohno et al. (1988) [22] employed a low-level gamma-ray detection system with a detection limit of 0.1 Bq/kg dry weight. In contrast, Kagawa et al. (2002) [26] and Fogh et al. (2001) [24] examined both gymnosperms and angiosperms. Kagawa et al. (2002) [26] and Fogh et al. (2001) [24] both utilized neutron activation analysis (NAA) combined with gamma spectrometry. Despite the different methodologies and tree types studied, all researchers arrived at a similar conclusion: ^{137}Cs exhibited high mobility within the tree rings, making it undetectable in specific rings. The isotope penetrated into the trunk, preventing its use as a dendrochemical tracer for nuclear fallout.

5.2.2 $^{239,240}\text{Pu}$

The mobility of $^{239,240}\text{Pu}$ within tree rings are quite similar for all reported studies. Hölgye et al. (2016) conducted an analysis of $^{239,240}\text{Pu}$ in a Norway spruce using an alpha spectrometric system equipped with 1200 mm² PIPS (Passivated Implanted Planar Silicon) detectors. Their findings indicated that all samples analyzed contained concentrations of $^{239,240}\text{Pu}$ that were below the detection limit and could therefore not be analyzed. This is partly explained by the low uptake by the tree due to its heavy mass and the chemical soil composition at the tree site [27]. Furthermore Kudo et al. (1993) [28] analyzed a Nagasaki tree using alpha particle spectrometry and came to the conclusion that, while the radioisotope appeared to be immobile and showed a clear signal, a delayed uptake by the roots through the soil and the faster uptake by the tree leaves leads to a blurry signal in the tree chronology. Furthermore the highest concentration found in the tree rings was $(30 \pm 1.5)\text{mBq kg}^{-1}$ which can be considered rather low in comparison to other radioisotopes [28].

5.2.3 $^{234,235,236,238}\text{U}$

McHugh et al. (2018) [29] studied various uranium isotopes, using thermal ionization mass spectrometry, in three trees, one white ash (*fraxinus americana*, semi-ring porous), slippery elm (*Ubrus rubra*, semi-ring porous) and one black walnut (*Juglans nigra*, diffuse porous), that were located in a uranium contaminated region. Uranium concentrations inside the tree rings ranged from 116 to 1010 $\mu\text{g U/kg}$ ash for the black walnut, 228-11700 $\mu\text{g U/kg}$ ash for the slippery elm and 56.4-476 $\mu\text{g U/kg}$ ash for the white ash. While analysis of $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ showed clear presence of anthropogenic uranium inside the tree, no signal correlating with the contamination history could be detected in any analyzed tree [29].

5.2.4 ^{129}I

Some studies on signal tracking in trees with the radioisotope ^{129}I have already been carried out. ^{129}I is measurable with conventional AMS. With this method Rao et al. (2002) [30] measured ^{129}I concentrations in ring porous and diffuse porous wood to check

whether the distribution of nuclides in the tree rings is a reflection of the nuclear fallout. While the diffuse porous wood showed no clear signal, the signal could be traced in the ring porous trees. However even in the ring porous trees pre nuclear tree rings had ^{129}I concentrations that were above pre anthropogenic levels. This indicates that a small amount of Iodine does penetrate into the inner xylem, however the signal could be traced nevertheless [30]. Furthermore Zhao et al. (2019) [19] performed the same experiment using a coniferous tree. With accelerator mass spectrometry, ^{129}I concentrations in tree rings were analyzed and Zhao et al. (2019) [19] came to the same conclusion that the fall out signal as well as the later emitted radioisotopes by nuclear fuel reprocessing plants were traceable. This is explained by the direct absorption of gaseous ^{129}I through the leaves stomata by the tree and the immediate implementation into the xylem. Furthermore the good traceability is explained by the immobility of ^{129}I within the tree rings [19]. Another study supporting the usage of ^{129}I to trace radioactive pollution in the environment with trees is Wershofen et al.(1989) [31].

5.2.5 ^{90}Sr

Kagawa et al. (2002) [26] suggested ^{90}Sr as a potential tracer for radioactive pollution when analyzing both ^{90}Sr and ^{137}Cs in tree rings. Their study included one gymnosperm and one angiosperm, utilizing instrumental neutron activation analysis (INAA) along with a germanium detector for γ event detection. A clear bomb peak from global nuclear fallout was observed in the gymnosperm, and although elevated strontium concentrations were detected in the angiosperm, no distinct signal could be identified. The study found ^{90}Sr to have low mobility within the tree rings, leading to its recommendation for future dendrochemical studies. Chigira et al. (1988) [23] also analyzed ^{90}Sr , using a Japanese gymnosperm and a low-background "pico γ " GM counter for ^{90}Sr activity detection. They found that tree rings formed before anthropogenic nuclear emissions contained no ^{90}Sr . A noticeable ^{90}Sr peak was detected during the nuclear bomb testing period, with elevated concentrations also present in later tree rings. The highest concentration was observed in the bark, measuring (1.776 ± 0.74) Bq/kg, followed by activity levels of (1.665 ± 0.148) Bq/kg in rings from 1958-1962. Hölgye et al. (2016) [27] further confirmed the low mobility of ^{90}Sr within gymnosperm tree rings, as measured using gamma spectrometry.

Table 5.2: Summary of studies on radioisotope mobility and detectability in tree rings.

Radioisotope	Study	Tree Types	Findings
^{137}Cs	Barci-Funel et al. (1995) [25], Kohno et al. (1988) [22]	Coniferous	High mobility, no detectable signal
	Kagawa et al. (2002) [26], Fogh et al. (2001) [24]	Gymnosperms and Angiosperms	High mobility, no detectable signal
$^{239,240}\text{Pu}$	Hölgye et al. (2016) [27]	Norway spruce	Below detection limit, low uptake
	Kudo et al. (1993) [28]	Nagasaki tree	Immobile, clear but blurry signal due to delayed uptake
			Highest concentration: $(30 \pm 1.5) \text{ mBq/kg}$
$^{234,235,236,238}\text{U}$	McHugh et al. (2018) [29]	White ash, Slippery elm, Black walnut	Uranium concentrations: Black walnut: 116 – 1010 $\mu\text{g U/kg ash}$ Slippery elm: 228 – 11700 $\mu\text{g U/kg ash}$ White ash: 56.4 – 476 $\mu\text{g U/kg ash}$ No correlation with contamination history
^{129}I	Rao et al. (2002) [30]	Ring porous, Diffuse porous	Detectable in ring porous, not in diffuse porous
	Zhao et al. (2019) [19]	Coniferous	Traceable fallout signal
			Direct absorption through leaves stomata
^{90}Sr	Kagawa et al. (2002) [26]	Gymnosperm, Angiosperm	Bomb peak visible in gymnosperm, elevated concentration in angiosperm, low mobility, recommended for dendrochemical studies
	Chigira et al. (1988) [23]	Japanese gymnosperm	No ^{90}Sr before anthropogenic emissions, peak during bomb testing, elevated ^{90}Sr in later rings. Highest in bark: $(1.776 \pm 0.74) \text{ Bq/kg}$, rings from 1958-1962: $(1.665 \pm 0.148) \text{ Bq/kg}$
	Hölgye et al. (2016) [27]	Gymnosperm	Low mobility within tree rings

6 Iodine

I 127	I 128	I 129	I 130	I 131
100	25.0 m	$1.61 \cdot 10^7$ a	9.0 m	12.36 h
	β^- 2.1...	β^- 0.151	β^- 1.0	β^- 0.6, 0.8...
	ϵ, β^+ ...	γ 40, e^-	1.8...	γ 364, 637
	γ 443, 527...	g	γ 536, 669	284..., g
σ 6.2	σ 22	σ 17.8 + 12.5	σ 18	σ ~0.7

Figure 6.1: Karlsruhe chart of nuclides showing strontium isotopes, ^{127}I , ^{128}I , ^{129}I , ^{130}I , and ^{131}I , 8th edition (2012).

Iodine is an element of the 17th group of the periodic table, the halogens. It has an atomic number of 53 and is naturally found in oxidative states like iodide (I^- , -1) elemental iodine (I_2 , 0) or iodate (IO_3^- , +5). Additional states in which Iodine can occur are +1, +3 and +7. There are 36 known iodine isotopes but normally, iodine only appears as two isotopes, one stable ^{127}I isotope with a natural abundance of 100% and one radioactive trace ^{129}I isotope with a half-life of $1.57 \cdot 10^7$ years. An overview of the most relevant iodine isotopes for this thesis, ^{127}I , ^{128}I , ^{129}I , ^{130}I , and ^{131}I , is presented in the excerpt from the Karlsruhe Nuclide Chart in [7.1](#).

The largest source of iodine is the ocean, which contains average concentrations of 50-60 $\mu\text{g/L}$. It is transferred from the ocean to the atmosphere as an organic compound, for example as iodomethane (CH_3I) or diiodmethane (CH_2I_2). Once evaporated, the iodine compounds are photolyzed in the upper atmosphere, creating iodine atoms which react with oxygen and hydrogen atoms. Subsequently, it is deposited onto land through wet and dry deposition, where it is absorbed into the soil. The retention and binding of iodine in the soil depend on various factors, like pH value, presence of soil microorganisms, and the organic matter content. In the soil, iodine binds to organic matter compounds or to iron and aluminum oxides.

Exposure to radioactive iodine, specifically ^{131}I , can have significant health effects on the human body. After a nuclear fallout, these radioactive iodine isotopes are released into the environment. This is concerning because the thyroid gland is highly efficient at absorbing iodine, regardless of its isotopic form. The accumulation of radioactive iodine in the thyroid can significantly increase the risk of developing thyroid cancer [\[32\]](#).

6.1 ^{129}I in the environment

Naturally, ^{129}I is produced by interaction of cosmic rays with atmospheric ^{129}Xe in the atmosphere and by spontaneous fission of ^{238}U in the lithosphere [32]. It decays back to ^{129}Xe through β -decay [33]. A decay diagram of ^{129}I can be seen in Fig. 6.2.

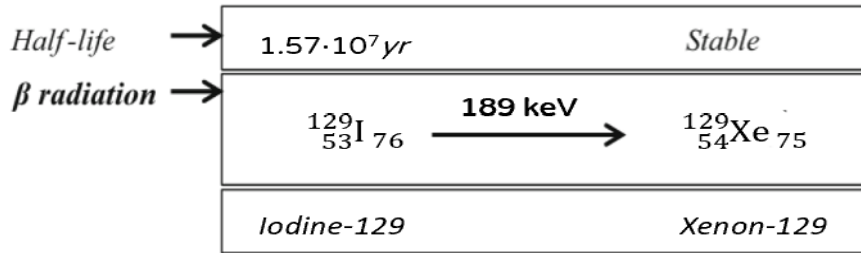


Figure 6.2: Decay chain diagram of ^{129}I .

The amount of naturally produced ^{129}I in the environment is negligible compared to the anthropogenically produced ^{129}I by sources like nuclear accidents (e.g. Chernobyl), atmospheric nuclear weapon testing and present discharges from nuclear fuel reprocessing plants (NFRP). Presently, european NFRPs in operation are located in La Hague and Marcoul (France), Sellafield (England) and Belgium. Others can be found in Pakistan, China, Japan, Mayak (Russia), Israel, India and the USA. The primary pathway for the release of ^{129}I during nuclear fuel reprocessing via the PUREX (plutonium uranium reduction extraction) process is through the oxidation of iodine to volatile I_2 as the fuel is dissolved with nitric acid [32].

La Hague and Sellafield NFRPs are responsible for the release of large amounts of ^{129}I . Until 2007 La Hague NFRP has discharged 3800 kg of ^{129}I into the English Channel, while Sellafield discharged 1400 kg ^{129}I into the Irish sea. Additionally 75 and 180 kg were released into the atmosphere by La Hague NFRP and Sellafield NFRP respectively. The NFRP in Marcoule released 145 kg ^{129}I into the atmosphere and 45 kg into the Rhine river [34]. Together, Sellafield and La Hague NFRPs accounted for more than 95% of marine ^{129}I . In comparison, during the nuclear bomb testing period an estimated amount of 50 kg were released and the Chernobyl reactor accident released 1-2 kg. The annual marine discharge and the total marine and atmospheric emissions by La Hague and Sellafield can be seen in Fig. 6.3 [32].

Additionally, NFRPs such as the Savannah River fuel-reprocessing plant in South Carolina, USA, and the Hanford Reservation in Washington, USA, have released approximately 23 kg in 1954-1989 and 290 kg in 1944-1995 of ^{129}I respectively [32]. A table of the ^{129}I releasing sources can be seen in Tab. 6.1. The NFRP in Tokai, Japan released 1.0 kg of ^{129}I into the environment from 1997 to 2005 and the NFRP in Karlsruhe, Germany

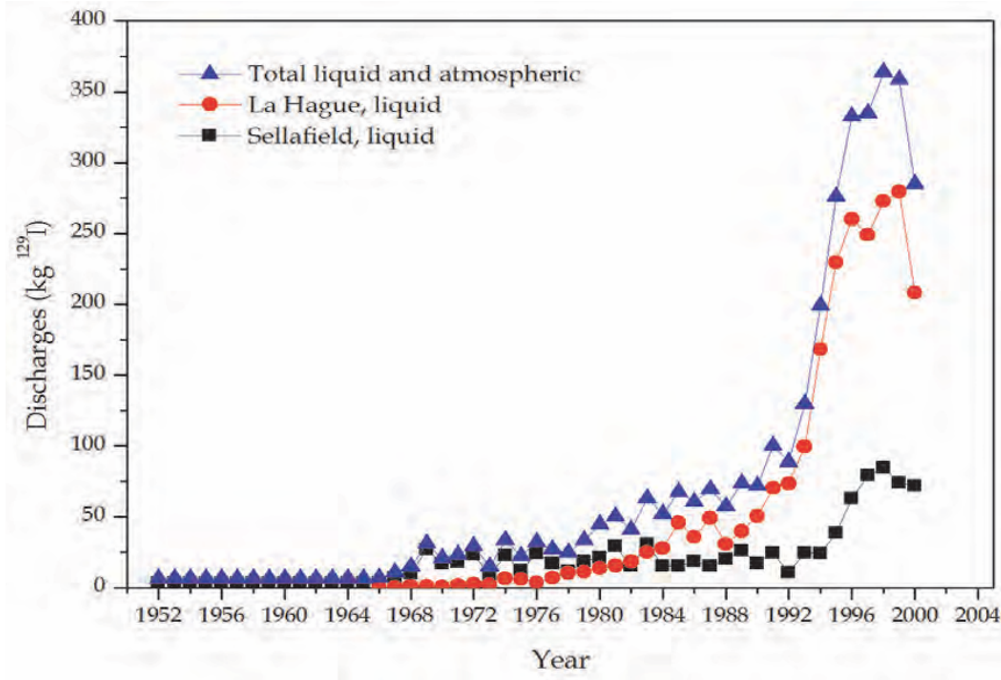


Figure 6.3: Annual liquid releases of ^{129}I and total liquid and atmospheric discharges by La Hague and Sellafield NFRP from 1952 to 2000, taken from [32].

released 1.1 kg into the atmosphere from 1971 to 1987. ^{129}I releases from NRFPs in Russia, China and India are unknown [34].

Table 6.1: Annual releases of ^{129}I from various sources.

Source	Total discharged ^{129}I [kg]
La Hague (1963-2007) [34]	3875
Sellafield (1963-2007) [34]	1580
Chernobyl (1986) [32]	1-2
Nuclear Bomb Tests (1945-1980) [32]	50
Savannah River NFRP, South Carolina (USA) (1954-1989) [32]	23
Hanford Reservation, Washington (USA) (1944-1995) [32]	290
Tokai, Japan (1997-2005) [34]	1
WAK Karlsruhe, Germany (1971-1987) [34]	1.1

These releases led to a severe elevation of the environmental isotopic ratio of $^{129}\text{I}/^{127}\text{I}$. Prior

to anthropogenic ^{129}I emissions, the ratio of natural $^{129}\text{I}/^{127}\text{I}$ in the marine environment was determined to $1.5 \cdot 10^{-12}$. This ratio was elevated to $10^{-11} - 10^{-10}$ and $10^{-8} - 10^{-5}$ in nordic sea regions. While no fixed pre-nuclear ratio value was agreed on for the terrestrial environment, high values were found ranging from $10^{-9} - 10^{-7}$ and even $10^{-6} - 10^{-4}$ near NFRPs after the beginning release of anthropogenic ^{129}I . A table of $^{129}\text{I}/^{127}\text{I}$ measurements of environmental samples measured over the past can be found in [32].

Both ^{129}I and ^{127}I behave similarly in environmental processes due to their comparable chemical properties, as they are isotopes of the same element. However, ^{129}I , which has been released primarily from reprocessing plants and other anthropogenic sources in the past, can be found in different chemical forms compared to ^{127}I because of its different sources. Since it is emitted in a volatile form, it behaves more mobile than ^{127}I . This difference in volatility may influence their biogeochemical behaviors, making one form more readily available for plant uptake and consequently more prevalent in plants [32].

6.1.1 ^{127}I and ^{129}I uptake by plants

"Owing to the complex physiological structure of terrestrial higher plants, understanding detailed metabolic process of iodine is difficult."
(Zhang et al. 2023, [35].)

The concentration of iodine can vary depending on whether the soil is located near a marine area or in an area contaminated by NFRPs. However, iodine content in soil has been found in a range from $1\text{-}5 \mu\text{g g}^{-1}$. Iodine in soil mainly appears as I^- , IO_3^- and organic iodine. While I^- is mobile in the soil because it is likely to combine with metal cations in soil, IO_3^- and organic iodine are less mobile and typically bound to solid components of the soil. The main factors impacting the behavior of iodine in the soil is the soils pH, redox conditions, oxygen levels, electrical conductivity, microbial activity and the soils organic matter content [35].

The exact pathways through which iodine enters plants, particularly trees, are not yet fully understood. The interactions between iodine molecules and the roots and other organs of trees remain largely unexplored. However, simulations and concentration measurements have provided valuable insights, allowing researchers to estimate which iodine compounds are preferentially absorbed by plants and the likely mechanisms involved in this uptake are explained in the following paragraphs. Iodine was found in cell walls and inside of the cells in the xylem, showing that it is actively and passively transported into the tree, through selective proteins and diffusion respectively [35].

Plants are estimated to absorb iodine through both their roots and via foliar uptake. While plant roots primarily take up iodine in the form of iodide I^- , some plants have been found to absorb iodine in the form of organic compounds as well. Additionally, under certain soil conditions, specific enzymes in plant roots can reduce iodate IO_3^- to iodide I^- ,

enabling the uptake of iodate. Active transport of iodide in trees is facilitated by carrier proteins and chloride ion transport proteins within plant cells. Furthermore, aqueous iodide can be passively absorbed through diffusion, indicating that both active and passive iodine uptake mechanisms operate in plants [35]. Additionally, iodide is soluble, allowing foliar uptake through wet deposition. For example, in the scope of precipitation, iodine dissolved in rainwater is deposited on leaves and absorbed. In very humid areas, stomatal uptake is also likely. Moreover, gaseous iodine can be taken up by the stomata of leaves [35].

The primary method by which trees absorb iodine is not clear [36]. However, it is known that iodine transport through terrestrial areas is inefficient, with significant amounts of iodine being lost when passing through forests. This suggests that trees may take in iodine through the leaves, reducing the amount that reaches inland areas. Additionally, root uptake of iodine might be limited due to the lack of dissolved iodide and the rapid binding of iodine to organic compounds in the soil, which makes it less available for absorption by the tree [35].

Stable iodine is found in low concentrations inside of tree wood. Pisarek et al. (2022) analyzed Douglas fir, pine, spruce, beech and oak and found iodine concentrations of $\text{LOD} > 16.5 \mu\text{g kg}^{-1}$. Zhao et al. (2019) measured $6\text{--}100 \mu\text{g kg}^{-1}$ in the xylem of spruce wood located at the Northeast Qinghai-Tibet Plateau [19] and Rao et al. found low concentrations of $3.4\text{--}13 \mu\text{g kg}^{-1}$ in the inner xylem as well. The highest iodine values were found in the bark with values up to $0.35\text{--}2.19 \mu\text{g g}^{-1}$ [23]. A table listing iodine concentrations found in tree xylem at different locations is seen in Tab. 6.2

Table 6.2: Stable iodine concentrations in different tree species.

Study	Tree Species	Location	^{127}I concentration ($\mu\text{g/g}$)	Tree organ
Zhao et al. 2019 [19]	Spruce	Northeast Qinghai-Tibet Plateau	0.006 - 0.1	Xylem
Rao et al. 2002 [30]	Elm, locust, oak, cherry, maple	Rochester, NY and West Valley, NY	0.09 - 1.25	Xylem
			0.35-2.19	Bark
Pisarek et al. 2022 [37]	Douglas fir, Corsican pine, Norway spruce, European beech, Sessile oak	Breuil-Chenue in Bourgogne, France	$< \text{LOD } 0.0165$	Xylem

Zhao et al. (2019) measured $^{129}\text{I}/^{127}\text{I}$ ratios in deep and surface soil and compared it to

6 Iodine

the $^{129}\text{I}/^{127}\text{I}$ ratio measured in tree rings. Here a value of $(0.01 - 3) \cdot 10^{-9}$ was found in the surface and deep soil respectively, while values ranging between $(6 - 15) \cdot 10^{-9}$ and $(4 - 20) \cdot 10^{-9}$ for tree rings in two different Qinghai spruce trees. The fact that the values measured in the tree rings are even higher than the surface soil value is explained by increased iodine uptake from the atmosphere through the leaves. Gaseous iodine can be taken up directly via the leaf stomata or bound as an aerosol via foliar uptake (5.1.4) and integrated into the xylem via the phloem. If there are higher concentrations of gaseous iodine in the atmosphere, it is mainly absorbed by the leaves of the trees. This would also confirm that anthropogenic radioactive iodine is released into the environment in a different chemical form and is therefore absorbed differently than stable iodine [19].

Hausschild et al. (1985) analyzed the soil and the tree rings of a black locust that grew in the vicinity of the Nuclear Fuels Reprocessing plant of Karlsruhe. They measured a ratio of $6.7 \cdot 10^{-5}$ and $1 \cdot 10^{-5}$ in the surface and deep soil after major ^{129}I releases, respectively. The $^{129}\text{I}/^{127}\text{I}$ ratio in the tree rings before the excessive release of ^{129}I by the nuclear reprocessing plant had a mean value of $0.23 \cdot 10^{-6}$ and a mean ratio of $5 \cdot 10^{-6}$ after the ^{129}I release. The ^{129}I concentrations remained constant, even after a filter for ^{129}I was installed at the facility in 1975. Hausschild et al. suggest that iodine is mainly absorbed via the roots and not through foliar absorption [38].

Rao et al. (2002) analyzed both surface and deep soil as well as tree rings of different ring porous and semidiffuse trees from different locations in the USA. They reported different iodine concentrations for various trees. The $^{129}\text{I}/^{127}\text{I}$ ratios of trees located in West Valley ranged between $(9 - 390) \cdot 10^{-8}$ in the xylem and $1.7 \cdot 10^{-5}$ in the bark. Correspondingly, the soil from West Valley showed ratios ranging between $(9 - 151) \cdot 10^{-7}$. Trees located in Rochester showed significantly lower values, ranging between $(6.08 - 249) \cdot 10^{-10}$ in the xylem and $2.1 \cdot 10^{-7}$ in the bark. The soil contained ratios between $(0.03 - 3.0) \cdot 10^{-7}$. Here the uptake of iodine through the roots is suggested as the main pathway into the trees xylem [30].

It can be concluded that the iodine uptake by trees depends on the availability of soluted iodine in the soil and the soil quality as well as gaseous iodine in the atmosphere but especially the tree species itself. Summarising, various literatures suggest different pathways of iodine uptake in trees. A compiled list of the $^{129}\text{I}/^{127}\text{I}$ ratios can be found in Tab. 6.3.

As can be seen in Tab. 6.3, the $^{129}\text{I}/^{127}\text{I}$ ratio in the environment exhibits significant variability. This is likely due to the complex environmental chemistry of iodine, which involves soluble, insoluble, volatile, and organic-bound species. The pathways by which anthropogenic ^{129}I and natural ^{127}I enter the samples are different and not fully understood. Despite this complexity, the wide dynamic range of ^{129}I concentrations, spanning several orders of magnitude, can still support robust conclusions when the data is analyzed on a logarithmic scale [39].

Table 6.3: $^{129}\text{I}/^{127}\text{I}$ Ratios in Soil and Tree Rings.

Study	Tree Species and Location	$^{129}\text{I}/^{127}\text{I}$ Ratio	Measurement
Zhao et al. (2019) [19]	Spruce; Northeast Qinghai-Tibet Plateau, China	$3 \cdot 10^{-9}$	Surface soil
		$1 \cdot 10^{-11}$	Deep soil
		$(6 - 15) \cdot 10^{-9}$	Tree rings (1. Spruce)
		$(4 - 20) \cdot 10^{-9}$	Tree rings (2. Spruce)
Hausschild et al. (1985) [38]	Black locust; Karlsruhe, Germany	$6.7 \cdot 10^{-5}$	Surface soil
		10^{-5}	Deep soil
		$0.23 \cdot 10^{-6}$	Tree rings (before ^{129}I release)
		$5 \cdot 10^{-6}$	Tree rings (after ^{129}I release)
Rao et al. (2002) [30]	Elm, locust, oak, cherry; maple, West Valley NY, USA	$(0.09-3.9) \cdot 10^{-6}$	Tree rings
		$1.7 \cdot 10^{-5}$	Bark
	Rochester, NY	$(0.09-1.51) \cdot 10^{-5}$	Soil
		$(0.061-2.49) \cdot 10^{-8}$	Tree rings
		$2.10 \cdot 10^{-7}$	Bark
		$(0.03-3.0) \cdot 10^{-7}$	Soil

7 Strontium

Sr 85	Sr 86	Sr 87	Sr 88	Sr 89	Sr 90
67.7 m	64.850 d	9.86	2.81 h	7.00	82.58
$t_{1/2}$ 232...	$t_{1/2}$ 388	$t_{1/2}$ 388	$t_{1/2}$ 388	$t_{1/2}$ 388	$t_{1/2}$ 388
ϵ , β^+ ...	ϵ , β^+ ...	ϵ , β^+ ...	ϵ , β^+ ...	ϵ , β^+ ...	ϵ , β^+ ...
γ 151...	γ 514...	γ 388	γ 388	γ 388	γ 388
σ 0.81 + 0.23	σ 0.0058	σ 0.0058	σ 0.0058	σ 0.0058	σ 0.0058
β^- 1.5...	β^- 0.5	β^- 0.5	β^- 0.5	β^- 0.5	β^- 0.5
γ (909)	γ (909)	γ (909)	γ (909)	γ (909)	γ (909)
g	g	g	g	g	g
σ 0.42	σ 0.010	σ 0.010	σ 0.010	σ 0.010	σ 0.010

Figure 7.1: Karlsruhe chart of nuclides showing strontium isotopes, ^{90}Sr , ^{89}Sr , ^{87}Sr , ^{86}Sr and ^{85}Sr , 8th edition (2012).

Strontium appears as a group 2 alkaline earth metal and typically shows similar chemical properties to its homologues calcium and barium. It has an atomic number of 38 and in the naturally occurring stable isotopes are: ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr with a natural abundance of 0.56 % 9.86 % 7.00 % and 82.58 % respectively [40]. In nature, strontium occurs abundantly in the earth's crust, with approximately 340 parts per million (ppm), placing it in close proximity to barium with 500 ppm. Strontium is predominantly present within minerals such as strontianite, existing as carbonate (SrCO_3), and celestite, existing as sulfate (SrSO_4) [41].

Radioactive strontium isotopes are naturally produced on earth only in very rare cases, like spontaneous fission [42]. Strontium isotopes with mass numbers $A \leq 85$ or less commonly experience electron capture or β^+ -decay, while those with $A \geq 89$ and higher usually undergo β^- -decay. The most abundant radioactive isotopes are ^{85}Sr , ^{89}Sr and ^{90}Sr . While the first two typically have applications in nuclear medicine, the latter was released into the environment due to nuclear weapon testing and nuclear accidents in the past.

Because of the similar chemical properties of strontium to calcium, radioactive strontium can pose a high risk to human health. The human body absorbs and integrates strontium instead of calcium and elevated ^{90}Sr concentrations in the body can lead to skeletal diseases, anaemia, leukaemia and metabolic imbalances [40].

7.1 ^{90}Sr in the environment

^{90}Sr has a half-life of 28.90 [43] years and is as a fission product of uranium or plutonium. It decays to ^{90}Y ($T_{1/2} = 64.1\text{h}$) through β^- -decay, which subsequently also decays through β^- -decay to ^{90}Zr , which is stable. Its decay chain is shown in Fig. 7.2 [40].

7 Strontium

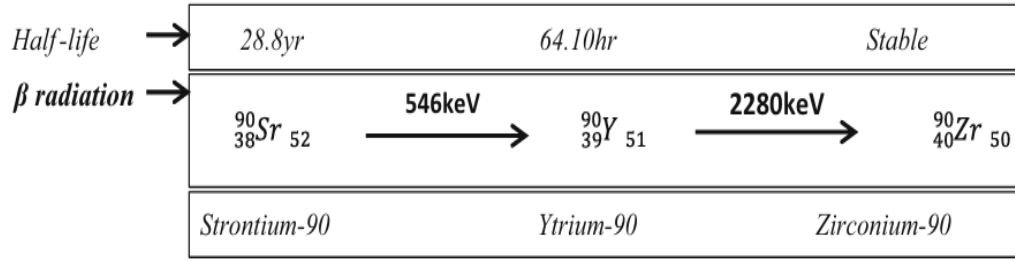


Figure 7.2: Decay chain diagram of ^{90}Sr taken from [40].

In 1986, the Chernobyl power plant accident contaminated at least 30.000 km^2 with 10 kBq m^{-2} of radioactive strontium. In 2011 the Fukushima nuclear power plant accident released ^{90}Sr activities in seawater of up to 1500 kBq m^{-3} at the Fukushima plant port. The highest amount of ^{90}Sr however, was spread by the nuclear weapon testing with an estimated value of roughly $6 \cdot 10^{14}\text{ kBq}$ [44].

Table 7.1: ^{90}Sr contamination from different nuclear incidents.

Incident	Contaminated Area/Release	Activity Level
Chernobyl (1986)	Estimated global spread	10 kBq m^{-2}
Fukushima (2011)	Released in seawater at Fukushima plant port	1.500 kBq m^{-3}
Nuclear Weapon Testing (1950-1963)	Estimated global spread	$6 \cdot 10^{14}\text{ kBq}$

An investigation on the behavior of radionuclides in the environment by Von Gunten et al. (1995) ([45]) lead to the conclusion that under environmental conditions, radioactive strontium behaves identically to its stable isotopes in the atmosphere. ^{90}Sr is a constituent within small particles, stemming from the nuclear explosions. It is dominantly found as strontium oxide (SrO) bound to form aerosols and it reacts rapidly with hydrogen to Sr^{2+} and SrOH^+ .

Its deposition on the earths surface usually is carried out by precipitation [41] and the ^{90}Sr distribution depends on the spreading event. If the emitted ^{90}Sr -containing aerosols are released by a nuclear plant, depending on their size they can travel tens to hundreds of kilometers, causing a local to semi-global fallout zone. If the ^{90}Sr particles reach the stratosphere, through a major explosion, depending on their size, the ^{90}Sr aerosols can travel for years around the globe, causing a global fallout. When aerosols containing

radioactive strontium settle on the Earth's surface, the strontium is released from the aerosols. This release process depends on weather conditions and the composition of the soil. Once released, the radioactive strontium dissolves into the soil, making it available for plant uptake [41].

7.1.1 Stable Sr and ^{90}Sr uptake by plants

Stable strontium is found in trees, where the concentration depends on the plant itself and the plant part analyzed. A table of typical Sr concentrations found in trees can be seen in Tab. 7.2. In soil, metal availability and plant uptake are influenced by various factors including pH, humidity, and soil organic content. The process is facilitated by root exudates-substances such as organic acids, sugars, and amino acids secreted by plant roots which enhance the uptake of strontium from the soil by transforming minerals into forms that are easier for plants to absorb. While strontium is also deposited in leaves, the majority of strontium found in the tree's stem primarily originates from uptake by the roots [40].

Table 7.2: Stable strontium concentrations in different tree species.

Study	Tree Species	Location	Concentration Measurement ($\mu\text{g/g}$)	
Kagawa et al. (2002)	Japanese cedar	Hiroshima	4-7	Tree rings
	Japanese cedar	Yamagata	8-9	Tree rings
	Japanese persimmon	Kyoto	10-11	Tree rings
Chigira et al. (1988)	Japanese cedar	Takao	4.5-13	Tree rings
	Japanese cedar	Tsukui	3.4-7	Tree rings
	Japanese cedar	Takao	116	Bark
	Japanese cedar	Tsukui	25	Bark
Miller et al. (2014)	Engelmann spruce, located on quartzite	Little Cottonwood Canyon	5.2-10.49	Tree rings

The "Transfer Factor" (TF), defined by Burger et al. (2019), represents the ratio of the concentration of strontium in the plant to the concentration of strontium in the soil:

$$TF = \frac{\text{Sr conc. in plant}}{\text{Sr conc. in soil}} \quad (7.1)$$

The TF depends on the solubility of strontium in the soil, since metals are taken up in soluted form. Plants growing in wet environments have a significantly higher TF factor than compared to plants in dry regions.

Furthermore, competing ions like calcium, potassium and magnesium can interfere with

7 Strontium

strontium uptake, due to competitive inhibition at the root uptake sites. Plant cells use specialized systems to absorb essential minerals. While no unique transporting channels for strontium are known, due to the chemical similarities it can utilize channels, meant for calcium and potassium to enter the plant cells. When abundant calcium or potassium is present in the soil, plants may absorb less strontium because they share the same pathways for uptake. This competition can result in a reduced intake of strontium [41].

Various studies have investigated strontium concentrations in different plant types, including crops, algae, trees and others. The conclusion reached was that strontium uptake and its incorporation into plant tissues vary significantly among different plants, with even subtle differences observed among trees. A comprehensive list compiling these studies, which details the strontium uptake for various plants, can be found in [41].

Using Ca to track Sr uptake by trees

Calcium and strontium are chemically homologue elements, each forming divalent cations (Ca^{2+} and Sr^{2+}) and exhibiting similar ionic radii, with strontium having a radius of 113 pm and calcium of 99 pm. Due to these similarities, the behaviors of these elements within biological systems, particularly plants, often display notable parallels. This congruence has lead researchers to explore the uptake and incorporation mechanisms of these elements in greater detail [46].

Calcium, as a macro-nutrient, is abundant in trees and has been extensively studied for its essential roles in cellular processes and structural functions within plant tissues. The well-documented pathways and mechanisms of calcium uptake and transport within trees provide a valuable framework for understanding how strontium, too, might be assimilated into plant biomass.

While leaves can absorb alkali earth metals such as calcium and strontium, further transport within the phloem is negligible. This implies that despite the absorption capabilities of leaves, transportation into the xylem is unlikely because it relies on the phloem (see chapter 5.1.4), which does not effectively convey these minerals to the xylem. However, calcium is also absorbed through the root system, where it serves as an essential macro nutrient crucial for plant health. In healthy trees, for instance, as much as $5000 \text{ mg Ca kg}^{-1}$ dry matter can be present [17]. Calcium, once absorbed through a plant's roots, is incorporated into the xylem cell walls, enhancing the plant's structural integrity and overall health. Due to its integration into the xylem, calcium exhibits low long-term mobility within the plant. Similarly, if strontium behaves like calcium and is available in a soluble form in the soil, it too could be expected to show low mobility in the xylem while being continuously absorbed through the roots [47].

Furthermore, it is important to consider whether isotopic fractionation influences the uptake of strontium by plants, as this could significantly impact the accuracy of dendro-chemical analyses.

Sr isotopic fractionation in the environment

Speciation studies on the uptake of radiostrontium are lacking in the scientific community. This is due to the difference of chemical preparation methods and the applied measurement techniques between the measurement studies of ^{90}Sr [16]. The kinetic fractionation factor of stable $\delta^{88}\text{Sr}/^{86}\text{Sr}$ in soy sprout beans was analyzed by Choi et al. (2023) [48]. Additionally $\delta^{88}\text{Sr}/^{86}\text{Sr}$ was analyzed in soil and aqueous solutions by Shalev et al. (2013) [49] and Alkhatib et al. (2022) [50] respectively. It was concluded that plants favored the uptake of the lighter ^{86}Sr isotope. This conclusion was based on the analysis of the nutrient solution before and after the plants uptake period. The remaining nutrient solution showed an increased $\delta^{88}\text{Sr}/^{86}\text{Sr}$ value, ranging from +0.25 ‰ to +0.42 ‰ relative to the standard, indicating preferential absorption of the lighter isotope by the plants [48].

The mentioned studies all confirm an isotope fractionation based on the mass of the isotopes between ^{88}Sr and ^{86}Sr , with the fractionation factor typically found in the first decimal place of ‰. In comparison, the $\delta^{13}\text{C}$ factor in trees averages around 25 ‰, which is a factor of 100 times larger. Furthermore, Miller et al. (2014) measured $\delta^{88/86}\text{Sr}$ values at various mountain regions in the Little Cottonwood Canyon area in Utah, USA. They found minimal differences in $\delta^{88/86}\text{Sr}$ values for trees located within the same forest mountain site. It is also noted that the study did not include fractionation factors in their calculations [51]. Furthermore Von Guten et al. (1995) made the assumption that under environmental conditions heavier radioisotopes acquire the speciation of their stable isotopes over a range of time [52]. Therefore, the fractionation of Sr in this study is considered negligible.

8 Measurement techniques and sample preparation

8.1 Samples

In the scope of this thesis, coniferous trees were investigated. The trees chosen were three spruces and one larch for dendrochronological analysis. One birch was used for test samples.

Two spruces (*Picea abies*) were provided by BOKU (University of Natural Resources and Applied Life Sciences, Vienna) from Rosalia, Burgenland. The ages of the spruces were determined by Elisabeth Wächter B.Sc. to be 87 and 89 years old. The year of death is known to be 2020 for both, which allows for accurate dendrochemical analysis with the additional help of a program that uses reference tree discs as a comparison for synchronisation. These can be seen in Fig. 8.2a and Fig. 8.2b. However, as visualized in Fig. 8.1, the annual rings are cut out with a scalpel, and since one gram is needed for each sample in the case of iodine and strontium measurements, the uncertainty of one annual ring must be taken into account, as a single annual ring may not yield sufficient material for analysis.

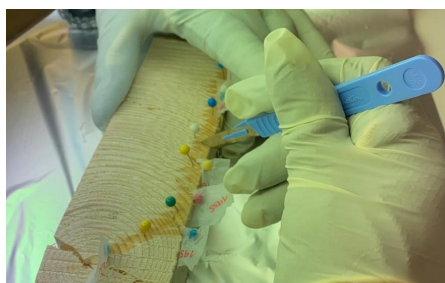


Figure 8.1: Cutting Spruce.1.

Another spruce tree was kindly provided by Mag. Dr. Stephanie Neuhuber of BOKU, from the Viennese woods in Vienna. It was dendrochronologically dated by Elisabeth Wächter B.Sc. and the year of death was determined to be 2023. It should be noted that some parts of the tree consist of very fine rings, as can be seen in Fig. 8.3a, adding years to the uncertainty when cutting out rings from these thinned areas. Furthermore, six years are estimated to be missing in the pointed out area in Fig. 8.3a. The tree's growth was likely impeded during this period, possibly due to the presence of a larger tree blocking

8 Measurement techniques and sample preparation

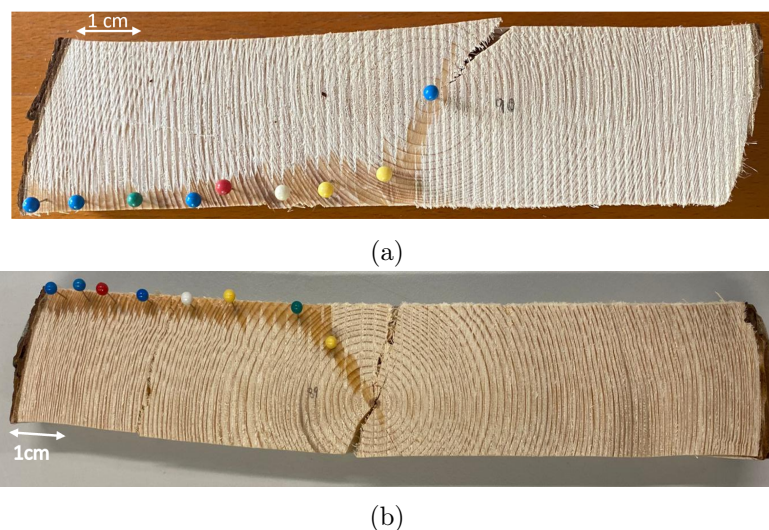


Figure 8.2: Coniferous trees: (a) Spruce.1 (*Picea abies*), estimated age: 90 years old; (b) Spruce.2 (*Picea abies*) age: 89 years old.

its sunlight and space. This tree is estimated to be 107 years old.

In addition, a 76-year-old larch (*Larix decidua*) from Zeltweg in Styria, Austria, shown in Fig. 8.4b, was kindly provided by Paul Horn. By showing clear rings and the exact death year of the tree being known, the tree could be well dendrochronologically analyzed.

Lastly, a birch tree originating from Dresden, Germany, was used as a test sample for iodine measurements to evaluate the effectiveness of the applied preparation chemistry. The age of the tree could not be determined as it had been severely decayed, likely due to poor environmental conditions and fungal infestation, which also obscured the clarity of its annual rings. It is expected to contain higher concentrations of radioisotopes because it comes from an area that may have been contaminated by a nuclear research reactor and radiochemical laboratories. Therefore, this tree was used as a test sample to evaluate the iodine chemistry preparation method, as it was highly likely to contain, among other elements, elevated iodine concentrations. This tree can be seen in Fig. 8.5a.



Figure 8.3: Coniferous trees: (a) Spruce.3 (*Picea abies*), estimated age: 105 years old; circled area points out the thinness of some tree rings; (b) Spruce.3 (*Picea abies*) as a whole piece, estimated age: 105 years old.



Figure 8.4: Coniferous tree: (a) Larch.1 tree-disc (*Larix Pinacae*) estimated age: 76 years old; (b) Larch.1 (*Larix Pinacae*) estimated age: 76 years old.



Figure 8.5: Birch trees from two different point of views, possibly contaminated with radioisotopes: (a) Tree disc as entire piece from above; (b) Section of tree disc prepared for sample examination, with red circles highlighting the selected rings.

For a clearer structure within the Master's thesis, the trees are given abbreviated names. The following table (Tab. 8.1) provides a summarized overview of the key characteristics and sampling details of the trees investigated in this study. It lists each tree by its designated ID, specifies its species and age, identifies the location where it was sourced, and outlines the specific years and conditions under which samples were taken for analysis.

Larch.1: The first tree to be analyzed was Larch.1. Two test samples for the first try were taken, one gram from the last 15 years (2009-2024) and 0.3 grams from the bark. Less material was taken out of the bark, because it was expected to have significantly higher radioisotope concentrations than in the xylem. Since its youngest tree ring was determined to be from the year 1948, one gram from each 1950, 1955, 1963, 1970, 1986, and 1990 were carved out.

Spruce.1, Spruce.2: Six rings were taken out of Spruce.1 and Spruce.2 as well, from the years 1950, 1955, 1963, 1970, 1986, and 1990, to have comparable data.

Spruce.3: Spruce.3 is significantly older and ten samples were taken, covering the years: 1920, 1930, 1940, 1950, 1955, 1963, 1986, 1990, and 2000.

Birch.1: Birch.1 was used as a test sample, providing a piece of wood, as it could not be dendrochronologically dated. Four samples were taken from this tree piece; the sample examination area can be seen in Fig. 8.5b.

Table 8.1: Summary of trees analyzed in the study.

ID	Species	Age	Location	Notes
Spruce.1	Spruce	86 y.o.	Rosalia, Burgenland, Austria	sampled for rings from 1950, 1955, 1963, 1970, 1986, 1990
Spruce.2	Spruce	90 y.o.	Rosalia, Burgenland, Austria	sampled for rings from 1950, 1955, 1963, 1970, 1986, 1990
Spruce.3	Spruce	105 y.o.	Viennese woods, Vienna, Austria	sampled for rings from 1920, 1930, 1940, 1950, 1955, 1963, 1986, 1990, 2000
Larch.1	Larch	76 y.o.	Zeltweg, Styria, Austria	sampled from 2009-2024; additional grams from bark and years 1950, 1955, 1963, 1970, 1986, 1990
Birch.1	Birch	N/A	Dresden, Germany	Test sample, not dendrochronologically dated; four samples taken

8.2 Chemical sample preparation

For both the strontium and iodine chemistry, a stable isotope carrier is added at the beginning of the chemistry process since the samples are expected to have very low concentrations of both elements. This method allows for the extraction chemistry to be performed through column exchange, enabling the determination of chemical yield from the precipitation process. Consequently, the concentration of ^{90}Sr in the sample can be calculated at a later stage. The chemical yield is determined through the following equation:

$$\text{chem. yield [\%]} = 100 \cdot \frac{\text{dry precipitate mass}}{\text{expected dry precipitate mass}} \quad (8.1)$$

The expected mass of the dry precipitate is calculated by multiplying the mass of the added isotope carrier by the ideal precipitate mass. This calculation provides an estimate of how much of the carrier was effectively transported through the chemical process, and how much was lost, rather than simply leached from the sample. However, caution should be exercised when interpreting the yield value, as it does not guarantee that all the dried precipitate consists solely of the target element.

8.2.1 Carbon

The ABA (Acid-Base-Acid) method is the most common method for pretreating wood samples, and it involves three steps: First, the sample is exposed to hydrochloric acid (1 M HCl) to remove carbonates, then in sodium hydroxide (0.1 M NaOH) to remove humic acids, and finally again in hydrochloric acid to eliminate CO_2 that may have been absorbed from the air during the alkaline treatment. Between each step, the sample is washed with deionised water for neutralization, and finally, the sample is placed in the oven to dry. The dried sample is weighed into tin foils and loaded into the AGE (Automated Graphitization Equipment). The graphitization process begins with the combustion of the sample in the Elemental Analyzer (EA), where the sample is oxidized to CO_2 . This CO_2 is then transferred to the AGE unit. In the AGE, the CO_2 is converted into elemental carbon by catalytic reduction at around 580°C . This process uses iron as a catalyst and hydrogen as a reducing agent. The reaction:



is controlled by selectively cooling the upper reactor tubes to -25°C to freeze out the resulting water and effectively shift the reaction to the right, favoring graphitization of the carbon. A schematic view of the AGE system can be seen in Fig. 8.6 [53]. The graphitized carbon sample is then pressed into an aluminium target holder, before being measured with AMS.

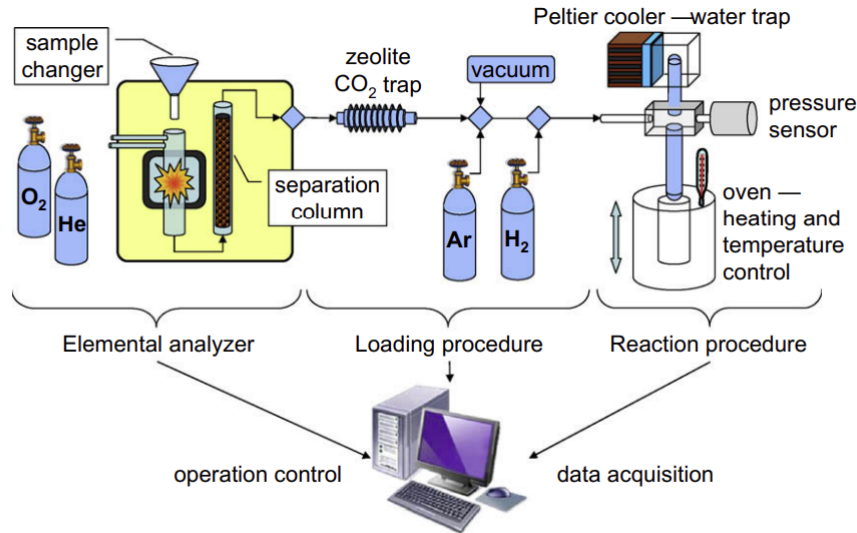


Fig. 1. Simplified operational scheme of the graphitisation line.

Figure 8.6: Simplified schematic view of the AGE system at VERA [53].

8.2.2 Strontium

The chemical method was adapted from Landstetter et al. (2016) [54], with slight modifications to accommodate the differences in sample material. It can be roughly divided into four steps: leaching, filtration, ion exchange and precipitation. A schematic diagram of the chemical process can be seen in Fig. 8.7. For each sample, one gram of wood was carved out of each tree ring. A stable strontium carrier, consisting of 0.1 g solution containing $(9773 \pm 50) \mu\text{g Sr/g}$ solution in 5% HNO_3 , was added to the sample.

Leaching: Each sample was leached in 15 ml 8 M HNO_3 (p.A. $\text{Sr} < 0.002 \text{ ppm}$). During the leaching process, the sample was gradually heated in a sand bath. It was exposed to temperatures of 50°C, 60°C, and 70°C, each maintained for one hour. After the heating cycle, the setup was turned off and allowed to rest overnight.

Filtering: The leached solution was centrifuged (4000 rpm) for five minutes before being separated from the wood sample by a filtering syringe with a $0.45 \mu\text{m}$ PTFE filter. Each sample was washed with 1-3 ml 8 M HNO_3 to make sure that as much leached solution was extracted from the wood as possible.

Ion exchange: The extracted solution is now loaded onto a 2 ml ion exchange column filled with 100-150 μm strontium specific 4,4(5)-di-*t*-butylcyclohexane-18-crown-6 (Eichrom Industries, Inc). The resin is pre-washed with 0.05 M HNO_3 to clean it from any unwanted strontium it may contain, and then conditioned with 8 M HNO_3 . After filling the column

8 Measurement techniques and sample preparation

with the sample solution, the column is first rinsed with 3 M HNO_3 to extract Ca from the resin. Afterwards, strontium is extracted from the resin with 10 ml 0.05 M HNO_3 into a PFA (perfluoralkoxy) container.

Precipitation: The PFA container with the Sr containing solution is placed on a hotplate and evaporated to dryness at 90°C . The residue is dissolved in $250\ \mu\text{l}$ sub-boiled water, and the container is washed three times with $130\ \mu\text{l}$ sub-boiled water. The solution is transferred into a reaction tube, where $130\ \mu\text{l}$ HF (40%) is added to precipitate SrF_2 . After allowing the reaction to proceed for at least 24 hours, the mixture is centrifuged (4000 rpm, 5 min), washed with 3x20 drops ethanol and then dried in a drying cabinet at 50°C . Lastly, SrF_2 is mixed with PbF_2 powder in an 1:8 ratio by weight and subsequently pressed into a copper target holder.

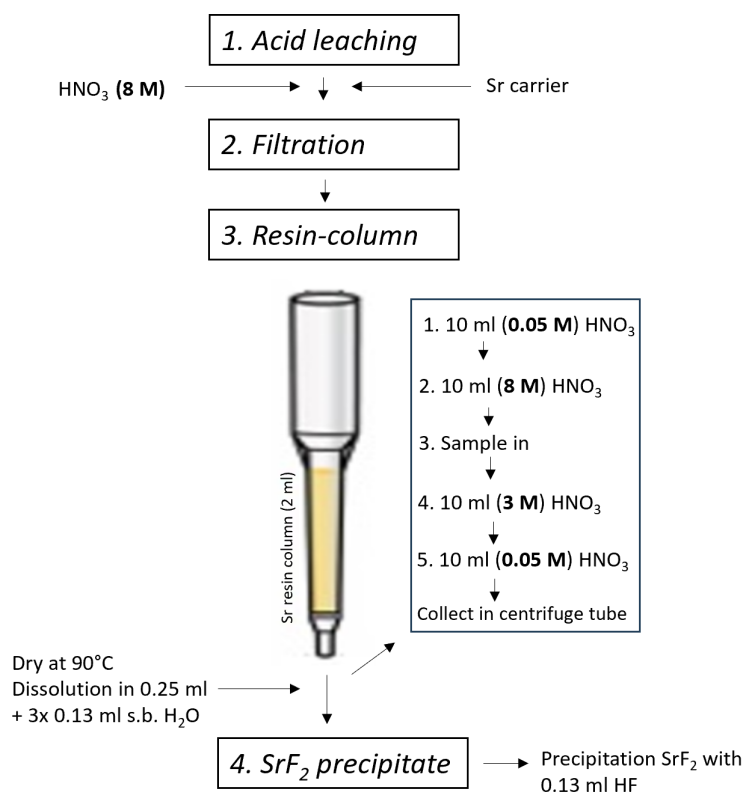


Figure 8.7: Schematic diagram for strontium preparation chemistry.

8.2.3 Iodine

Several methods have been developed for the extraction of iodine out of different matrices. While for solid environmental samples, an oxidative combustion method [19] as well as acid leaching and fusion methods [30, 55] have been used in the past, an acid leaching approach was attempted in this thesis. The leached solution underwent treatment following the method outlined by [39] with slight modifications, as part of the chemical extraction process for iodine from water samples. The chemical process can be divided into six steps: leaching, filtration, oxidation, reduction, anion exchange and precipitation, as seen in Fig. 8.8.

Leaching: Two samples were taken from the same part of the tree to facilitate comparison, as two different concentrations were tested in the leaching process (Fig. 8.5a). A stable ^{127}I isotope carrier with a concentration of 10.091 mg ^{127}I /g is added to each sample. To leach iodine from the wood samples, HNO_3 is used. Each sample was leached once with 15 ml of 0.1 M HNO_3 and 1 M HNO_3 respectively, to evaluate which concentration performs better. For the leaching process, the same procedure as in section 8.2.2 was used. The samples were leached in a sandbath for three hours, starting with a temperature of 50°C and increasing it by 10°C each hour, up to 70°C.

Filtration: The residues were separated from the leached solution using a filtering syringe, and the sample was washed three times with 2 ml of 0.1 M HNO_3 and 1 M HNO_3 . 120 ml of deionised H_2O together with 5-10 ml of 0.1 M NaOH were added to the samples leached with 0.1 M HNO_3 , until a pH value of 6-7 was achieved. The samples leached with 1 M HNO_3 were filled with 135 ml of 0.1 M NaOH and pH-stripe tested until the solution had a pH value of 6-7. The samples were then stirred for 15 minutes using a magnetic stirrer.

Oxidation: For the oxidation of I^- and organic iodine compounds to I^{5+} , 5 ml of saturated $\text{Ca}(\text{ClO})_2$ solution is added to the samples during the stirring process. The samples are stirred for another 15 minutes. This step is important to destroy organic iodine compounds and allow all iodine in the sample to transform to IO_3^- [56].

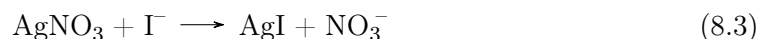
Reduction: To reduce I^{5+} to I^- 20 ml of (1M) $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 1 g of $\text{Na}_2\text{S}_2\text{O}_6$ was added to the solution and stirred for 45-60 minutes. This step is necessary to create a uniform oxidation state, i.e. I^- charged iodine ions in the solution, to facilitate anion exchange and subsequent precipitation as AgI , since in environmental samples, iodine can exist in different valence states as organic compounds [57].

Anion exchange: For the anion exchange, 6 ml 1*8 (100-200 mesh) Dowex resin per column is treated with 2.25 M KNO_3 to eliminate any iodine contained in the resin and then conditioned with 0.5 M KNO_3 . The sample is then adjusted with 7 M NaOH to achieve a pH value of 5-6, before loading it onto the column. The anion exchange resin

8 Measurement techniques and sample preparation

contains functional groups that act selectively towards different anions based on their electron affinities. It specifically targets ions for separation from other non-binding sample components, making the resin preserve the I^- and washing out impurities and other ions [39]. Each column is then washed with 50 ml of 0.5 M KNO_3 before the trapped iodide is rinsed out with 15 ml (2.25M) KNO_3 and collected in centrifuge-tubes.

Precipitation: 0.5 ml of 0.1 M AgNO_3 is added to the I^- containing solution in the centrifuge tubes to precipitate AgI , see equation 8.3:



The solution is stored in the dark for at least 24 hours. The solution is then centrifuged, and the precipitate is separated from the solution, transferred to a weighed, dark reaction tube, dried at 50°C , and mixed with Ag-powder (99% purity) at a 1:1 ratio, by weight. The mixture is finally pressed into a copper target holder, to be measured by Accelerator Mass Spectrometry.

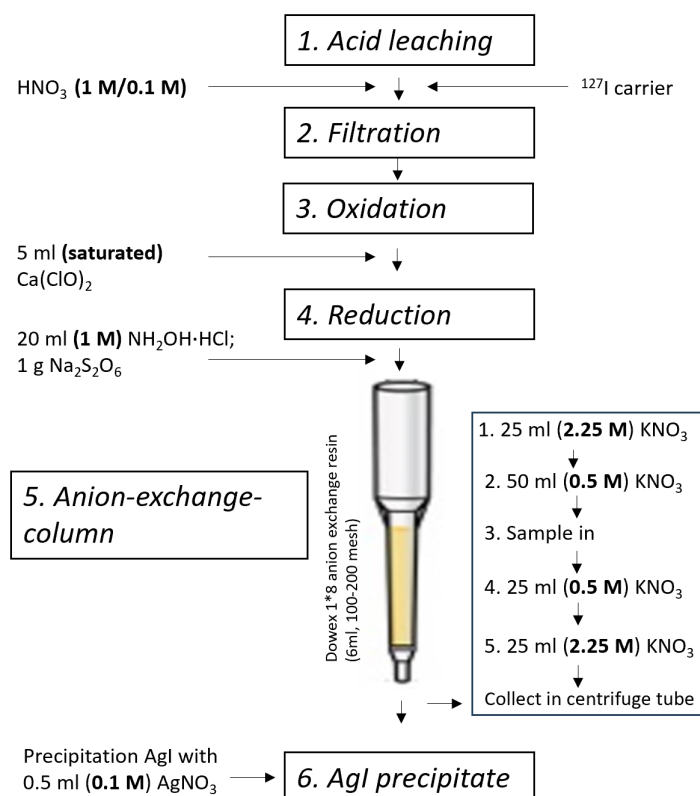


Figure 8.8: Schematic diagram for iodine preparation chemistry.

8.3 Accelerator Mass Spectrometry (AMS) at VERA (Vienna Environmental Research Accelerator)

All radioisotopes measured in this thesis were measured at VERA with either Accelerator Mass Spectrometry (AMS) or Ion-Laser InterAction Mass Spectrometry (ILIAMS). The basic goal of AMS is to measure isotopic ratios of long-lived radioisotopes with low abundances, by succession of energy and momentum filters. In many cases, an isobar with the same mass as the desired isotope must be suppressed using additional components integrated into the beamline. A typical setup for conventional AMS consists of an ion source, magnetic and electrostatic components, a tandem accelerator, and a detector. To follow and detect the ion beam through the beamline, Faraday Cups (FC), which measure the ion currents of the stable ion beam, are placed within the beamline. In the following paragraphs, a short overview of the components at VERA is given [58].

Ion source VERA uses two ion sources, both being MC-SNICS (Multi Cathode Source for Negative Ions by Cesium Sputtering) sources, using positive Cs^+ ions, with an energy of a few keV to sputter negative ions out of a sample target and thus forming a negatively charged ion beam. The ionization yield strongly depends on the ionized atom's or molecule's electron affinity. In some cases, the ion source already serves as a isobar suppression tool, since no interfering, negative ions are formed for certain elements like ^{14}C , ^{129}I , and ^{26}Al [58].

Electrostatic Analyzer (ESA) The Electrostatic Analyzer (ESA) usually consists of two electrodes in a spherical shape with a radius r , which are at a distance d from each other. A charged particle's trajectory in an electric field is dependent on its E/q ratio, and its bending radius is connected to the ESA parameters according to the following equation:

$$U = \frac{2Ed}{qr} \quad (8.4)$$

where E is the ion energy, q is the ionic charge, and U is the voltage potential. At constant values of q , r and d the ESA at AMS facilities is used to select wanted isotopes according to their energy-charge ratio (E/q) [59].

Bending Magnet (BM) The deflection angle of the bending magnet at VERA is $\Omega = 90^\circ$, therefore the Lorentz force can be used to calculate the magnetic field acting on an incoming ion:

$$B = \frac{\sqrt{2mE}}{qr} \quad (8.5)$$

At fixed energy E and charge, q the BM is used to filter isotopes by their momentum over charge ratio (p/q) [59].

Tandem accelerator The tandem accelerator at VERA is a 3 MV accelerator which consists of two pellet chains and a positive terminal. The anion beam is accelerated towards the positively charged terminal, where, due to collisions with stripping gas atoms, (depending on the measured element, helium or argon) the ions are stripped to positive charge states. Due to stripped off valence electrons, molecular bonds are broken up. The beam is accelerated at the second part of the accelerator again, now by repulsion of the positively charged terminal:

$$E_{HE} = (E_{inj} + q_{LE} \cdot U_{term}) \cdot \frac{m_{HE}}{m_{LE}} + q_{HE} \cdot U_{term} \quad (8.6)$$

where "HE" and "LE" stand for high energy and low energy sides. The low energy side being the beam line before the accelerator and the high energy side being the beam line after the accelerator. E_{inj} is the injection energy of the ions, m is the mass, and q is the charge. U_{term} is the terminal voltage [60].

Detectors For the detection of rare isotopes, suitable detectors are used for each radioisotope. Depending on the wanted isotope and the existence of an isobar in the beam line, a gas ionization chamber (GIC) or solid state detectors are used for detection [60].

8.4 Ion-Laser Interaction Mass Spectrometry (ILIAMS)

Behind the second ion source and the bending magnet, a laser setup connected to a radio frequency quadrupole (RFQ) cooler system, filled with buffer gas (He, HeO₂) can be seen in Fig. 8.10. The ILIAMS setup is used to suppress unwanted isobars from wanted isotopes. Through interactions between the ions and the buffer gas molecules, the kinetic energy of the ions that pass through is lowered, and the beam is cooled inside the RFQ. A continuous-wave-laser is guided into the RFQ system, where unwanted isobars are selectively neutralized by photo-detachment. The difference in detachment energy between the unwanted isobar and the wanted isotope is made use of in this method, allowing to detach an electron from an unwanted isobar and thus removing it from the beamline [61]. A schematic overview of AMS at VERA is shown in Fig. 8.9.

8.4 Ion-Laser Interaction Mass Spectrometry (ILIAMS)

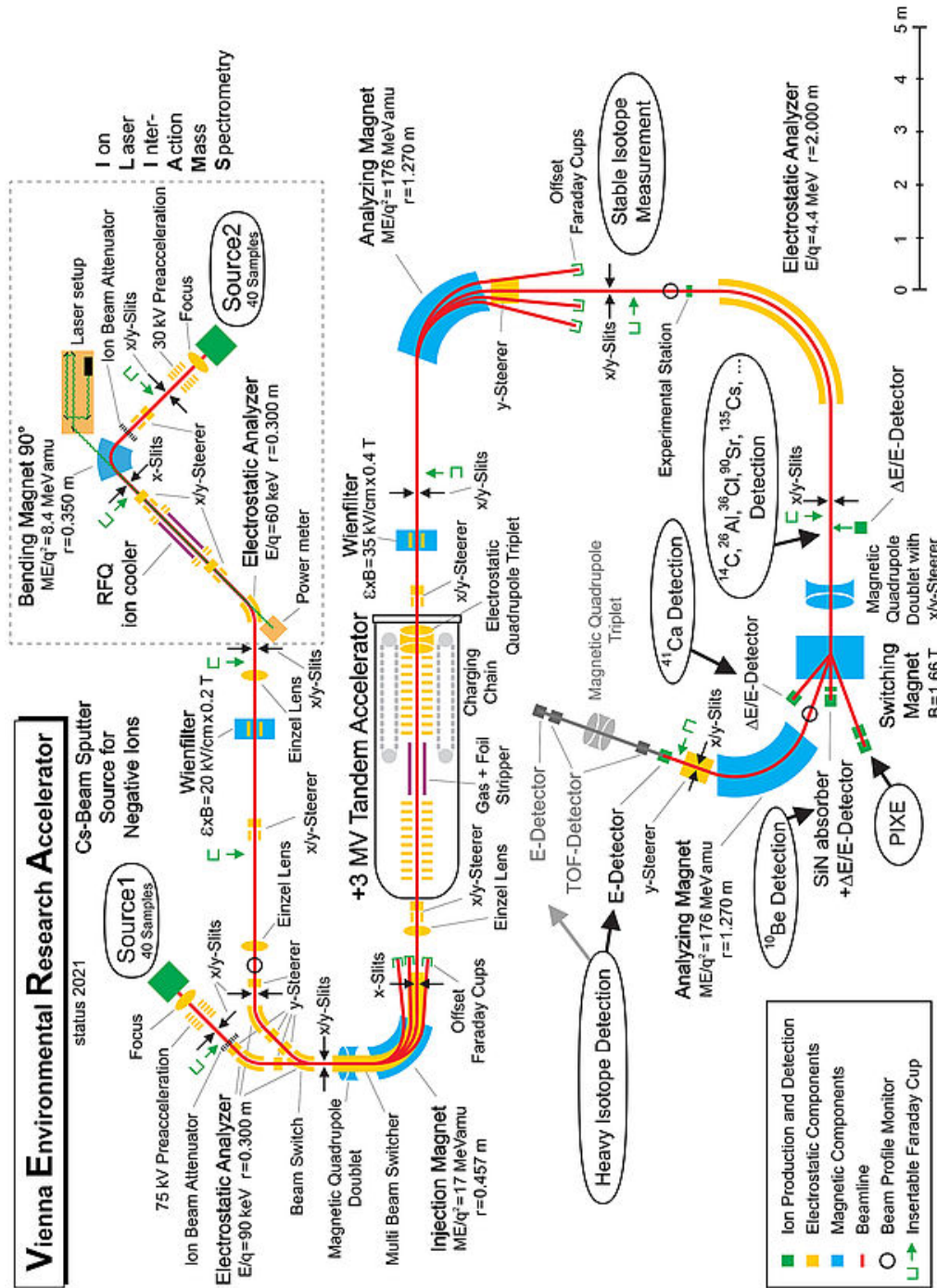


Figure 8.9: Schematic overview of Vienna Environmental Research Accelerator (VERA); 2024.

8.5 ^{14}C measurement with AMS

The ^{14}C measurement at VERA starts with Source 1 where the samples are sputtered with Cs^+ ions and accelerated to 70 keV. The ions are separated by their E/q and m/q ratio accordingly to their mass of ^{12}C , ^{13}C and ^{14}C . In the accelerator molecular isobars ($^{12}\text{CH}_2^-$, $^{13}\text{CH}_2^-$, Li_2^-) are broken up. [62] The magnet is used to separate ions by their mass-to-charge (m/q) ratio, selecting a 3+ state for the ^{14}C ions on the high energy side. Subsequently, the electrostatic analyzer (ESA) is used to sort them by their energy-to-charge (E/q) ratio. A multi-beam switcher is used to switch between ^{14}C , ^{13}C and ^{12}C ions, and for each ^{13}C and ^{12}C the ion current is measured in a Faraday cup while ^{14}C is measured in a gas ionization detector.

percentage modern carbon (pMC [%]), $\delta^{13}\text{C}$ One important factor to consider is isotope fractionation, particularly the varying incorporation of carbon isotopes into the environment. This is why, in the case of carbon the second stable isotope ^{13}C is additionally measured. For instance, during the process of photosynthesis, ^{12}C is absorbed slightly more readily than ^{13}C , and ^{13}C more than ^{14}C . Both chemical and physical isotope fractionation can alter the isotope ratio within the sample, necessitating correction. This correction is achieved by calculating the fractionation factor, which is done by dividing the sample's or standards blank corrected $^{14}\text{C}/^{12}\text{C}$ ratio with the square of its corresponding $^{13}\text{C}/^{12}\text{C}$ ratio, as seen in [8.7], [8.8].

$$F_{12,13,14,\text{sample}} = \frac{\left(\frac{^{14}\text{C}^{3+}}{^{12}\text{C}^{3+}}\right)_{\text{sample, blankcorr}}}{\left(\frac{^{13}\text{C}^{3+}}{^{12}\text{C}^{3+}}\right)_{\text{sample}}^2} \quad (8.7)$$

$$F_{12,13,14,\text{standard}} = \frac{\left(\frac{^{14}\text{C}^{3+}}{^{12}\text{C}^{3+}}\right)_{\text{standard, blankcorr}}}{\left(\frac{^{13}\text{C}^{3+}}{^{12}\text{C}^{3+}}\right)_{\text{standard}}^2} \quad (8.8)$$

Using the fractionation factors of both standard and sample; the sample percentage of modern carbon (pMC[%]) value can be calculated [63, 59], as seen in [8.9]. A list of Standards used for the measurement can be seen in Tab. [8.2]

$$\text{pMC}_{\text{sample}} = \frac{F_{12,13,14,\text{sample}}}{F_{12,13,14,\text{standard}}} \cdot \text{pMC}_{\text{standard, nominal}} \quad (8.9)$$

Additionally the $\delta^{13}\text{C}$ value can be calculated, dividing the samples measured $^{13}\text{C}/^{12}\text{C}$ with a measured standard and multiplying it with a fixed, nominal standard $\delta^{13}\text{C}$ value. This value gives information on the ^{13}C deviation of the measured sample compared to a given nominal value $^{13}\text{C}_{\text{standard,nominal}}$. $\delta^{13}\text{C}$ is calculated with:

$$\delta^{13}\text{C} = 1000 \cdot \left(\left(\frac{\left(\frac{^{13}\text{C}^{3+}}{^{12}\text{C}^{3+}}\right)_{\text{sample}}}{\left(\frac{^{13}\text{C}^{3+}}{^{12}\text{C}^{3+}}\right)_{\text{standard}}} \right) \left(1 + \frac{\delta^{13}\text{C}_{\text{standard,nominal}}}{1000} \right) - 1 \right) \quad (8.10)$$

Table 8.2: Standards and Blanks Used for Correction.

Name	Material	pMC [%]
OX-II	Oxalic acid	134.07 ± 0.1
IAEA-C3	Cellulose	129.41 ± 0.06
IAEA-C6	Saccharose	150.61 ± 0.11
ETH WinC	Wood	95.87 ± 0.049
Lab Blank 1	Black coal	-
Lab Blank 2	Charcoal	-
Machine Blank	Charcoal	-

All standards listed in Tab. 8.2 are used to correct for systematic checks within the AMS instruments. Additionally, the black and charcoal blanks are particularly useful for identifying contamination during the chemistry preparation process or within the ion source itself. Furthermore, cellulose and wood standards provide an effective method for accounting for isotopic fractionation.

8.6 ^{90}Sr measurement with ILIAMS at VERA

The ^{90}Sr measurements at VERA were performed under the supervision of Mag. Dr. Martin Martschini. Cs^+ ions are used to sputter a $\text{PbF}_2 + \text{SrF}_2$ (8:1) target in the ion source, before the beam is accelerated to 30 keV and sorted by its mass-to-charge ratio for $^{90}\text{SrF}_3^-$ and $^{88}\text{SrF}_3^-$, i.e. mass 147 and 145 respectively. The beam is decelerated before being injected into the RFQ cooler, filled with buffer gas and further decelerated to less than 1 eV. For the measurement of ^{90}Sr , a combination of O_2 and He (1:30) is chosen as buffer gas [65].

A 12 W laser (VERDI V18, Coherent Inc., 532 nm (2.33 eV)) is used for photodetachment to remove an electron from the isobar ZrF_3^- , due to its lower detachment energy (<2.33 eV) compared to SrF_3^- , thereby eliminating it from the ion beam line. Additionally, chemical reactions between O_2 and the isobar $^{90}\text{ZrF}_3^-$ also lead to the separation of $^{90}\text{ZrF}_3^-$ [65]. Afterwards, the beam is reaccelerated to 30 keV and sorted by its E/q ratio using an electrostatic analyzer after the RFQ cooler. It is then further sorted by its m/q ratio using a magnet. The beam is then directed into an accelerator where $^{90}\text{SrF}_3^-$ and any remaining molecules are fragmented before the ions in the 3+ state are sorted by mass 90 using a magnet. Next, the beam is sorted by its E/q ratio using an ESA before $^{90}\text{Sr}^{3+}$ is measured in a two anode gas ionization detector (GIC), allowing for differentiation between $^{90}\text{Sr}^{3+}$ and any residual $^{90}\text{Zr}^{3+}$ based on the differences in Z-dependent energy loss characteristics $\Delta E - E$ [64]. The pathway of SrF_n from the ion source to the detector can be seen in Fig. 8.10.

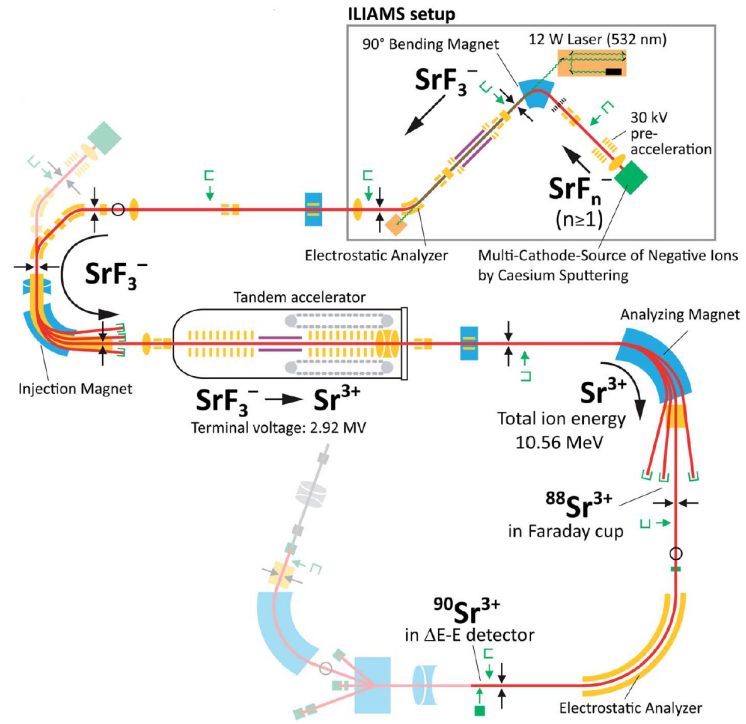


Figure 8.10: Schematic view of VERA and the pathway to measure $^{90}\text{Sr}^{3+}$ with ILIAMS [64].

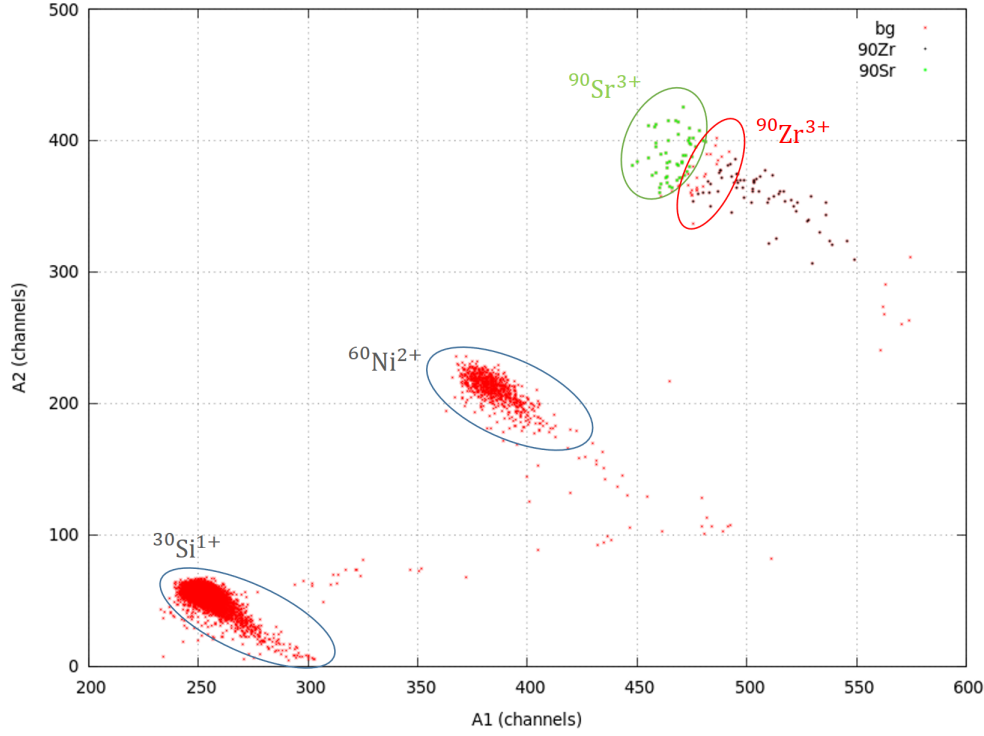


Figure 8.11: $^{90}\text{Sr}^{3+}$ (green circle, upper right) and $^{90}\text{Zr}^{3+}$ (red circle, upper right) isobar separation within the GIC-detector containing two anodes for isobar separation. All events for $^{90}\text{Sr}^{3+}$ and $^{90}\text{Zr}^{3+}$ originate from run 2. for the year 1970 ring of sample Spr.1.

An example spectrum from one run is shown in Fig. 8.11, illustrating the distinction between ^{90}Sr and ^{90}Zr in the GIC. To be able to define the energy area of ^{90}Zr in the spectrum, a target containing ZrF_4 and no ^{90}Sr is measured. In the Faraday cup positioned before the detector, the current of $^{88}\text{Sr}^{3+}$ is measured. This allows for the calculation of an isotopic ratio from the ^{90}Sr counts obtained from numerous runs and the currents of $^{88}\text{Sr}^{3+}$. An in-house standard Sr-12J with a defined $^{90}\text{Sr}/\text{Sr}$ ratio of $(3.75 \pm 0.09) \cdot 10^{-12}$ was measured for the normalization of the obtained ratios. Furthermore a machine blank containing a mixture of SrF_2 and PbF_2 , and no ^{90}Sr , is measured to monitor instrumental contamination.

^{90}Sr value determination To determine the ^{90}Sr concentration in the sample, the following method is used:

$$^{90}\text{Sr} = \frac{^{90}\text{Sr}}{^{88}\text{Sr}_{\text{sample}}} \cdot (^{88}\text{Sr}_{\text{carrier}} + ^{88}\text{Sr}_{\text{sample}}) \quad (8.11)$$

Table 8.3: Measured standards and their properties for ^{90}Sr measurements with ILIAMS.

Standard	$^{90}\text{Sr}/\text{Sr}$ Ratio	Composition	Purpose
Zircon Target	N/A	ZrF_4	Define energy area of ^{90}Zr
Sr-12J	$(3.75 \pm 0.09) \cdot 10^{-12}$ (Reference date: 18.10.2021)	SrF_2	Normalization of obtained ratios
Machine Blank	N/A	SrF_2 , PbF_2 (1:8 mass ratio)	Correct for instrumental contamination
Procedure Blank	N/A	SrF_2 , PbF_2 (1:8 mass ratio)	Ensure no contamination from the preparation procedure

The known added amount of stable $^{88}\text{Sr}_{\text{carrier}}$ was introduced into each sample. No additional methods were used to determine the content of stable $^{88}\text{Sr}_{\text{sample}}$ already present in the samples. One mg of ^{88}Sr was added as a stable carrier to each sample. According to the literature [23, 26], the stable strontium content varies between trees, ranging from 5-10 $\mu\text{g Sr/g}$ of wood. However, the natural stable strontium content remains significantly lower in magnitude compared to the amount of stable ^{88}Sr added as a carrier to the sample, which is sufficiently accurate for this study to conduct a qualitative analysis. Therefore the ^{90}Sr concentration is calculated with:

$$^{90}\text{Sr} = \frac{^{90}\text{Sr}}{^{88}\text{Sr}_{\text{sample}}} \cdot ^{88}\text{Sr}_{\text{carrier}} \quad (8.12)$$

Where the $^{90}\text{Sr}/^{88}\text{Sr}_{\text{sample}}$ ratio is taken from the measurement, and $^{88}\text{Sr}_{\text{carrier}}$ is taken as the 1 mg added in the preparation process. The data is decay corrected to reconstruct the original amount of ^{90}Sr that the wood contained. This is done with:

$$N(t) = N_0 \cdot e^{-\lambda t} \quad (8.13)$$

The samples activity is calculated with:

$$A = N \cdot \lambda \quad (8.14)$$

8.7 ^{129}I measurement with AMS at VERA

Attempts to measure ^{129}I at VERA started in 1998 and following modifications of the beam line at VERA in 2001, the precise measurement of trace elements like ^{129}I and other heavier isotopes was made possible [66]. As AMS only delivers relative measurement values, the isotopic ratio $^{129}\text{I}/^{127}\text{I}$ is measured in the case for iodine.

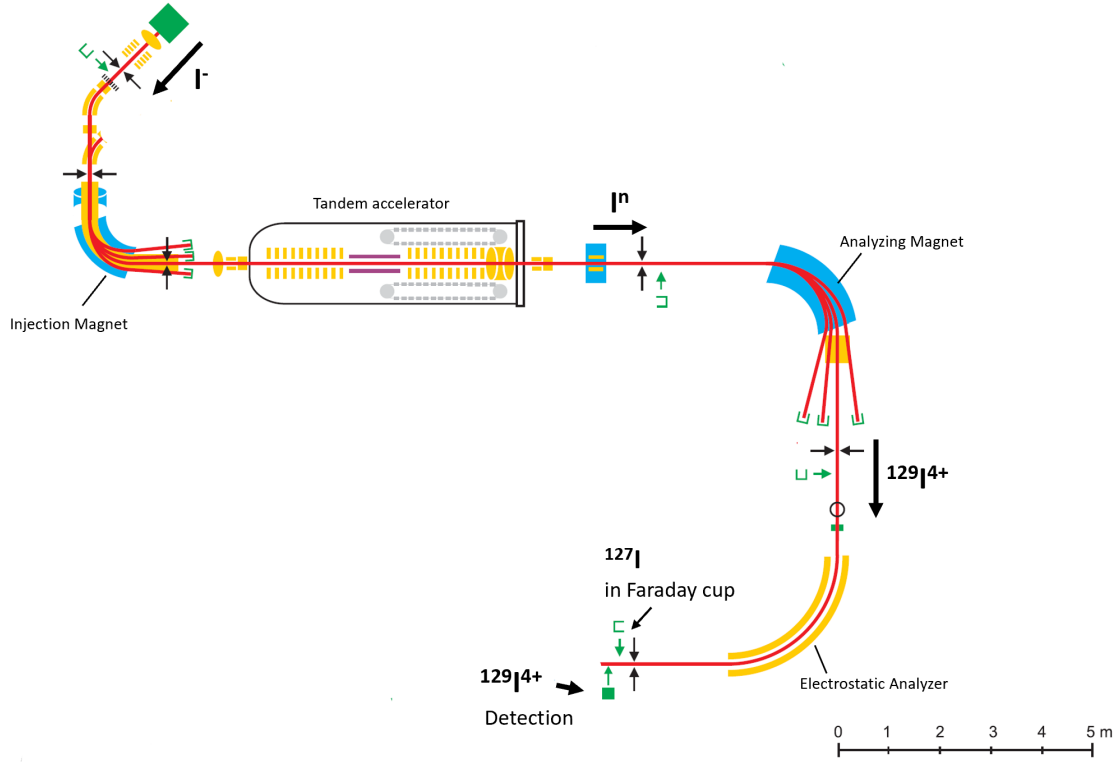


Figure 8.12: Schematic view of VERA to measure $^{129}\text{I}^{4+}$ with AMS.

The described setup of VERA (Fig. 8.9) was used to determine the isotopic $^{129}\text{I}/^{127}\text{I}$ ratio of the wood samples. Cs^+ ions are used to sputter AgI targets at Source 1 as I^- , and the electrostatically extracted anion beam is pre-accelerated to 57 kV before being electrostatically analyzed according to its E/q ratio. The ions are further separated by mass with the bending magnet for the atomic masses of ^{127}I and ^{129}I . The isobar ^{129}Xe does not form any long-lived negative ions, which makes the measurement of ^{129}I possible with conventional AMS [67]. For the stripping procedure argon gas is used.

The terminal voltage is set to 3 MV and a 4+ charge state is chosen to separate the ions by the magnetic and electrostatic analyzer on the high energy side. A multi-beam switcher is used to switch between ^{127}I and ^{129}I ions, where $^{129}\text{I}^{4+}$ is counted in a gas ionization chamber while ^{127}I currents are measured in a Faraday cup after the electrostatic analyzer. This way a $^{129}\text{I}/^{127}\text{I}$ ratio can be determined. A schematic view of the iodine measurement with VERA can be seen in Fig. 8.12.

^{129}I concentration determination To correct the $^{129}\text{I}/^{127}\text{I}$ ratio, two in-house standards were measured. The standard, SM-I-11, has a $^{129}\text{I}/^{127}\text{I}$ ratio of $(1.083 \pm 0.015) \cdot 10^{-11}$ and was used to normalize the sample data, accounting for variations and fluctuations

8 Measurement techniques and sample preparation

in beam current, inherent to the AMS method caused during long-term measurements. Additionally, a machine blank (NaI) with a ratio of $< 2 \cdot 10^{-14}$ was utilized to correct for any instrumental or memory-related ^{129}I background [39]. Furthermore, another standard (AgI 111) is used for further quality control, with a known ratio of $(1.80 \pm 0.20) \cdot 10^{-13}$. To ensure the accuracy of the chemical procedures, a procedural blank containing 1 mg of ^{127}I was processed alongside the samples. This blank underwent the same chemical treatments as the samples, allowing for the detection and correction of any potential contamination introduced during the extraction and measurement processes. By measuring the procedural blank, any extraneous iodine contamination in the sample results can be effectively corrected [66, 39].

Table 8.4: Standards and Blanks Used for Correction.

Item	Ratio	Purpose
SM-I-12 (Standard)	$(7.59 \pm 1.032) \cdot 10^{-13}$	Normalize sample data, correct for AMS specifications and long-term fluctuations
AgI 111 (Standard)	$(1.8 \pm 0.2) \cdot 10^{-13}$	Normalize sample data, correct for AMS specifications and long-term fluctuations, quality control
NaI (Machine Blank)	$< 2 \cdot 10^{-14}$	Correct for instrumental and memory-related ^{129}I background
Procedural Blank	N/A	Detect and correct for contamination during chemical procedures

$$^{129}I_{\text{sample}} = \frac{^{129}I}{^{127}I_{\text{sample}}} \cdot (^{127}I_{\text{carrier}} + ^{127}I_{\text{sample}}) \quad (8.15)$$

The ^{129}I concentrations can be calculated with equation 8.15. No additional method was employed to determine the stable content of $^{127}\text{I}_{\text{sample}}$ in the sample. As with ^{88}Sr , the amount of $^{127}\text{I}_{\text{sample}}$ was expected to be significantly lower than the 1 mg of carrier added to the samples. The average concentration of stable iodine in wood varies between 0.006 and 0.1 $\mu\text{g/g}$ according to Zhao et al. (2019) [19] and between 0.09 and 1.25 $\mu\text{g/g}$ according to Rao et al. (2002) [30]. Although the uptake of trace elements can vary between different trees, depending on factors such as soil quality, tree location, and species, it is reasonable to assume that the iodine content in most trees remains significantly lower than the added ^{129}I concentration from the 1 mg of carrier. This approximation was considered sufficiently accurate.

9 Results

9.1 ^{14}C Measurement

The years assigned to each tree ring sample described in all ^{14}C and ^{90}Sr chapters were determined by dendrochronology by Elisabeth Wächter. The samples were measured with AMS by Peter Steier and Stephanie Adler (Ch. 8.5). The same ring samples used for the ^{14}C measurement, were used for the other following ^{90}Sr measurements. This was done to determine the approximate age of a ring, as several tree rings were too thin to be cut apart from each other. Furthermore, the dendrochronological synchronization of Spruce.3 showed that six years of tree rings are missing in the approximate time period between 1970 and 1980. The radiocarbon peak analysis also serves to determine if the tree has experienced any damage or disease, as these factors could affect the tree's nutrient uptake. Such disturbances can alter the environmental conditions within the tree, potentially impairing the accuracy of dendrochemical analysis [68].

Table 9.1: Comparison of percent modern carbon (pMC) and uncertainties for different tree samples.

Years	Larch.1	Spruce.1	Spruce.2	Spruce.3
	pMC [%]	pMC[%]	pMC [%]	pMC [%]
1920	-	-	-	98.17 ± 0.45
1930	-	-	-	97.37 ± 0.44
1940	-	-	-	97.35 ± 0.60
1950	97.27 ± 0.31	98.11 ± 0.18	97.21 ± 0.35	97.01 ± 0.42
1955	100.64 ± 0.33	100 ± 0.20	103.45 ± 0.41	102.76 ± 0.45
1958	-	-	-	121.67 ± 0.49
1963	171.47 ± 0.49	173.13 ± 0.31	122.33 ± 0.47	-
1970	155.01 ± 0.55	151.09 ± 0.28	152.93 ± 0.48	-
1970-1978	-	-	-	136.37 ± 0.56
1986	119.70 ± 0.53	120.75 ± 0.23	118.65 ± 0.42	115.08 ± 0.49
1990	114.96 ± 0.54	117.38 ± 0.21	114.12 ± 0.37	112.6 ± 1.3
2000	-	-	-	106.1 ± 1.3

The pMC values of Tab. 9.1 are also shown in Fig. 9.1. The peak values of Spruce.3 and Spruce.2 are significantly lower than those of Spruce.1 and Larch.1. An uncertainty of six years was added in this area, since the tree rings were too fine to be precisely cut out and six years are estimated to be missing in this time period.

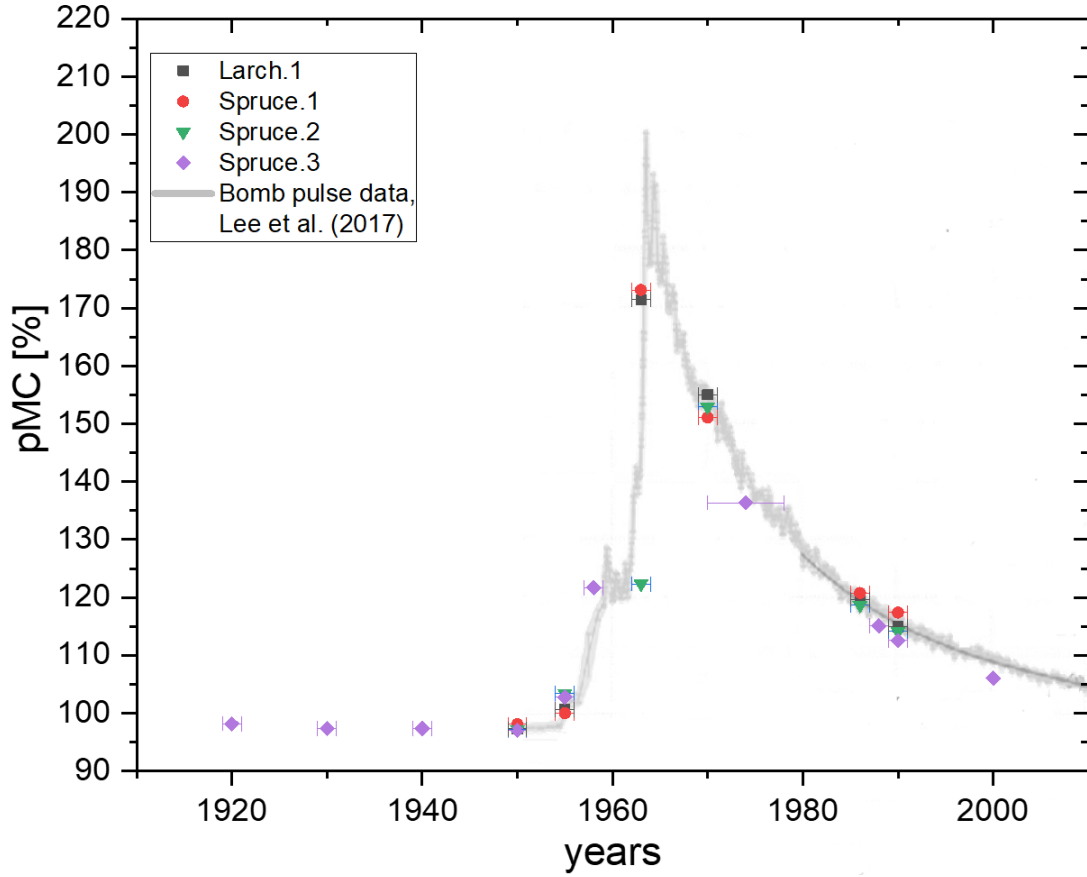


Figure 9.1: Percent modern carbon of samples Spruce.1, Spruce.2, Spruce.3, Larch.1. The polynomial bomb pulse fit (grey line) was presented by Lee et al. (2017) [69] using ^{14}C data of Levin and Kromer (2004) [70], Levin et al. (2013) [71] and CALIBomb (2015).

Finally, maxima of ^{14}C released by nuclear weapon tests, were visible in all trees and no extreme damage was found. For comparison, a polynomial bomb pulse fit (grey line), made by Lee et al. (2017) [69], is illustrated in Fig. 9.1. This fit illustrates the bomb peak in the tree rings and shows how well the data align with the expected curve. This alignment confirms that the trees experienced normal nutrient uptake during the relevant time periods, validating the selected rings for dendrochemical analysis. Consequently, these trees, measured for ^{14}C , are also suitable for analyzing the pathways of other radionuclides.

9.1.1 ^{14}C Discussion

The ^{14}C samples analyzed comprise Larch.1 from a Larch tree, along with three spruce samples: Spruce.1, Spruce.2, and Spruce.3, spanning periods from the 1920s to the 2000s. The bomb peak is clearly visible in all the trees analyzed, and within the uncertainties, all data align well with the expected bomb pulse curve. Although, the pMC values for Spruce.2 and Spruce.3 show slightly lower peak concentrations in the years 1963 and 1970, these differences are within the uncertainties. For Spruce.1, dendrochronological analysis revealed that the tree rings became increasingly narrow between 1960 and 1975, making them nearly indistinguishable. This could be attributed to local environmental factors, such as competition for sunlight from larger surrounding trees, which likely impacted the growth of Spruce.1. One reason the values might differ slightly from each other is due to local variations in uptake, as well as the impact of CO_2 emissions in populated areas. These emissions lower the $^{14}\text{C}/^{12}\text{C}$ ratio in trees, resulting in a seemingly lower ^{14}C concentration in trees located in densely populated regions [72].

Additionally, Spruce.3 shows a six-year uncertainty for the year 1970 due to the extreme narrowing of the tree rings during that period, making precise identification of individual rings difficult. Despite these challenges, the tree rings were accurately selected to distinguish between pre- and post-nuclear times, allowing the identification of the nuclear bomb peak within the expected timeframe.

Therefore, it can be concluded that the selected tree ring material and the resulting radiocarbon data are reliable and suitable for further analysis, including the interpretation of ^{90}Sr levels.

9.2 ^{90}Sr Measurement

9.2.1 Decay-correction

All ^{90}Sr activities of the samples are decay-corrected to their respective dendro-chronologically determined year.

Determining a specific year to use as a reference date for decay-correction is challenging due to the complexity of strontium movement within tree rings. Two factors must be considered: First, the environmental factor, the timing of radiostrontium release into the environment and its subsequent uptake by the tree. There may be a delay of several years between the release of the radionuclide, its absorption by the tree's root system,

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and its incorporation into the cell walls of the tree trunk [16]. Additionally, the duration that radiostrontium remains in the soil before being absorbed by the tree is also crucial. Second, the radial movement of strontium within the trunk. It is important to understand whether strontium only moves inward, becoming incorporated into the heartwood, or if it also moves radially outward as new rings are formed. These factors contribute to the complexity of accurately assessing and correcting for decay. For all samples originating from before 1950, the corresponding year should not be used for decay-correction since no significant amount of ^{90}Sr would originate from pre-nuclear times. For all data from before 1950, the correction year 1950 could be used as it marks the boundary when the first significant amounts of ^{90}Sr entered the biosphere. In 1963, the highest amount of radionuclides was released into the biosphere. In this thesis, it is assumed that the highest amount of ^{90}Sr found in the rings within the nuclear bomb period and also from before 1963 originates from that year, and the ^{90}Sr amounts before 1963 are considered negligible in comparison. Therefore any ^{90}Sr found before 1963 is decay-corrected with the year of 1963. This decay-correction assumes that all ^{90}Sr produced before 1963 is not significantly high. While this assumption is not entirely accurate, it is unlikely that very high amounts of ^{90}Sr were present before 1963. If such large amounts are found in the pre-nuclear rings of the tree, the majority must come from the emissions in the year 1963.

If the entire ^{90}Sr amount found in a year like 1950 were to be decay-corrected to its corresponding year, it would result in an overcorrection. This is because a significant portion of the strontium must have migrated from the 1963 ring. Therefore, applying the decay-correction this way would inaccurately inflate the ^{90}Sr levels for earlier years.

Furthermore, after 1963, it is assumed that no radial movement into newly formed rings occurs, and the radiostrontium found in rings after this year is decay-corrected to its corresponding dendrochronological year.

For a precise evaluation of this data, it would be necessary to conduct modeling that incorporates the factors mentioned above. However, this may present a challenge, as these factors can vary significantly depending on the specific tree being analyzed.

9.2.2 Results for applied strontium chemistry

For the chemical preparation of **Larch.1** for strontium, the method described in chapter 8.2.2 was used. Silke Merchel applied this chemical treatment to two test samples: one consisting of the rings of Larch.1 from the years 2014 to 2024, and another sample taken from the bark of Larch.1. The results were promising and provided successful values in subsequent measurements (see Tab. 9.3).

In the initial real batch, the chemical yields varied significantly. Three out of four samples showed almost no yield and subsequently produced no currents during the AMS measurement. The chemical procedure blank showed low currents as well, indicating that strontium was lost during the chemical preparation. To address this, an alternative approach was tried: combusting the sample at 650°C for five hours to reduce the organic components of the wood sample, which may interfere with chemical processes, such as the final precipitation step.

This new method applied to test samples taken from Larch.1, led to higher chemical yields and stable strontium currents during the ILIAMS measurement. The quality factor is defined as the ratio of each sample's stable strontium current during measurement to that of the standard (Sr-12J) and is plotted against the chemical yields in Fig. 9.2. Although high chemical yields were achieved compared to the previous measurement, the stable strontium currents were partially lower than that of the standard, and almost no ^{90}Sr counts were detected in any of the samples. The high uncertainties observed in Fig. 9.2 are due to significant fluctuations in the stable strontium currents during the measurement, caused, among other factors, by in-homogeneity in the cathode material.

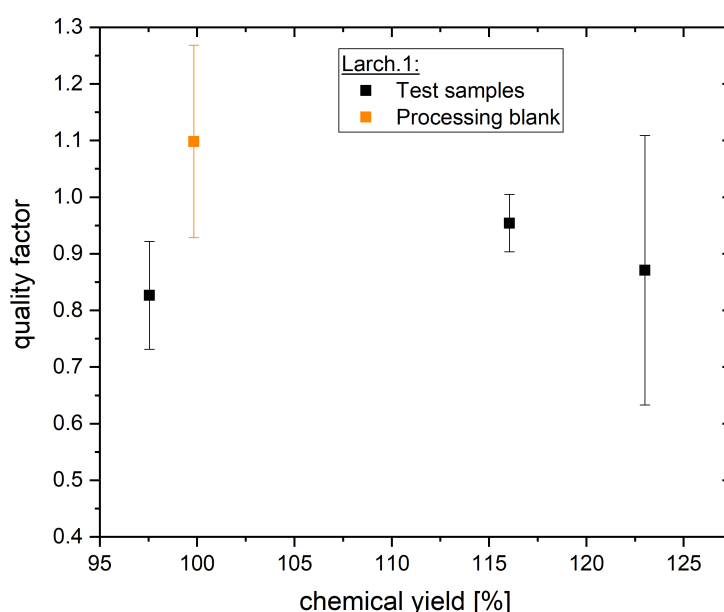


Figure 9.2: Comparison of the quality factor for three samples taken from **Larch.1**.

The combination of high chemical yields and lower currents may suggest that, despite the combustion process, residual organic compounds leached from the wood could have hindered strontium precipitation, leading to the co-precipitation of other substances. This argument is supported by the processing blank data point (orange) in Fig. 9.2, which shows an approximately 100% chemical yield and a strong strontium current relative to the standard. This indicates that, in the total absence of organic components, the chemical process worked effectively. Alternatively, this result could be attributed to the chemist's inexperience during the initial attempt. Therefore, no useful ^{90}Sr data in Larch.1 could be determined.

Consequently, the results for **Larch.1** will not be further discussed in this thesis.

Testing combustion method

After the initial unsuccessful attempt of chemical preparation with and without sample combustion, a third trial was conducted. In this trial, two identical samples, taken from **Spruce.1**, were processed—one combusted and one not-combusted each—to determine if consistent results could be achieved.

For the comparative experiment, rings from 1990 and 2000 were used, but these were taken from the opposite side of the tree disc to ensure variability and comprehensive testing. The sampling areas for Spruce.1 are shown in Fig. 9.6. A table of the $^{90}\text{Sr}/^{88}\text{Sr}$ ratios and the specific activities of Spruce.1 for the comparative test can be seen in Tab. 9.2.

All $^{90}\text{Sr}/^{88}\text{Sr}$ ratio values presented in the following chapters have been blank-corrected using the corresponding processing blank from the chemistry preparation. Additionally, the $^{90}\text{Sr}/^{88}\text{Sr}$ ratios include the contribution from the 1 mg of stable Sr carrier added during the preparation process.

In Fig. 9.3, the specific ^{90}Sr activities of combusted and not-combusted tree rings are analyzed to determine if there is a bias induced by the chemical preparation. This analysis examines whether combusting the sample at 650°C for less than 6 hours affects the results. The findings indicate no significant difference between the two methods. Within the uncertainties, the resulting specific activities are the same.

Therefore, for simplicity, the combustion step was left out in the chemical preparation for all following samples analyzed for ^{90}Sr .

Table 9.2: $^{90}\text{Sr}/^{88}\text{Sr}$ and ^{90}Sr [Bq/kg] for **Spruce.1**, combusted and non-combusted samples.

Sample [year]	Chemical preparation	$^{90}\text{Sr}/^{88}\text{Sr}$ [$\cdot 10^{-13}$]	^{90}Sr Decay-corrected [Bq/kg]
1990	Combusted	9.41 ± 0.73	8.94 ± 0.69
1990	Not-combusted	1.02 ± 0.92	8.33 ± 0.75
2000	Combusted	8.27 ± 0.74	6.24 ± 0.56
2000	Not-combusted	9.81 ± 0.91	6.26 ± 0.52

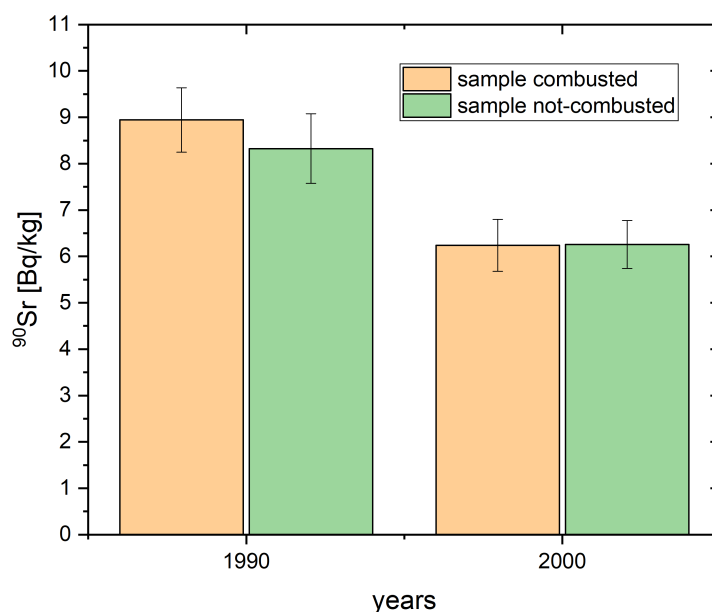
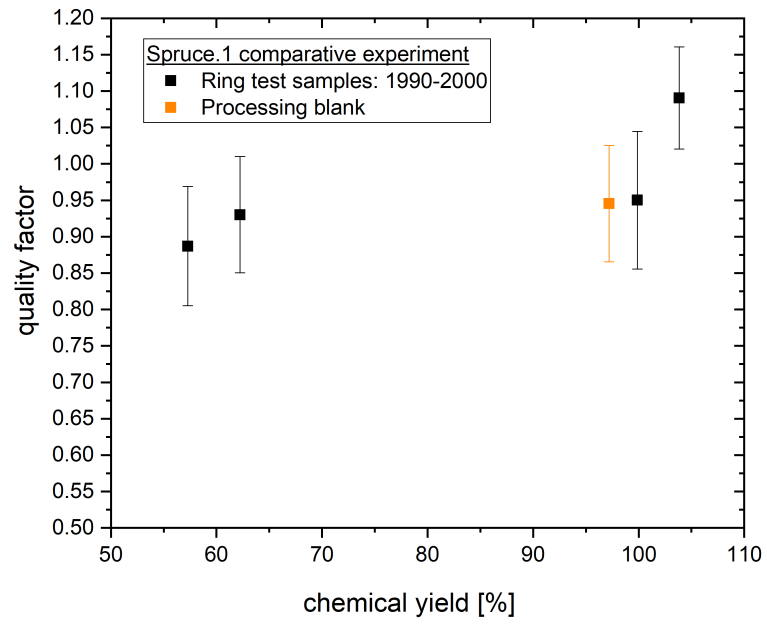


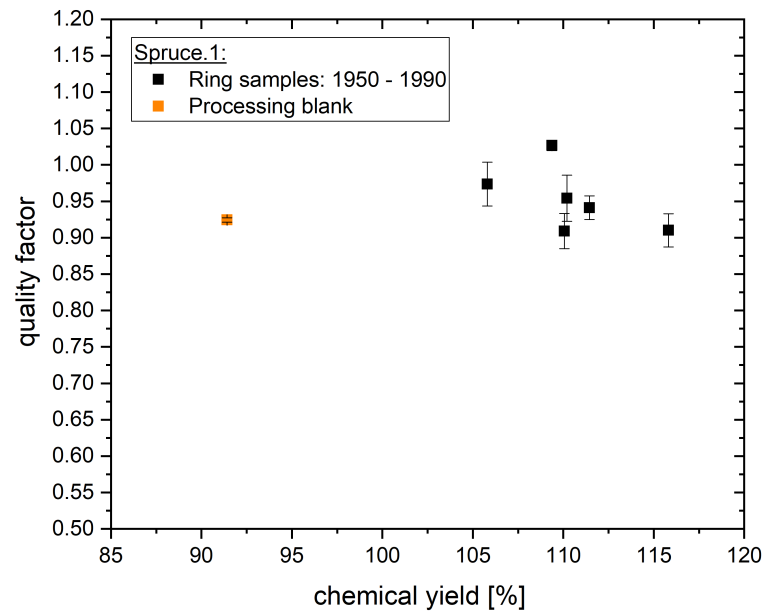
Figure 9.3: Comparison of two samples from tree rings 1990 and 2000 taken from **Spruce.1**, both combusted and not-combusted.

The chemical yields, relative to the quality factor of samples taken from Spruce.1, are presented in Fig. 9.4. The measurements of Spruce.1, along with the comparative experiment, demonstrated acceptable current values when compared to the standard. However, significant variability in the current values was observed across different runs for some samples, resulting in increased uncertainties. However ^{90}Sr could be detected and information over the ^{90}Sr content in a sample could be conducted for Spruce.1.

The chemical preparation for the samples taken from **Spruce.2** and **Spruce.3** resulted in varying chemical yields, with values as low as 52%. This loss could be due to strontium being lost at various stages of the chemical process, particularly in the first step after the carrier was added, during the leaching process. At this stage, the wood material soaks the acid, making it difficult to separate the wood from the solution quantitatively. Despite this variability, the strontium currents measured were consistently aligned with the standard currents of the measurement. This is illustrated by comparing the chemical yields of the Spruce.2 and Spruce.3 samples with the quality factor of the measurement in Fig. 9.5. As a result, reliable values for the ^{90}Sr concentrations were obtained for both Spruce.2 and Spruce.3.

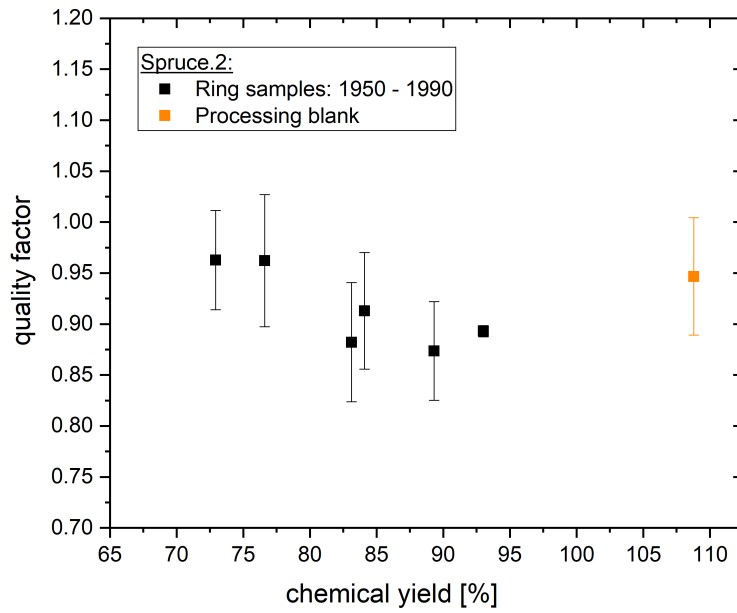


(a)

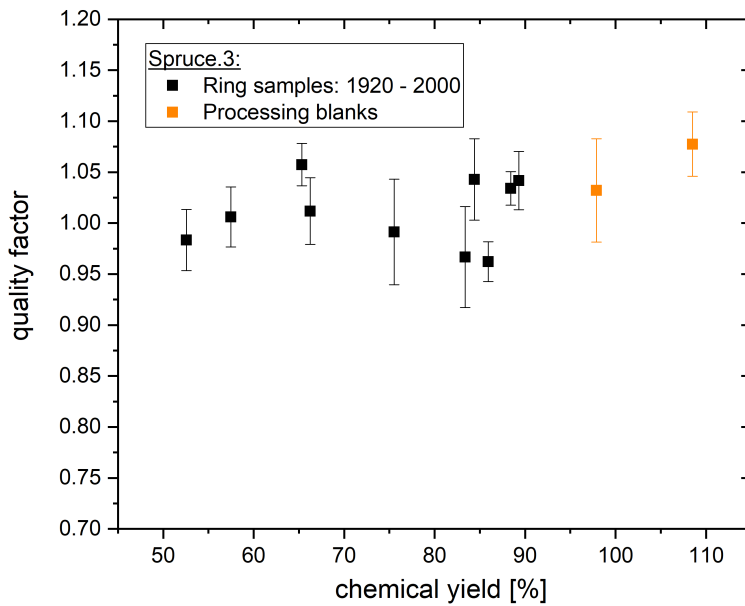


(b)

Figure 9.4: Comparison of the quality factors for samples taken from **Spruce.1**: (a) Two samples from each tree ring dated 1990 and 2000, combusted and not-combusted (b) Time series of rings dated from 1950 to 1990.



(a)



(b)

Figure 9.5: Comparison of the quality factors for samples taken from (a) **Spruce.2** and (b) **Spruce.3**.

9 Results

9.2.3 ^{90}Sr Results

Larch.1 Results

Two Larch.1 samples were analyzed as test samples to determine if the acid leaching chemistry method, when applied to wood material, leads to results. The $^{90}\text{Sr}/^{88}\text{Sr}$ ratios for Larch.1 can be seen in Tab. 9.3.

Table 9.3: $^{90}\text{Sr}/^{88}\text{Sr}$, sample mass, and specific ^{90}Sr activity in **Larch.1**.

Sample [year]	$^{90}\text{Sr}/^{88}\text{Sr}$ [10^{-13}]	Sample mass [g]	^{90}Sr activity [Bq/kg]
bark	2.46 ± 0.22	0.28	3.65 ± 0.40
2014-2024	2.14 ± 0.24	0.96	1.25 ± 0.11

The specific ^{90}Sr activity in the bark was found to be almost three times higher than that in the inner wood part from the outer rings of the xylem. This result was anticipated, as various experiments have reported that the bark contains higher radionuclide concentrations compared to other parts of the tree [51, 23]. After the method was successfully applied to Larch.1, it was also used on subsequent spruce samples. This involved measuring tree ring data to investigate the visibility of nuclear events, such as bomb tests or the Chernobyl incidence, within the tree rings. The conclusion from the literature review indicated that gymnosperms are better candidates for dendrochemical analysis due to their cell structures (see chapter 5.2). Consequently, three spruce trees were selected for further analysis.

Spruce.1 Results

The sampled area can be seen in Fig. 9.6. All values given in the following chapters were obtained with the method described in chapter 8.6 and blank-corrected with the respective processing blank used during the chemical preparation.

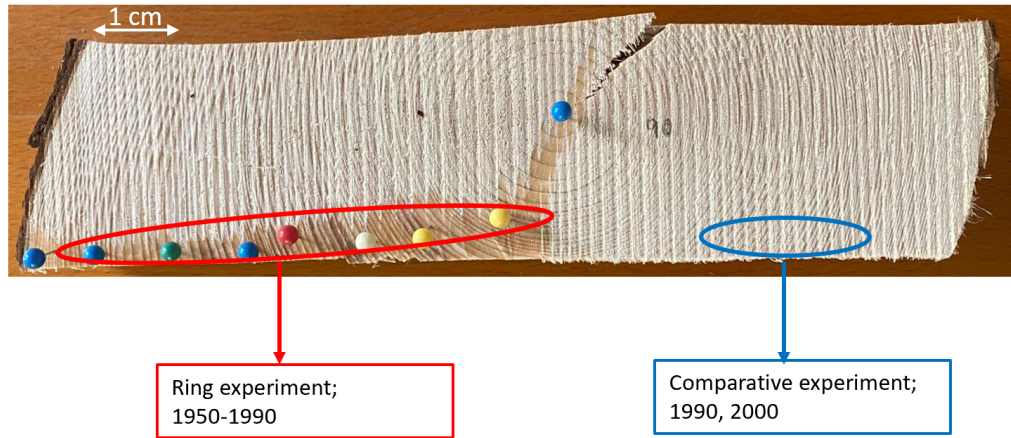
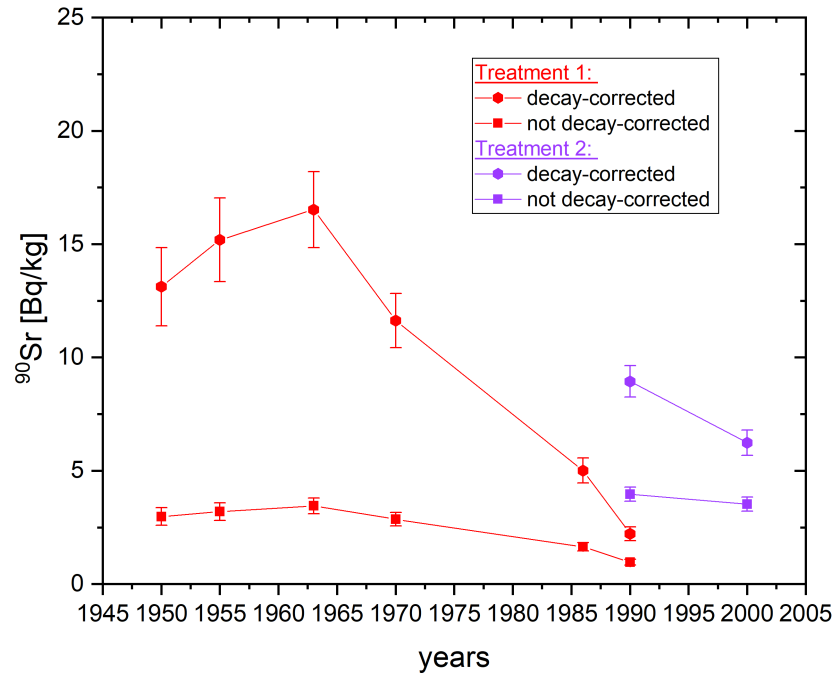


Figure 9.6: Spruce.1 sample region.

Processing blanks were measured to detect any potential contaminations introduced during the chemical procedure. The $^{90}\text{Sr}/^{88}\text{Sr}$ ratios given in [9.4] were blank-corrected using the two blank values of $(1.41 \pm 0.95) \cdot 10^{-14}$ (first batch) and $(5.02 \pm 8.47) \cdot 10^{-15}$ (second batch). Since these values are significantly lower than the sample values, it indicates that negligible contamination occurred during the chemical preparation. The specific activities for each tree ring are listed in Tab. [9.4] and visualized in Fig. [9.7]. All ^{90}Sr activity data described in Tab. [9.4] is decay-corrected. A comparison for not decay-corrected and decay-corrected data is shown in Fig. [9.7]. As expected, a huge difference between not decay-corrected data and decay-corrected data can be seen in Fig. [9.7]. For further graphs, only decay-corrected data will be shown.

Table 9.4: $^{90}\text{Sr}/^{88}\text{Sr}$ and ^{90}Sr [Bq/kg] for **Spruce.1**, years 1950-1990.

Treatment 1, ring experiment, circled red in Fig. 9.6		
Sample [year]	$^{90}\text{Sr}/^{88}\text{Sr}$ [10^{-13}]	^{90}Sr activity [Bq/kg], decay-corrected
1950	6.69 ± 0.88	13.1 ± 1.7
1955	7.60 ± 0.92	15.2 ± 1.8
1963	7.93 ± 0.80	16.5 ± 1.7
1970	6.71 ± 0.69	11.6 ± 1.2
1986	3.75 ± 0.41	5.01 ± 0.55
1990	2.27 ± 0.31	2.22 ± 0.31
processing blank	0.141 ± 0.095	0.061 ± 0.042
Treatment 2, comparative experiment, circled blue in Fig. 9.6		
1990	9.41 ± 0.73	8.94 ± 0.69
2000	8.27 ± 0.74	6.24 ± 0.56
processing blank	0.050 ± 0.085	$0.021 \pm \begin{smallmatrix} 0.036 \\ 0.021 \end{smallmatrix}$

Figure 9.7: Specific ^{90}Sr activity in Spruce.1 samples from 1950 to 2000, comparing decay-corrected and not decay-corrected data.

Surprisingly, different values for the same year 1990 were found in the same tree, only in other parts of the tree disc as seen in Fig. 9.7. The sample examination can be seen in Fig. 9.6. While the tree ring from 1990 on one side of the disc showed a specific activity of (2.22 ± 0.31) Bq/kg, the one on the opposite side is (8.94 ± 0.69) Bq/kg. This significant difference may be explained by the varying nutrient absorption rates on different sides of the tree. Prohaska et al. (1998) [73] suggested that due to unbalanced mechanical pressures, combined with environmental factors like wind, snow, or slope, trees can grow differently on one side compared to the other. The compressed side, which is more exposed to environmental conditions, is expected to have higher element concentrations. This is because its wood tissue develops similarly to juvenile wood, which has more binding sites and, therefore, binds more elements to the cell wall than wood under normal conditions. However, these higher ^{90}Sr concentrations on the opposite side should not affect the overall signal found in the tree rings. Instead, they indicate that significant concentration differences, of all trace elements including strontium, can occur within the tree itself, depending on the part of the tree that is sampled. Therefore, when conducting dendrochemical analysis, it is important to consider this factor and ensure that only rings from the same radial section of the tree are analyzed, rather than from opposite sides, to maintain consistency in the tree ring series.

Spruce.2 Results

To test the reproducibility of the method, a second tree of almost the same age as Spruce.1 was chosen and analyzed. The same tree rings as in Spruce.1 were chosen for the analysis of Spruce.2 and their isotopic ratios as well as their activities can be seen in Tab. 9.5. Interestingly, the highest value is found in the year of 1950, where (21.7 ± 1.1) Bq/kg was measured. This is also the highest value recorded across all samples. The graph shown in Fig. 9.8 shows an almost linear decline, which can be interpreted as strong migration of ^{90}Sr into the inner xylem. After measuring Spruce.1 and Spruce.2, it was discussed that the trees were maybe too young for dendrochemical measurements. Liu et al. (2024) [74] recommended using only older parts of tree rings for dendrochemical analysis, as juvenile wood tends to distribute elements more widely. This is because in the early years of a tree, sapwood is more likely to translocate elements due to the absence of heartwood. Understanding the time it takes for heartwood to develop is crucial to determining when a tree ring no longer transports nutrients and only serves as structural support. At this stage, wood is estimated to stop relocating elements radially as the parenchyma cells die off. However, there is no consensus on this in the literature. A review by Taylor et al. (2002) [20] concluded that heartwood forms gradually each year, but the exact formation period remains debated. To further investigate the influence of heartwood formation on the translocation of ^{90}Sr , an additional, over thirty years older Spruce.3 was chosen for analysis. This was done to determine whether an older tree, with established heartwood, would exhibit less translocation of ^{90}Sr during the bomb-peak period.

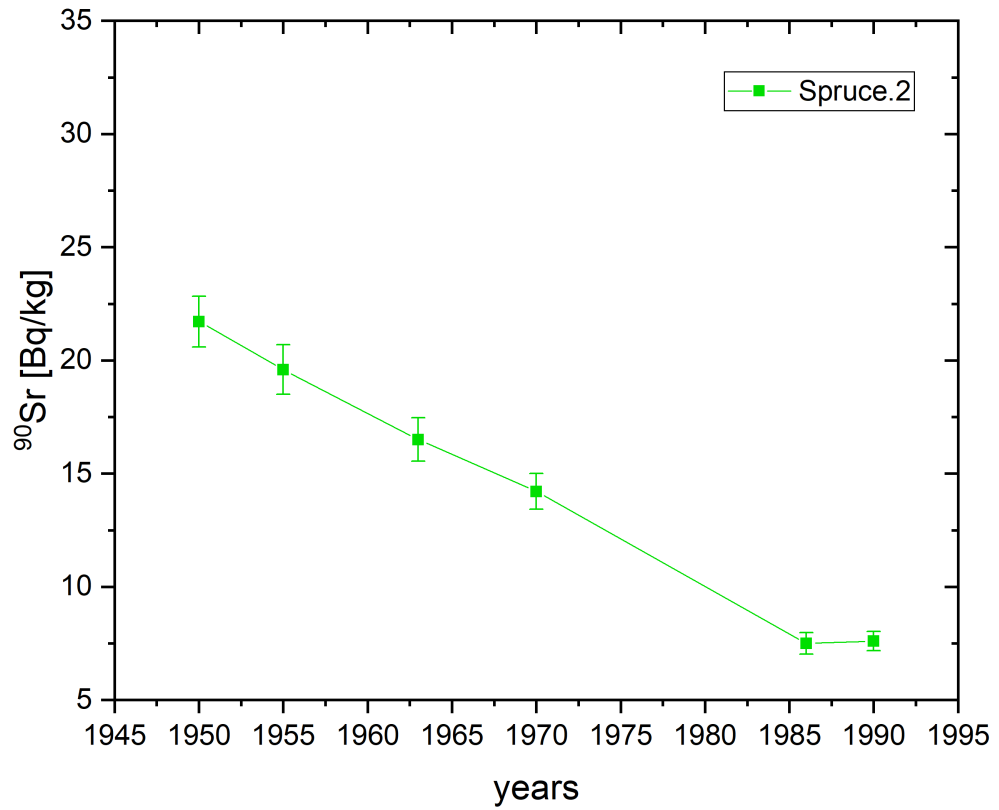


Figure 9.8: Specific ^{90}Sr activity in Spruce.2 samples from 1950 to 1990.

Spruce.3 Results

The isotopic ratios and the decay-corrected specific activities of the tree rings of Spruce.3 are shown in Tab. 9.6. High specific ^{90}Sr activities were observed in the years before 1963, indicating that ^{90}Sr migrated into the inner xylem, also in Spruce.3. The values remained relatively constant until 1970, suggesting that the migration primarily occurred inward, rather than outward, as the activity levels drop significantly after this period. This observation suggests that strontium itself may not be inherently mobile but is rather redistributed by the tree into its inner layers.

Table 9.5: $^{90}\text{Sr}/^{88}\text{Sr}$ and ^{90}Sr [Bq/kg] for **Spruce.2**, years 1950-1990.

Sample [year]	$^{90}\text{Sr}/^{88}\text{Sr}$ [10^{-13}]	^{90}Sr activity [Bq/kg], decay-corrected
1950	12.17 ± 0.63	21.7 ± 1.1
1955	10.67 ± 0.59	19.6 ± 1.1
1963	9.29 ± 0.54	16.51 ± 0.96
1970	10.01 ± 0.55	14.21 ± 0.78
1986	7.25 ± 0.46	7.49 ± 0.48
1990	9.66 ± 0.54	7.61 ± 0.42
processing blank	0.055 ± 0.034	0.023 ± 0.014

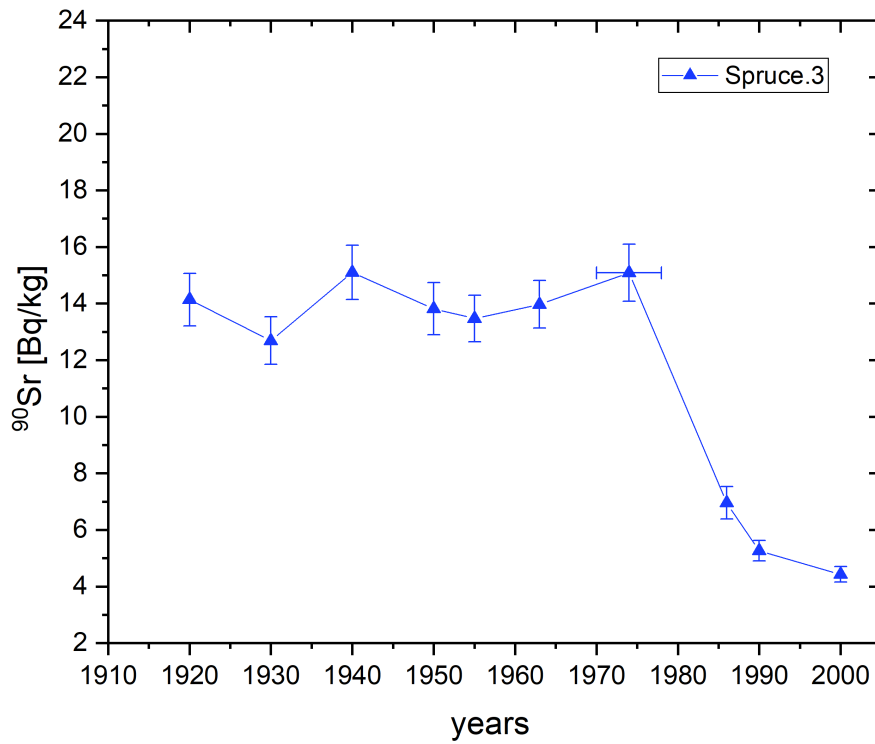
Figure 9.9: Specific ^{90}Sr activity in Spruce.3 samples from 1950 to 1990.

Table 9.6: $^{90}\text{Sr}/^{88}\text{Sr}$ and ^{90}Sr [Bq/kg] for **Spruce.3**, years 1920-2000.

Sample [year]	$^{90}\text{Sr}/^{88}\text{Sr}$ [10^{-13}]	^{90}Sr activity [Bq/kg], decay-corrected
1920	7.56 ± 0.49	14.14 ± 0.93
1930	6.75 ± 0.45	12.69 ± 0.84
1940	8.32 ± 0.53	15.10 ± 0.96
1950	6.93 ± 0.46	13.82 ± 0.92
1955	5.41 ± 0.33	13.47 ± 0.82
1958	7.74 ± 0.47	13.97 ± 0.82
1970-1978	9.21 ± 0.62	15.09 ± 1.01
1986	6.95 ± 0.57	6.96 ± 0.57
1990	6.22 ± 0.42	5.26 ± 0.36
2000	7.10 ± 0.44	4.43 ± 0.27
processing blank	$0.0000 \pm \begin{smallmatrix} 0.0412 \\ 0.0000 \end{smallmatrix}$	-

Spruce.1, Spruce.2, Spruce.3: The data of all trees measured can be seen in Fig. [9.10](#) for comparison. The highest values measured originate from Spruce.2, reaching (21.7 ± 1.1) Bq/kg in the year of 1950. This is surprising since Spruce.1 and Spruce.2 originate from the same location in Rosalia, Burgenland, and would therefore be expected to show similar patterns. The rest of the data aligns well within the uncertainties, in all trees from around 1963 onwards. While Spruce.1 shows a decreasing value in 1950, Spruce.2 exhibits increasing values towards the tree center until 1940, and these elevated values do not decline significantly until 1920.

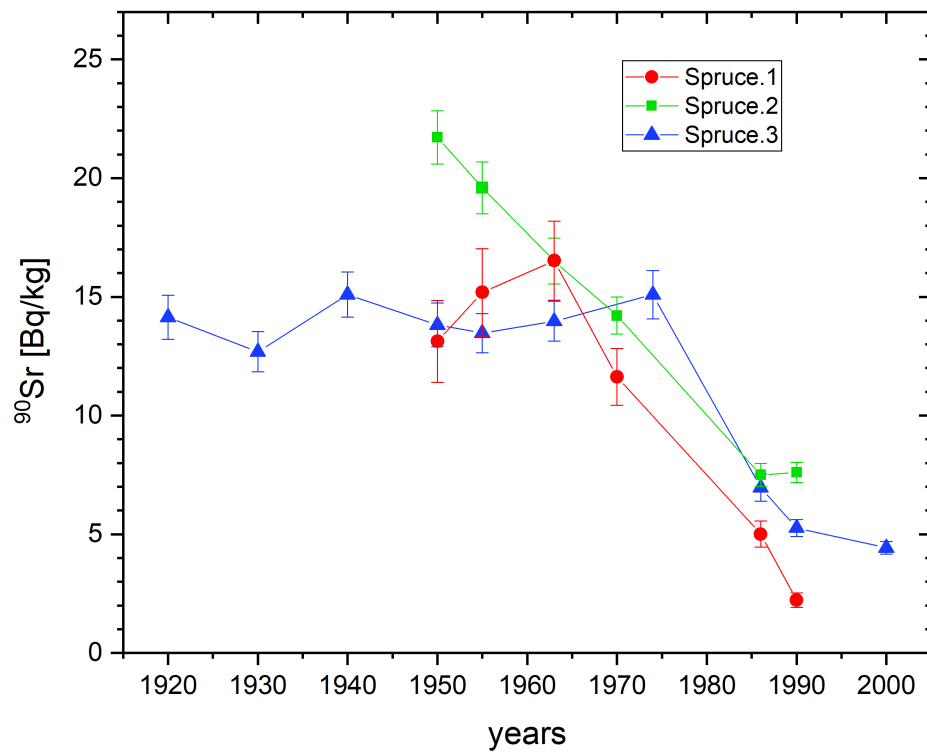


Figure 9.10: Specific ^{90}Sr activity of Spruce.1, Spruce.2 and Spruce.3 samples from 1920 to 2000.

Comparison with literature data

A graph showing data measured by Chigira et al. (1988) [23] on two Japanese cedars, one in Takao and one in Tsukui, Japan, can be seen in Fig. 9.11. Because it was not stated in the study, whether the data was decay-corrected, a decay-correction of the given data was performed and compared with the estimated not corrected data, the data being taken from Chigira et al. (1988). The sample mass for each tree ring period was reported to range between 0.2 and 1 kg [23].

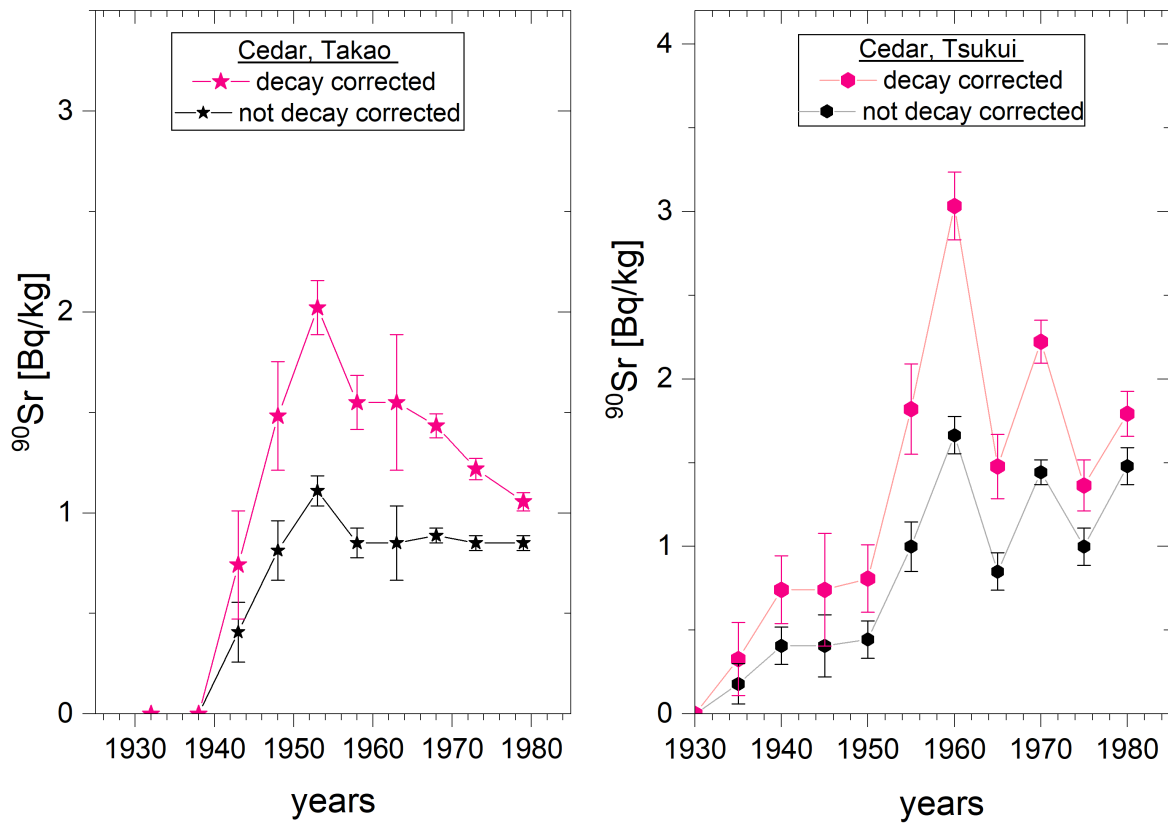


Figure 9.11: Specific ^{90}Sr activity of two Japanese Cedars, one originating from Tsukui and one from Takao, Japan. Since no specification was made in the study whether the data was decay-corrected, a comparison of decay-corrected and not decay-corrected ^{90}Sr values is shown, data taken from [23].

The data is compared with measurements taken from Spruce.1, Spruce.2, and Spruce.3, as shown in Fig. 9.12. For this comparison, the decay-corrected data from Chigira et al. was used.

No ^{90}Sr was found in the years until 1940 and only low values were found until the year of 1950. Since the tree analyzed was a Japanese cedar, finding small amounts of ^{90}Sr in the years between 1940 and 1945 do not come as a surprise, due to the nuclear bombing of Hiroshima and Nagasaki in 1945 in Japan.

It is suggested by Chigira et al. (1988) [23] that no significant translocation of ^{90}Sr into the sapwood took place for both trees analyzed, and this is explained by the completion of growth and the ceasing of cell function in the heartwood in comparison to the sapwood. Any ^{90}Sr found in the years before 1945 is said to originate from the nuclear bombings in Japan. Furthermore, elevated ^{90}Sr values in the following years and a clear bomb peak can be seen in Fig. 9.12 [23]. However, no clear sign and strong translocation of ^{90}Sr was found in Spruce.1, Spruce.2 and Spruce.3. For Spruce.2 the highest value being found in the year 1950. It is notable that the ^{90}Sr concentrations in Chigira's data are significantly lower compared to the data of all trees measured in this study. However, since the uptake of strontium in the soil is highly dependent on various environmental factors, this discrepancy could be understandable.

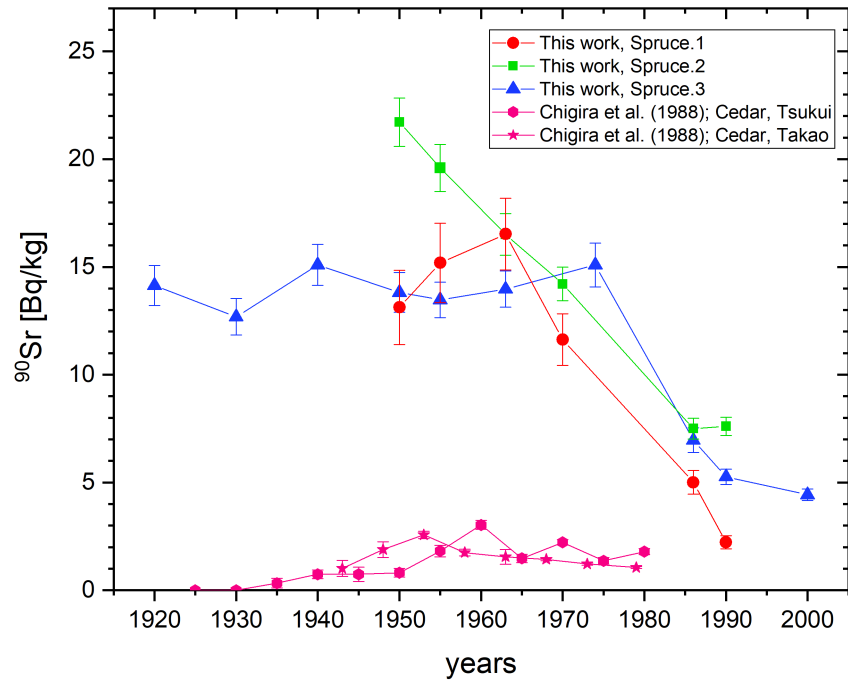


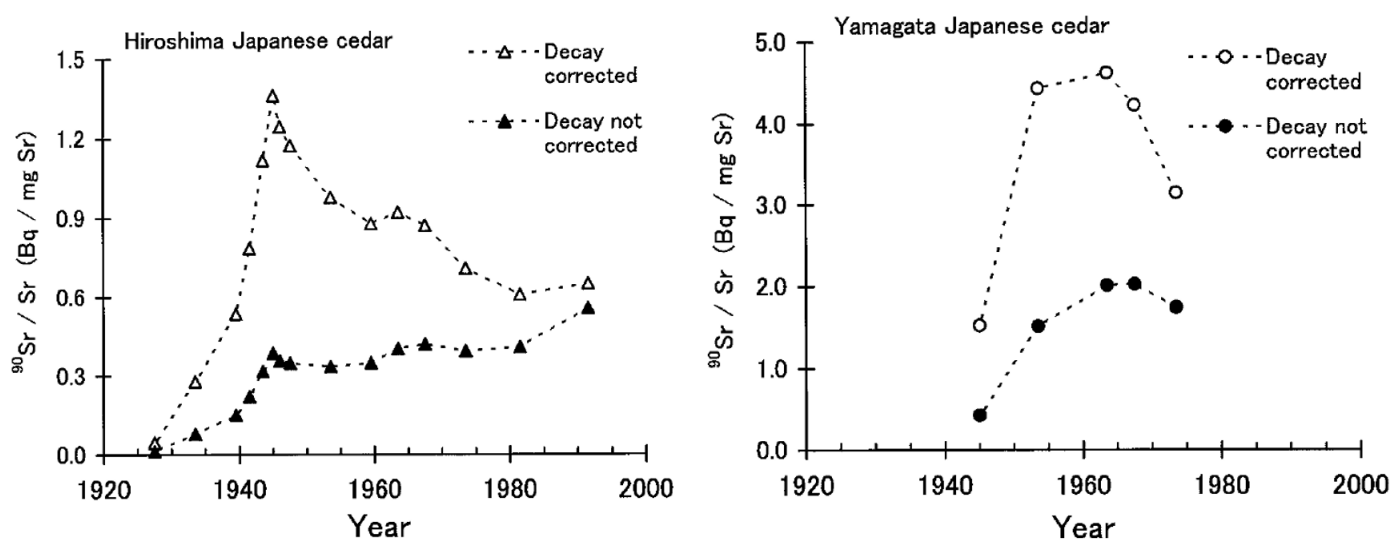
Figure 9.12: Comparison of specific ^{90}Sr activity data of Spruce.1, Spruce.2 and Spruce.3 of this thesis with decay-corrected data of two Japanese Cedars (pink line), one originating from Tsukui and one from Takao, Japan, measured by Chigira et al. (1988) [23].

For comparison with the literature data of **Kagawa et al. (2002)** [26], the evaluated values are expressed as $^{90}\text{Sr}/\text{Sr}$, as Kagawa et al. (2002) did not provide the necessary data to directly compare the values in Bq/kg. An approximate sample mass of 100 g was provided for each tree sample. For these calculations, an approximate stable strontium content of $0.062 \mu\text{g/g}$ was used. Since the stable strontium content of the samples was not directly determined, an average value derived from the literature data in Tab. 7.2 was used. Although the stable strontium content reported in three studies analyzing tree xylem ranges from 3.4 to $11 \mu\text{g/g}$, the discrepancy is at most a factor of 10. Importantly, this factor does not affect the observed trend over the years.

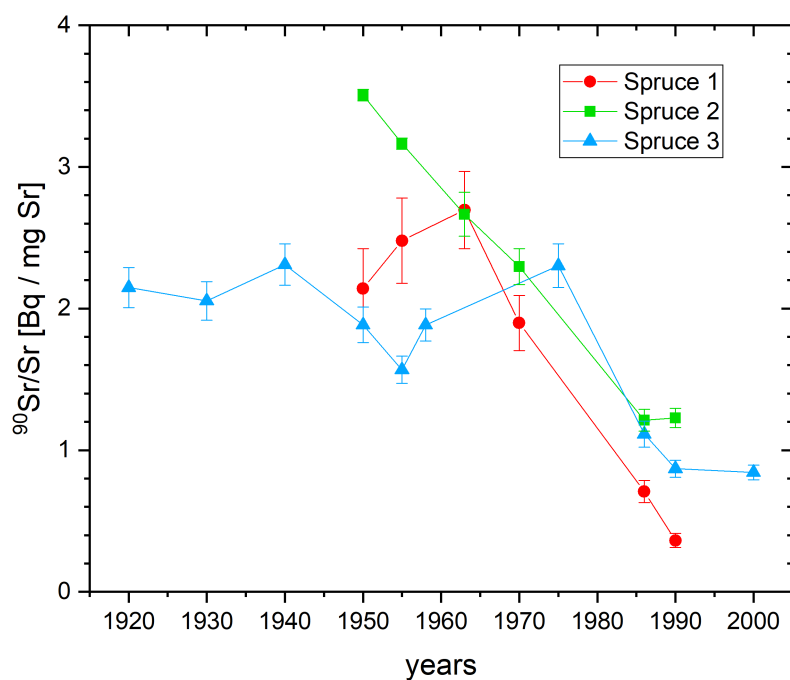
The trend of $^{90}\text{Sr}/\text{Sr}$ in two Japanese cedar trees, one from Hiroshima and the other from Yamagata, is illustrated in Fig. 9.13a. The data has been decay-corrected and clearly reflects the environmental circumstances. In the Hiroshima cedar, a distinct peak is visible in 1945, marking the year when the first nuclear bomb was dropped on Hiroshima. Subsequent peaks from nuclear bomb tests are also evident in both trees from Hiroshima and Yamagata.

Interestingly, the ^{90}Sr concentrations between the two trees vary significantly. When comparing the Hiroshima Japanese cedar to the Yamagata Japanese cedar, the latter exhibits concentrations up to three times higher. The magnitudes reported by Kagawa et al. generally align well with our findings, particularly for the Yamagata cedar. Kagawa et al. suggested that there is no migration of ^{90}Sr in the heartwood region and considered the ^{90}Sr radial migration factor negligible.

As shown in Fig. 9.13b, the environmental circumstances are not accurately reflected in the tree rings of the spruces, unlike in the Japanese cedars studied by Kagawa et al. In the spruces, no clear peak is visible in the year 1963, and concentrations remain elevated before 1950.



(a)



(b)

Figure 9.13: Comparative analysis of ^{90}Sr activity data: (a) ^{90}Sr activity in $\text{Bq}/(\text{mg Sr})$ in two Japanese cedars, one from Hiroshima and one from Yamagata, Japan. The figure compares both decay-corrected and not decay-corrected ^{90}Sr values. Figure taken from Kagawa et al. (2002) [26]; (b) ^{90}Sr activity in $\text{Bq}/(\text{mg Sr})$ of Spruce.1, Spruce.2, and Spruce.3 from this work, assuming natural strontium to be $6.2 \mu\text{g/g}$.

In the study published by Hölgye et al. (2016) [27], ^{90}Sr concentrations were measured in the tree rings of a Norway spruce at different heights, ranging from 1.3 meters above the ground up to 22 meters. A sample mass of 200–850 g of dried wood was used. The 103-year-old spruce was analyzed, and the results remained uniform across all heights. For comparison, the data from 1.3 meters above the ground was used, as this height contained the oldest parts analyzed. The ^{90}Sr data was originally decay-corrected to the year 2012, the year the tree died, but for this comparison, the data was decay-corrected to the corresponding year of each tree ring. Additionally, a three-year uncertainty was added to the year axis, as the sampled tree rings always consisted of seven rings. A comparison of Spruce.1, Spruce.2 and Spruce.3 with the decay-corrected data taken from Hölgye et al. (2015) [27], can be seen in Fig. 9.14.

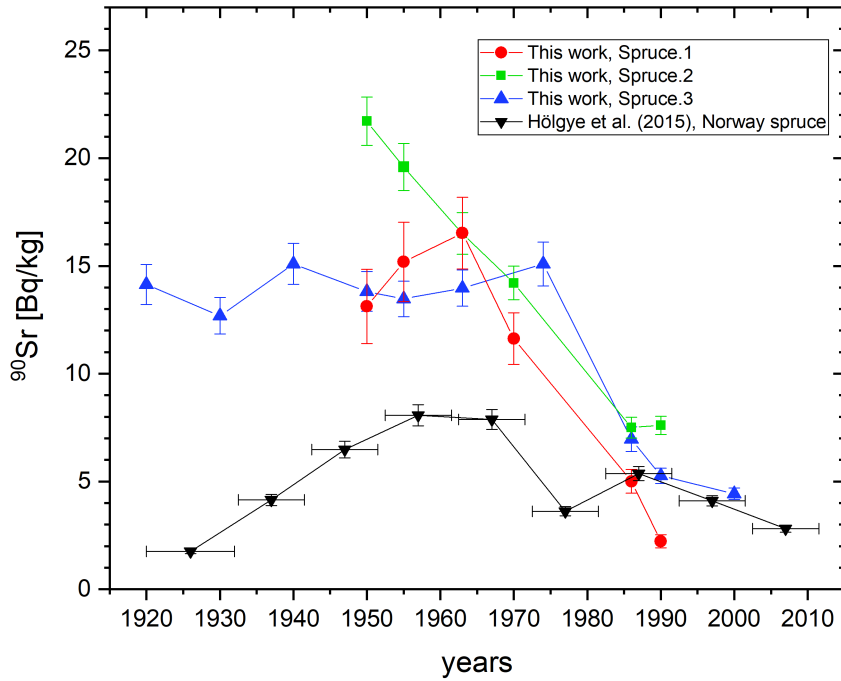


Figure 9.14: Comparison of decay-corrected ^{90}Sr specific activity between a Norway spruce, measured by Hölgye et al. (2015) [27] (black symbols), and Spruce.1, Spruce.2, and Spruce.3.

A clear ^{90}Sr peak is visible in the year 1960 in Fig. 9.14, accompanied by low values in the years before 1950. While the tree rings from 1986 to 2000 align well with the data from this study, the data from before the 1980 years show significant differences. All Austrian spruces exhibit considerably higher ^{90}Sr concentrations and evidence of radial migration.

9.2.4 ^{90}Sr Discussion

The samples analyzed in this study included three Austrian spruce trees named Spruce.1, Spruce.2, and Spruce.3. Spruce.1 and Spruce.2 were of similar age, with rings spanning from the 1950s to the 1990s, while Spruce.3 was older, covering a period from the 1920s to the 2000s. The evaluated data from all Austrian tree samples—Spruce.1, Spruce.2, and Spruce.3— show elevated ^{90}Sr concentrations from 1920 until 1970. Notably, Spruce.2 exhibits significantly higher values between 1950 and 1960. However, all trees display decreasing ^{90}Sr concentrations in the post-nuclear era. Radiocarbon measurements did not show any elevated concentrations before the nuclear era, suggesting healthy nutrient uptake by the trees. This strongly indicates that ^{90}Sr migrates into the inner xylem.

Spruce.3 was specifically chosen to investigate the migration of ^{90}Sr into the inner xylem due to its age of 105 years, allowing analysis of tree rings formed long before the nuclear period. The data shows that even in the 1920 ring, high ^{90}Sr values were found. This implies a migration period of at least 30 years must be considered when conducting dendrochemical analyses with ^{90}Sr , as no significant ^{90}Sr should have entered the tree before 1950. Hölgye et al. (2016) and Kagawa et al. (2002) [26, 27] stated that the heartwood, the dead xylem part of the tree, lacks living parenchyma cells responsible for radial nutrient transport. Due to the low mobility of strontium in wood tissue, ^{90}Sr was considered a suitable radionuclide for dendrochemical analysis.

However, this assumption has been proven incorrect in the case of these Austrian spruce trees. By 1920, the trees should have consisted only of heartwood, and by 1930, heartwood should have been present at the time of measurement, with no expected nutrient transport through it. Consequently, no ^{90}Sr concentrations were expected in these tree rings. Nevertheless, the highest ^{90}Sr values in all measured spruce trees were found before 1963, indicating that ^{90}Sr does migrate, even within heartwood.

While the decay correction is more significant for earlier years, applying a correction factor is necessary. One might try correcting the ^{90}Sr values based on their respective years, considering most ^{90}Sr entered the environment in 1963. However, this does not change the fact that ^{90}Sr migrated strongly into the heartwood.

Three trees were chosen, and all showed good ^{14}C uptake, indicating healthy nutrient pathways. Moreover, it is highly unlikely that all three chosen trees would exhibit the same pattern if it were due to a defect.

Lastly, the findings on Spruce.1 revealed the importance of selecting the specific part of the tree for examination. The results indicated that for accurate dendrochemical analysis, only rings from the same radial part of the tree should be analyzed.

9.3 ^{129}I Measurement

9.3.1 Challenges in ^{129}I measurements with AMS

Challenges in measuring ^{129}I have persisted over time, both in terms of AMS measurements and the associated chemical preparation. Roberts et al. (1997) [55] conducted a comparative study where the same environmental and synthetic materials, such as AgI, were distributed to various laboratories for analysis. These laboratories employed different chemical preparation methods, including acid leaching, dry combustion, and wet acid digestion. Despite using these established methods, the results varied significantly, particularly for environmental samples, with differences of two to three orders of magnitude in ^{129}I concentration observed between laboratories for the same sample.

The study concluded that several factors contributed to these discrepancies. Cross-contamination during chemical preparation, variability in preparation methods, the complexity of the sample matrix, and inconsistent recovery rates were identified as key influences. For instance, during the chemical leaching process, incomplete extraction of ^{129}I was a concern, especially in samples with high organic content. Similarly, the dry combustion method sometimes failed to completely oxidize organic matter, leading to incomplete iodine recovery. Additionally, organic matter in environmental samples can bind with iodine, making it difficult to break down complex compounds and fully recover ^{129}I [55].

Furthermore, there is concern that the added carrier and the iodine in the sample might not be in equilibrium during the leaching process, which could result in the loss of ^{129}I . The volatile nature of iodine also poses a challenge, as it may lead to the loss of iodine during the preparation process, particularly if it is not fully stabilized.

Additionally, the measurement process using AMS presents its own challenges, particularly with cross-contamination between samples and long-term memory effects within the ion source. These issues are especially problematic for low-level samples, as highlighted in studies by Vockenhuber et al. (2015) [75] and Rugel et al. (2016) [76]. These challenges can significantly affect the accuracy and reliability of ^{129}I measurements, making it difficult to achieve consistent results across different experiments.

9.3.2 ^{129}I Results

Four birch test samples were analyzed to test the chemical preparation method. The samples were chemically prepared in the way described in Chapter 8.2.3 and measured with the AMS procedure described in Chapter 8.7, by Peter Steier.

The notation "Bir.ins" indicates the birch sample collected from the inner xylem, while "Bir.out" refers to the sample taken from the outer xylem. The numerical suffixes "0.1" and "1" in "Bir_1" denote the molar concentration of HNO_3 used to leach the respective sample during chemical preparation. An image containing the sample examination of the birch tree can be seen in Fig. 8.5b in chapter 8.1.

9 Results

To begin this results section, we will first examine the currents shown in Fig. 9.15, Fig. 9.16, and Fig. 9.17. These figures display the I^{4+} current on the high-energy side of the beamline, during the AMS measurement, as a function of the number of turns. It is evident that the standard currents fluctuate significantly, even between cathodes containing the same standard material. This pattern is particularly noticeable in both SM-I-11 and SM-I-12, seen in Fig. 9.15 and Fig. 9.16 respectively, where strong fluctuations occur during the first ten turns. Only in the final four turns does the current for the standards appear to stabilize. This pattern is also observable in Fig. 9.17 showing the currents for the samples. Therefore, the subsequent calculations will be based solely on the data from the last four turns.

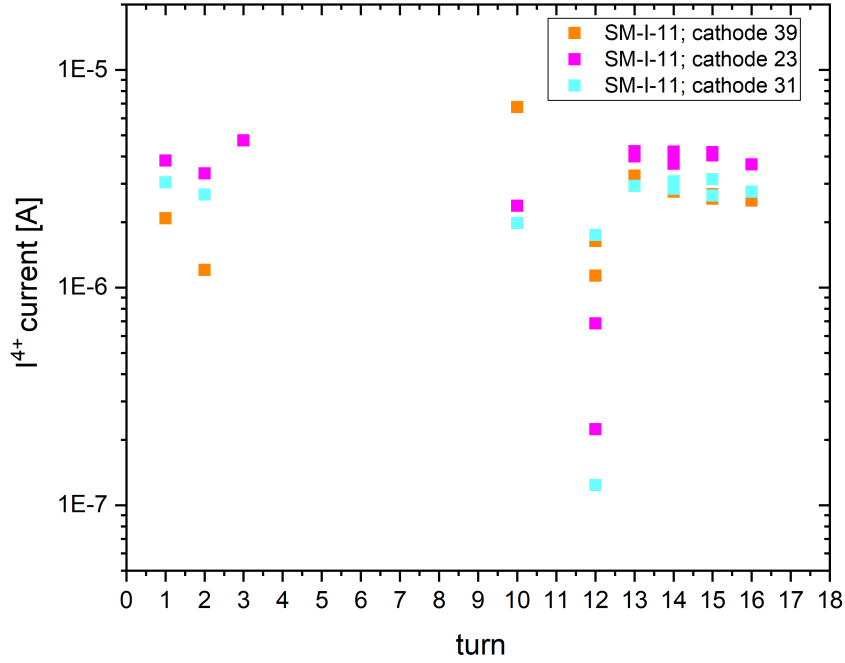


Figure 9.15: Average $^{127}\text{I}^{4+}$ current [A] as a function of the number of turns in the measurement, for the standard sample SM-I-11, measured across three different cathodes (39, 23, and 31).

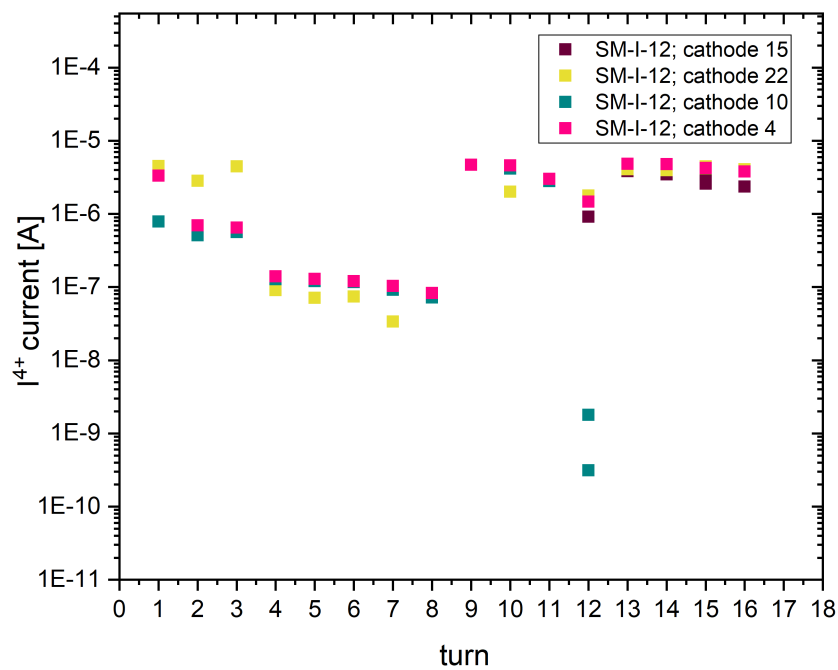


Figure 9.16: Average $^{127}\text{I}^{4+}$ current [A] as a function of the number of turns in the measurement, for the standard sample SM-I-12, measured across four different cathodes (4, 10, 15 and 22).

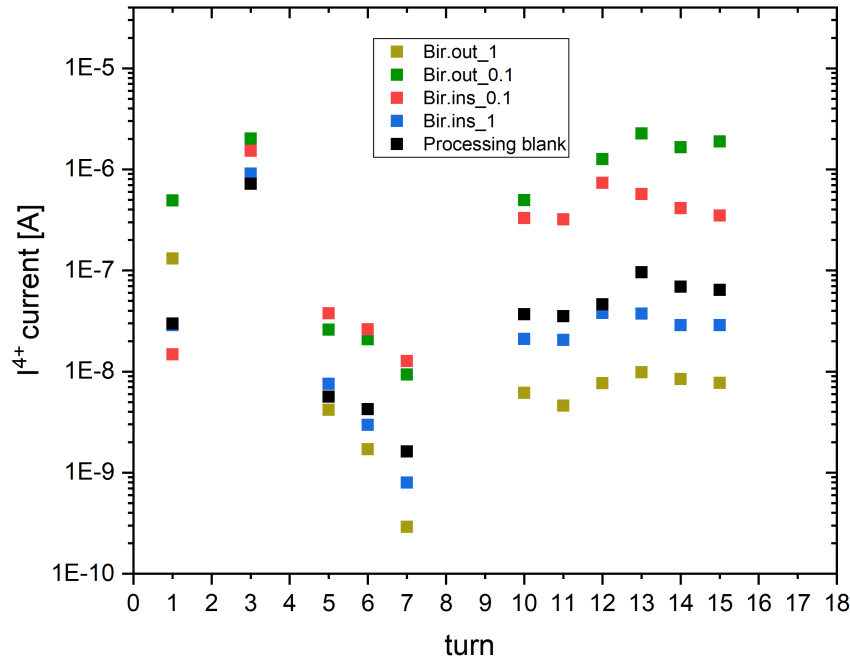


Figure 9.17: Average $^{127}\text{I}^{4+}$ current [A] as a function of the number of turns in the measurement, for various birch samples and the processing blank.

The average I^{4+} current is presented as the ratio of the sample currents to the processing blank, plotted against the chemical yields of the samples in Fig. 9.18. The quality factor, showing the average I^{4+} of the samples current relative to the average current of SM-I-11, can be seen in Fig. 9.19. The values for chemical yield of the samples and the according relative current values are shown in Tab. 9.8. Analyzing the chemical yields shows that the processing blank achieved approximately 80% chemical yield. However, it only produced $(2.17 \pm 0.58)\%$ of the current, relative to the standard SM-I-11, on average. Similarly, both samples, Bir.out_1 and Bir.ins_1, that were leached with 1 M HNO_3 show low I^{4+} current values relative to the standard.

The low current of the processing blank is likely due to significant losses during the chemical process. Since the processing blank underwent chemical preparation with 1 M HNO_3 , it is possible that the concentration of the acid played a role in this outcome. One hypothesis is that stable carrier iodine may have been oxidized, as all samples leached with 1 M HNO_3 exhibit extremely low currents relative to the standard. However, it is also plausible that the losses occurred during the various chemical steps, as this was the first attempt at chemical preparation, and preparing environmental samples with iodine chemistry requires practice. The chemical yields described in Tab. 9.7 were derived from

Table 9.7: Chemical yields and average $^{127}\text{I}^{4+}$ currents for various birch samples and the processing blank. The current values are shown as percentages relative to both the standard SM-I-11 and the processing blank (p.b.).

Sample Name	Chem. yield	Avg. $^{127}\text{I}^{4+}$ current	Avg. $^{127}\text{I}^{4+}$ current
	[%]	[%] (rel. to SM-I-11)	[%] (rel. to p.b.)
Bir.ins_0.1	43	0.20 ± 0.16	8.33 ± 4.38
Bir.ins_1	308	0.0122 ± 0.0077	0.52 ± 0.17
Bir.out_0.1	456	0.57 ± 0.17	26.11 ± 2.47
Bir.out_1	25	0.0029 ± 0.0013	0.127 ± 0.023
Processing blank	80	0.0217 ± 0.0058	0.01

the weighed precipitation mass in the Eppendorf tube. It is important to note that the final transfer step, where the material was moved from the Eppendorf tube to the cathode, was not included in the yield calculation. It's possible that some material was lost during this step, as this part of the process improves with time and practice.

Next, the samples leached with 0.1 M HNO_3 are considered. Both samples, Bir.out_0.1 and Bir.ins_0.1, show higher currents compared to the processing blank. However, the uncertainties for these samples are noticeably large. This is due to the fact that, even within the four runs selected for analysis due to the fluctuations in the standards, the currents vary significantly. One possible explanation is that along with iodine, other interfering elements may have co-precipitated and mixed into the cathode material. The chemical yield of 456% for Bir.out_0.1 suggests that co-precipitation occurred during the preparation process, possibly due to the co-precipitation of Ag_2S along with AgI , influenced by sulfur-containing chemicals like $\text{Na}_2\text{S}_2\text{O}_6$, or other organic compounds leached from the wood material.

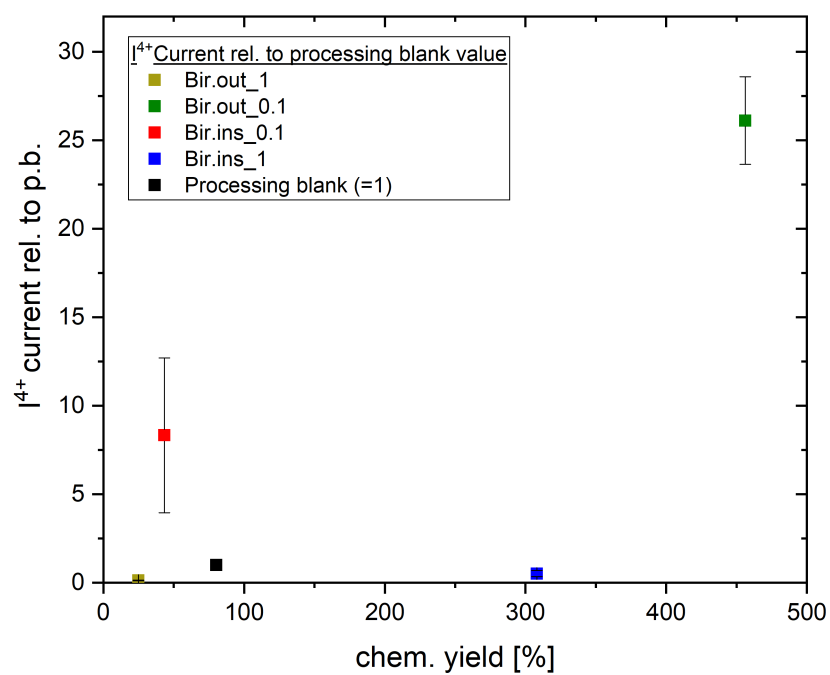


Figure 9.18: Average $^{127}\text{I}^{4+}$ current relative to the processing blank (p.b.) as a function of chemical yield for various birch samples and the processing blank.

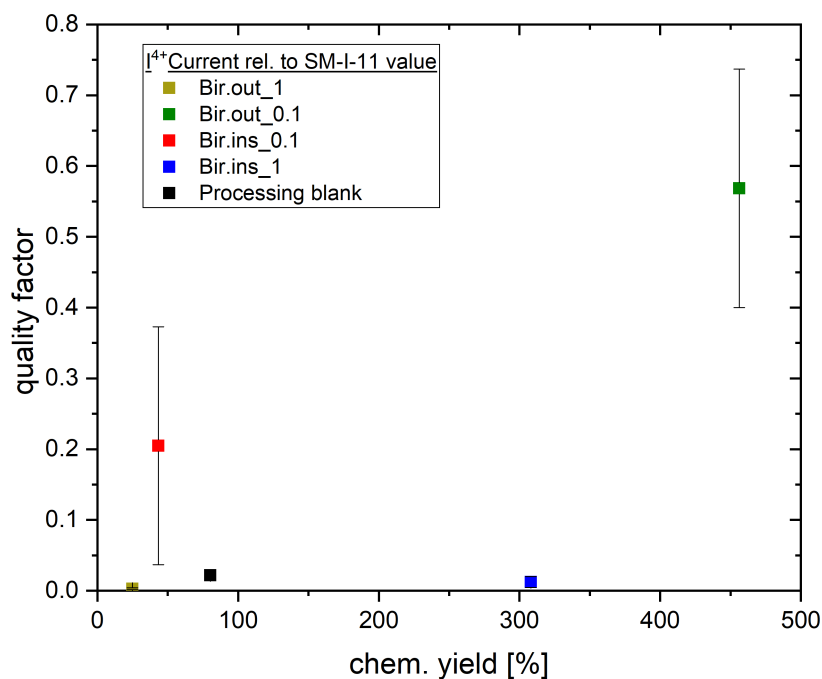


Figure 9.19: Average $^{127}\text{I}^{4+}$ current relative to the SM-I-11 standard, as a function of chemical yield for various birch samples and the processing blank.

This likely contributed to the inhomogeneity within the cathode material, leading to the observed fluctuations in current measurements. ^{129}I was detected in all samples, as shown in Tab. 9.8. The ^{129}I atoms found in the processing blank can be considered (cross-)contamination and should be subtracted from all sample measurements. This means that Bir.out_1 is excluded from further analysis. For the remaining samples, it can be reasonably concluded that the detected ^{129}I likely originates from the samples themselves.

Table 9.8: Sum of ^{129}I atom detections for **Birch.1** samples.

Sample Name	Sum of ^{129}I atom detections
Bir.ins_0.1	396 ± 19
Bir.ins_1	393 ± 19
Bir.out_0.1	925 ± 30
Bir.out_1	32 ± 5
Processing blank	72 ± 8

9.3.3 ^{129}I Discussion

Five samples from a Birch tree were analyzed for iodine content using a chemical leaching method with nitric acid (HNO_3) at concentrations of 1 M and 0.1 M, as indicated in the sample names. The terms "Bir.ins" and "Bir.out" denote the inner and outer xylem of the tree, respectively. To ensure accuracy in the analysis, a stable iodine carrier was added during the chemical preparation process. Since most of the carrier appears to have been lost during the preparation method for three out of five samples (Bir.ins_1, Bir.out_1, and the processing blank), there are two possible explanations. One possibility is that the carrier oxidized during the process, possibly due to the presence of 1 M HNO_3 . If this is the case, it would suggest that the iodine in the samples, including ^{129}I , may have also oxidized during leaching, leading to a loss of the iodine we intended to measure. Another theory is that the carrier was lost at some stage during the chemical preparation, which would imply that the ^{129}I in the samples could have been lost along with it. Additionally, co-precipitation likely disrupted the chemical procedure, possibly due to the presence of unknown organic compounds in the wood material or sulfur-containing chemicals like $\text{Na}_2\text{S}_2\text{O}_6$, which may have led to the co-precipitation of Ag_2S along with AgI .

Moreover, the chemical yields described in Tab. 9.7 were derived from the weighed precipitation mass in the Eppendorf tube. It's important to note that the final transfer step, where the material was moved from the Eppendorf tube to the cathode, was not included in the yield calculation. This means that some material could have been lost during this transfer, as this part of the process tends to improve with time and practice. Furthermore, the interlaboratory comparison study conducted by Roberts et al. (1997) [55] highlights the variability in ^{129}I measurements and suggests that acid leaching of ^{129}I from solid organic samples may result in incomplete extraction. This introduces an additional source of uncertainty to the measurement process.

Regardless of which theory is correct, the current results cannot provide reliable information on the iodine content in the wood samples. However, it is clear that ^{129}I was extracted and measured with this method. In future attempts, it may be beneficial to add the stable carrier after the leaching process and consider using only 0.1 M HNO_3 , as this concentration seems sufficient to extract ^{129}I from the samples, as seen in Bir.out_0.1. After refining the chemical method with further practice, it may be possible to achieve

more stable currents. If successful, this would allow for a more accurate assessment of the ^{129}I concentration in wood samples and enable a potential dendrochemical analysis. This approach has been successful in other studies, and this modified chemical method could offer a faster and more effective alternative to the methods previously used.

10 Conclusion and outlook

10.1 ^{14}C for age determination in modern wood samples

The samples were successfully measured with AMS, and the analysis highlighted some discrepancies in tree ring synchronization, particularly the six missing years between 1970 and 1980 for Spruce.3, which were adjusted in the data interpretation.

The variations observed in the percent of modern carbon across different samples and time periods, especially around the bomb-peak years, align with expected radiocarbon fluctuations caused by nuclear testing. This confirms that the selected trees have not experienced significant damage, making them suitable candidates for further analysis of other radionuclides in a dendrochemical study.

10.2 ^{90}Sr as a supplement to ^{14}C for dating modern wood

In conclusion, this thesis evaluated the potential of ^{90}Sr as a complementary method to ^{14}C for dating modern wood samples, particularly by examining its behavior in trees and its migration within tree rings.

The study revealed that ^{90}Sr does not remain fixed within the heartwood, as initially hypothesized, but migrates within the xylem. This migration, which was observed even in tree rings formed decades before the nuclear era, complicates the use of ^{90}Sr for dendrochronological dating. Notably, significant concentrations of ^{90}Sr were detected in rings from as early as 1920, despite the isotope being introduced in substantial quantities only during mid-20th century nuclear testing.

In contrast to ^{14}C , whose uptake by trees reliably correlates with atmospheric levels, ^{90}Sr 's variability and movement reduce its effectiveness as a precise dating tool. Levels of ^{90}Sr varied widely across trees of the same species and location, further diminishing its reliability for age determination. However, for samples predating the nuclear era, ^{90}Sr could still provide useful information, particularly in cases where ^{14}C levels may become indistinguishable from pre-industrial levels in the future.

Ultimately, the results show that ^{90}Sr is unsuitable for distinguishing post-nuclear from pre-nuclear materials due to its migration within trees. This holds true for both angiosperm and gymnosperm species, where no consistent bomb-peak pattern was preserved. While ^{90}Sr concentrations diminish over time, indicating its limited use in more recent periods, it may still be relevant for dating very old wood samples. Specifically, if an old tree had been exposed to environmental contamination from ^{90}Sr after its death, the isotope could penetrate the wood, necessitating careful analysis and removal of any contamination before reliable dating. Further research is needed to explore these conditions.

10.3 ^{129}I as a supplement to ^{14}C for dating modern wood

This study investigated the potential of ^{129}I for dendrochemical analysis and age determination in modern wood samples. The chemical preparation method was tested on four birch samples, with ^{129}I detected in nearly all of them. However, several challenges were identified during the process.

One significant issue was the loss of stable iodine carrier, which affected three out of five samples (Bir.ins_1, Bir.out_1, and the processing blank). This could be due to oxidation during the chemical preparation, possibly caused by the use of 1 M HNO_3 , or due to losses in various steps of the chemical process. This, in turn, may have led to the loss of ^{129}I from the samples as well. Additionally, co-precipitation likely interfered with the procedure, potentially caused by the presence of unknown organic compounds in the wood material. Despite these challenges, ^{129}I was successfully extracted and measured from the samples, indicating that the method has potential. Future studies could focus on refining the chemical preparation technique, possibly by introducing the stable carrier after the leaching process to minimize its loss. Using a lower concentration of HNO_3 , such as 0.1 M, might also be more effective, as seen in the Bir.out_0.1 sample. If these improvements result in more stable current measurements, this method could provide a faster and more effective approach for ^{129}I analysis in wood samples compared to other, more complex techniques.

It is notable that while Zhao et al. (2019) [19] reported results that demonstrate ^{129}I detection in tree rings, these findings differ significantly from those of Hausschild et al. (1985) [38] and Rao et al. (2002) [30]. Hausschild et al. analyzed trees near a nuclear reprocessing plant in Karlsruhe, which explains their higher ^{129}I values, reaching up to 10^{10} atoms/g wood. In contrast, the values reported by Rao et al. vary by a factor of up to 10^5 compared to those of Hausschild et al. Despite the fact that all these studies examined coniferous trees, the resulting ^{129}I concentrations varied considerably. This suggests that iodine uptake may be strongly influenced by factors such as tree species, geographic location, and the availability of iodine in the environment. Another possibility is that inconsistencies in the methods used to detect iodine in tree rings contributed to the discrepancies across these studies. Therefore, before conducting future dendrochemical analyses with iodine, it would be prudent to verify the reproducibility of the chosen detection method on wood material.

Although this study cannot conclusively determine the suitability of iodine for dendrochemical analysis, the results are promising. With further refinement, ^{129}I could serve as a valuable tool for tracing environmental changes and potentially as a supplement for ^{14}C age determination in modern wood samples.

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