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Uranium and Polonium concentrations in salt lakes of the Seewinkel region in Burgenland

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# Dedication

*Life had started to feel increasingly bitter, until the sweetest Muffin came along and reminded me just how sweet it can truly be.*

# Acknowledgements

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## Zusammenfassung

Die vorliegende Arbeit untersucht die Urankonzentrationen, das isotopische Aktivitätsverhältnis von $^{234}U/^{238}U$ und die $^{210}Po$-Konzentrationen, sowie die damit verbundene Ionenchemie in Proben von Porenwasser, Oberflächenwasser und Brunnenwasser an verschiedenen Standorten aus dem Seewinkel, Burgenland, und aus Hinterbrühl, Niederösterreich. Nach der Abtrennung von Uran über Anionenaustausch wurde mittels Mikropräzipitation eine dünne Messprobe hergestellt, die alpha-spektrometrisch gemessen wurde. $^{210}Po$ wurde durch Spontandeposition auf Cu-Plättchen abgeschieden und ebenfalls mittels alpha-Spektrometrie gemessen. In beiden Fällen wurde vor Beginn der Probenvorbereitung ein Spike zur Bestimmung der chemischen Ausbeute zugesetzt.

Die Urankonzentrationen variieren stark, wobei die Porenwasser die höchsten Konzentrationen aufweisen (51 µg/L - 802 µg/L) und mit hohen Salzgehalten (vor allem Sulfate) und hohen elektrischen Leitfähigkeiten korrelieren. Die hohen Uran-Konzentrationen können daher durch die Bildung von gut löslichen Uranyl-Sulfat-Komplexen erklärt werden.

Brunnen- und Oberflächenwasserproben zeigen relativ niedrigere Urankonzentraionen, mit Ausnahme des Oberflächenwassers Herrnsee (70,2 µg/L). Diese Konzentration wurde im alkalischen Milieu beobachtet (pH-Wert = 8,9), was die Bildung von ebenfalls gut löslichen Uranyl-Carbonat-Komplexen in Gegenwart erhöhter Bicarbonat- Konzentrationen begünstigt.

Die Aktivitätsverhältnisse von $^{234}U/^{238}U$ reichen von 0,50 ± 0,02 bis 1,68 ± 0,05, unabhängig von der Urankonzentration; die größten Schwankungen werden bei den niedrigsten Urankonzentrationen beobachtet. Generell bestätigen die hier präsentierten Ergebnisse eine frühere Arbeit, die ebenfalls am Institut für Anorganische Chemie durchgeführt worden ist.

# Abstract

The present work examines uranium concentrations, the isotopic activity ratio of $^{234}U/^{238}U$, and $^{210}Po$ concentrations, as well as the associated ion chemistry in samples of pore water, surface water, and well water from various locations in Seewinkel, Burgenland, and Hinterbrühl, Lower Austria. After uranium was separated using anion exchange, a thin measurement sample was prepared by microprecipitation, which was measured using alpha spectrometry. $^{210}Po$ was spontaneously deposited onto copper plates and also measured using alpha spectrometry. In both cases, a spike was added before sample preparation to determine the chemical yield.

The uranium concentrations vary significantly, with the pore waters showing the highest concentrations (51 µg/L - 802 µg/L), correlating with high salt contents (mainly sulfates) and high electrical conductivities. The high uranium concentrations can thus be explained by the formation of highly soluble uranyl sulfate complexes.

Well and surface water samples show relatively lower uranium concentrations, except for the surface water of Herrnsee (70.2 µg/L). This concentration was observed in an alkaline environment (pH = 8.9), which favors the formation of highly soluble uranyl carbonate complexes in the presence of elevated bicarbonate concentrations.

The activity ratios of $^{234}U/^{238}U$ range from 0.50 ± 0.02 to 1.68 ± 0.05, independent of uranium concentration; the greatest fluctuations are observed at the lowest uranium concentrations. Overall, the results presented here confirm an earlier study conducted at the Institute of Inorganic Chemistry.

# Content

# 1 Introduction

Measurements carried out by the Environment Agency Austria (Umweltbundesamt) have shown that the Seewinkel (Burgenland, Austria) is affected by high concentrations of uranium in groundwater. The cause of this is unknown. Due to the geology of the area, a geogenic cause has been thought to be unlikely, on the other hand no indications were found for an anthropogenic pollution (e.g. from radioactive repositories or from fly ash from meanwhile closed down coal-fired power plants) of the groundwater with uranium. The only possible anthropogenic impact might be from using phosphate fertilizers in the neighboring fields or wine yards.

As groundwater is a major source of drinking water in Austria, uranium in groundwater might pose a health risk especially to children, the most radiosensitive group (Frisbie et al., 2013; Steffanowski, et al. 2017). Uranium concentrations exceeding the legal limit of 15 µg/L are usually only found in the uranium bearing granite and gneiss regions of the Alps and in the Bohemian Massif (Krachler, et al. 2017).

Aim of the thesis: The planned master thesis is intended to clarify whether ascending deep groundwater / mineral waters are the cause of the increased uranium content in the shallow groundwater. The sampling sites used are selected field irrigation fountains (Well), Seewinkel brines (pore water), as well as surface waters and a spring (Hinterbrühl, Vienna Woods) for comparison. The uranium concentration as well as the activity ratio of the uranium isotopes $^{234}U/^{238}U$ will be measured on the water samples thus obtained. From the $^{234}U/^{238}U$ activity ratios possible hints of the uranium origin is expected and results will be compared with the study of Krachler et al. (2018). Additionally, the $^{210}Po$ activity concentration and the mineral composition of the waters will also be investigated.

## 1.1 Uranium

Uranium (U) is a heavy metal that has served as a significant source of concentrated energy for over 60 years. It is commonly found in most rocks and soils at concentrations ranging from 2 to 4 parts per million (ppm), making it as prevalent in the Earth's crust as tin, tungsten, and molybdenum. Additionally, much higher amounts of dissolved uranium are present in seawater and could be extracted from the oceans. (Nor, et al. 2012)

Discovered in 1789 by German chemist Martin Klaproth in the mineral uraninite, uranium was named after the planet Uranus, which had been discovered eight years earlier. Formed in supernovae approximately 6.6 billion years ago, uranium is relatively rare in the solar system. However, its slow radioactive decay together with the decay of its daughter products is a primary source of the Earth's internal heat, driving geological processes such as convection and continental drift.

Due to its high density (19,1 g/cm$^3$), uranium (or more exactly depleted uranium, a waste product of the nuclear industry) is used in yacht keels, aircraft control surface counterweights, and radiation shielding, as well as in armor piercing ammunition and armor shielding. It has a melting point of 1132°C.

Uranium exists in different isotopes, which vary in the number of neutrons in their nucleus. In the Earth's crust, uranium is primarily found in two isotopes: uranium-238 ($^{238}$U), which makes up about 99.3%, and uranium-235 ($^{235}$U), which accounts for about 0.7%.

$^{235}$U is particularly noteworthy because it can undergo fission under certain conditions, releasing a significant amount of energy. This property led Otto Robert Frisch to coin the term "nuclear fission." $^{238}$U decays very slowly, with a half-life approximately equal to the Earth's age (about 4.5 billion years). This slow decay rate means $^{238}$U is only mildly radioactive, less so than many other isotopes found in rocks and sand, among them also the $^{238}$U daughter nuclides, but it still generates enough decay heat (0.1 watts per ton) *(World Nuclear Association*) to contribute to warming the Earth's core. $^{235}$U, on the other hand, decays slightly faster (HWZ= 704 million years).

Radionuclides like uranium can enter the human body mainly through food and drinking water (Bansal, et al. 1992). Water, in contact with various underground minerals, can dissolve uranium, which then can be consumed by livestock or used for irrigation, potentially contaminating the food chain. Marine life can also be affected if seawater is contaminated with uranium. Surface water from rivers, lakes, and ponds should be considered as potential sources of contamination, making the determination of uranium in water crucial (IAEA Technical Report series No. 295). Table 1 (Suma, et al. 2016) provides data on the variability of uranium in natural water.

*Table 1: Uranium variability (µg/L) in natural water*

| Source | Uranium concentration (µg/L) |
|---|---|
| Lakewater | 8.4 - 3.7 |
| Groundwater | < 0.1 - 120 |
| River | 0.1 - 10 |
| Ocean | 3.3 |

Uranium exists in the natural environment in various oxidation states, with hexavalent uranium (U (VI)) and tetravalent uranium (U (IV)) being the most common (Wufuer et al. 2017). Hexavalent uranium minerals, such as carnotite, are highly soluble in water, whereas tetravalent uranium minerals, like uraninite and pitchblende, are less soluble and immobile, particularly under reducing conditions or in very acidic environments (Kirchheimer 1963).

The presence of sulfate ($SO_4^{2-}$), bicarbonate ($HCO_3^-$) and phosphate ($PO_4^{3-}$) in water influences the adsorption and desorption of uranium minerals into aqueous phases (Bachmaf, et al. 2008). The release of uranium from minerals is affected by the chemical properties of groundwater, including pH, redox potential, and the presence of these ions and natural organic substances.

Anthropogenic sources such as phosphate fertilizers, pesticides, coal combustion in thermal power plants, and depleted uranium can also increase uranium levels in water (Wazne, et al. 2003). A study indicates that uranium-containing rocks are predominantly found in Austria's Bohemian Massif and Alpine regions, where groundwater may naturally contain higher uranium concentrations (Berka, et al. 2014).

### 1.1.1 Uranium radiotoxicity

Uranium is known for its radiotoxicity and chemical toxicity. For most uranium series radionuclides, the radiation dose is more significant for human health than the chemical toxicity. However, for uranium itself, being a low-level radioactive heavy metal, the chemical toxicity is more critical (Sheppard, et al. 2005). The primary health effect from uranium exposure is renal toxicity, as ingested uranium is mainly excreted via the kidneys (EFSA 2009).

Using the MAK values (maximum allowable concentration in the workplace) as a reference, uranium has a value of 0.25 mg/m³, which is between mercury (0.1 mg/m³) and nickel (0.5

mg/m³) (Schnug, et al. 2016). Studies have shown that gamma radiation can increase the DNA-damaging effect in the presence of uranium, indicating a synergistic impact of these harmful factors (Smirnova et al., 2005). Additionally, aquatic organisms exhibit oxidative stress and genotoxicity at uranium concentrations as low as 10 µg/L.

Another study reported that increased uranium exposure through water uptake can lead to leukemia and an estrogenic effect (Raymond-Whish et al., 2007). Besides uranium, its decay products, such as polonium-210 ($^{210}$Po), radium-226 ($^{226}$Ra), radon-222 ($^{222}$Rn), and lead-210 ($^{210}$Pb), also exhibit both radiological and chemical toxicity (Wallner, et al. 2008), though these (with the exception of $^{210}$Po) are not considered in this work.

*Table 2: Uranium limits in drinking water (µg/L)*

| **Organization/Region** | **Uranium limit (µg/L)** |
|---|---|
| US-EPA (2000) | 30 |
| Health Canada (2001) | 20 |
| Australian Drinking Water Guidelines (2002) | 20 |
| WHO (2011) | 30 |
| India (AERB 2001) | 60 |
| Austria (BGBl. II 359/2012) | 15 |
| Germany (2013) | 10 |

Table 2 shows the limits for uranium in drinking water as established by various organizations (Suma, et al. 2016; Schnug, et al. 2008; US EPA 2000; WHO 2011; AERB 2010). In Austria, the limit of 15 µg/L is based on the chemical toxicity of uranium as a heavy metal (Humer, et al. 2019), as radiotoxicity occurs only at significantly higher concentrations (EFSA 2009).

### 1.1.2 Uranium decay series

Uranium-238 ($^{238}$U) is the parent nuclide of the 4n + 2 decay series found naturally in the environment. uranium-234 ($^{234}$U), a decay product of $^{238}$U, exhibits identical chemical behavior but can be naturally enriched or depleted (Steinhauser et al. 2009).

Figure 1 illustrates the decay series of $^{238}$U, showing its daughter nuclides along with their respective half-lives and types of radiation.

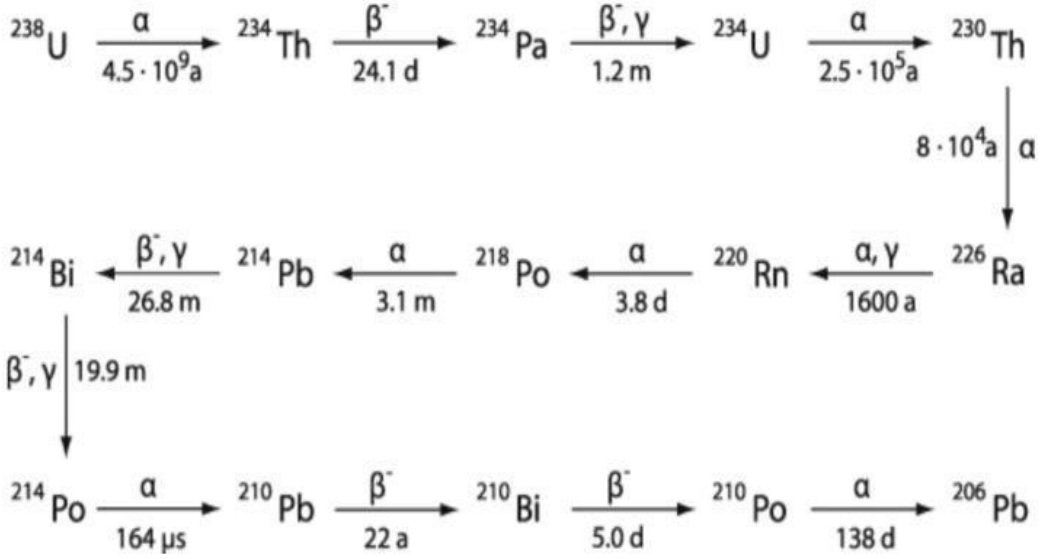



*Figure 1: Decay series of uranium*

A radioactive decay series is in equilibrium when all secondary products have the same activity as the long-lived parent nuclide. In a closed system, uranium-238 ($^{238}U$), the parent nuclide, should be in equilibrium with all its decay products, resulting in activity ratios of 1 (Khattab 2016). However, due to the α-particle recoil effect in the crystal lattice, uranium-234 ($^{234}U$) isotopes are more soluble and prone to leaching than $^{238}U$, leading to higher $^{234}U/^{238}U$ activity ratios in groundwater (Khattab 2016).

Because of this recoil effect, the activity ratio $^{234}U/^{238}U$ in natural groundwater is expected to be higher than in groundwater contaminated by depleted uranium from the nuclear industry, where the ratio should be much less than 1 (Rhodes, et al. 2007).

For these reasons, the activity ratio $^{234}U/^{238}U$, along with $^{238}U$ concentration and its other daughter nuclides, is used to assess geological processes and identify the type of groundwater contamination (Khattab 2016; Rhodes, et al. 2007). Table 3 describes the causes of changes in the activity ratio of these isotopes.

*Table 3: Causes for the changes of the activity ratio*

| **A ($^{234}U/^{238}U$)** | **Causes** |
|---|---|
| = 1 | Radioactive equilibrium, in an undisturbed place |
| < 1 | Contamination (waste products from nuclear industry) |
| >1 | Better solubility of $^{234}U$ as a result of alpha particle recoil effect |

### 1.1.3 Uranium in fertilizer

Anthropogenic inputs such as coal combustion in thermal power plants and depleted uranium (waste product from nuclear industry) are not significant in the tested water samples. However, fertilizers may be a potential contributing factor for some water samples due to the proximity of sampling sites to fertilized agricultural areas. uranium can reach shallow groundwater and drinking water through mineral or organic phosphate fertilizers (Schnug, et al. 2008).

The uranium content in phosphate fertilizers depends on the source of the raw phosphate, usually phosphate rock. Phosphate rock naturally contains uranium, along with other radionuclides, because it is a sedimentary rock and uranium and thorium - similar to phosphate - concentrate in marine sediments during the geological processes of rock formation. Even organic fertilizers (manure and sludge) can contain a certain amount of uranium. Table 4 provides an estimate of possible uranium inputs from different fertilizers, based on fertilization rates of 22 kg phosphate per hectare per year (Dienemann, et al. 2012; Kratz, et al. 2008). The $^{234}U/^{238}U$ activity ratio in phosphate rocks typically ranges from slightly below 1 to slightly above 1, with most values reported between 0.9 and 1.1. This range indicates that these isotopes are generally close to secular equilibrium in such rocks, although slight deviations can occur due to geological and environmental factors, such as uranium mobilization or weathering processes. (Boujelbane, et al. 2022)

As shown in Table 4, the uranium concentrations [mg/kg P] and resulting inputs [g/ha per year] are lower in soils treated with organic fertilizers compared to mineral fertilizers. Additionally, studies in Germany have demonstrated that 5 - 15 percent of the uranium present in agricultural soils originates from fertilization (Schnug 2016).

*Table 4: Uranium concentrations [mg/kg P] and resulting inputs [g/ha per year] (Dienemann, et al. 2012).*

| Typ | P-Konzentration [% P] Spannweite | U-Gehalt [mg/kg P] Spannweite | U.Eintrag [g/ha·a] Spannweite | U-Eintrag [g/ha·a] Mittelwert |
|---|---|---|---|---|
| TSP (Triple-Superphosphat) | 16,6 – 20,6 | 52,3 - 362 | 5,6 - 48 | 22 |
| NP (Stickstoff-Phosphat-Dünger) | 5,3 – 25,8 | 0,62 – 198 | 0,05 - 82 | 7,0 |
| PK (Phosphat-Kalium-Dünger) | 5,8 – 13,4 | 31,2 - 163 | 5,1 - 61 | 23 |
| NPK (Stickstoff-Phosphat-Kalium-Dünger) | 1,5 – 13,5 | 0,04 - 113 | 0,01 - 166 | 8,0 |
| Rindergülle | 0,43 – 2,1 | 0,15 – 1,4 | 0,16 - 7 | 2,9 |
| Klärschlamm | 2,1 – 2,2 | 0,0005 – 18,5 | 0,001 - 19 | 3,2 |

## 1.2 The influence of salinity-determining anions on uranium solubility

The main oxidation states of uranium in nature are U (IV) ([Rn] $5f^2$) and U (VI) ([Rn] $5f^0$). The oxidation state U(V) is very rare. uranium in fresh and mineral waters usually occurs in the U (VI) form (Ervanne 2004). The variability of uranium in natural water is given in Table 1. It has been reported that under reducing conditions, the uranium concentration is ~0.1 µg/L and can reach 120 µg/L under oxidizing conditions (Suma, et al. 2016).

These oxidation states of uranium are critical for its stability and mobility. U (IV) has much lower solubility than U (VI). The change in oxidation state from U (IV) to U (VI) usually occurs under oxidizing conditions at the geosphere/atmosphere interface or in the lithosphere by contact with oxygen-containing groundwater (Cumberland, et al. 2017).

According to Bruno and Puigdomenech, dissolved U (IV) in natural waters ranges between 3 - 30 µg/L if these waters contain a large amount of inorganic salts like $Na^+$, $Ca^{2+}$, $K^+$, and $Cl^-$ (Bruno, et al. 1988). Anaerobic systems with high carbonate alkalinity or high dissolved organic matter concentrations may also contain more dissolved U (IV) than commonly assumed (Ervanne 2004).

The tendency of uranium to combine with oxygen is more pronounced when it is in the hexavalent state. For most of the natural pH range (≈6-10), U (VI) forms strong complexes with oxygenated ions (such as $CO_3^{2-}$, $HCO_3^-$, $SO_4^{2-}$, $PO_4^{3-}$) found in most surface and groundwaters (Richardson, et al. 2003). The order of affinity for mono and dual charged species is as follows (Bourdon, et al. 2003):

- $F^- > H_2PO_4^- > SCN^- > NO_3^- > Cl^-$ for U (IV)
- $CO_3^{2-} > HPO_4^{2-} > SO_4^{2-}$ for U (VI)

Sulfate and phosphate are major ligands that influence the adsorption and transport of U (VI) in groundwater. Uranium can form complexes with these ligands, such as $UO_2SO_4$ and $UO_2HPO_4$ (Gorman-Lewis, et al. 2008).

Carbonate is the most important uranium ligand in natural water. Due to the ability of the uranyl ion to form soluble carbonate complexes, uranium mobility increases under alkaline, oxidizing conditions (Langmuir 1978). Table 5 illustrates various uranyl carbonate complexes in different pH ranges at 25°C.

*Table 5: Uranium-carbonate complexes in water*

| **Complex** | **pH range** |
|---|---|
| $UO_2CO_3$ | 5 - 6.5 |
| $UO_2(CO_3)_2^{2-}$ | 6.5 - 7.5 |
| $UO_2(CO_3)_3^{4-}$ | > 7.5 |

Carbonate complexes also play a crucial role in the removal of uranium from contaminated water, as they increase the solubility and mobility of uranium in water (Brown, et al. 2007).

## 1.3 The uranium determination methods for environmental monitoring

There are several methods for determining uranium concentration in water. Uranium can be measured in mass units using chemical-analytical methods such as mass spectroscopy, which primarily determines the major isotope $^{238}U$ and does not allow for the calculation of the isotope ratio $^{234}U/^{238}U$. It can also be measured in activity units through radiochemical analysis (Environmental Protection Agency 1997).

Radiochemical Analysis Methods:

- Alpha spectroscopy
- Liquid scintillation counting (LSC) (Tosheva, et al. 2003; Szabó, et al. 2013).
- Gamma spectroscopy

**Alpha Spectrometry:** Alpha spectrometry is utilized for determining uranium concentrations in water and environmental media. The advantages of alpha spectrometry include:

- **High Sensitivity:** It can detect very low levels of uranium isotopes, making it suitable for trace analysis.
- **Specificity:** It distinguishes between different alpha-emitting isotopes, allowing for precise identification of uranium isotopes such as $^{234}U$, $^{235}U$, and $^{238}U$.
- **Accuracy:** Provides accurate quantitative measurements of uranium concentrations due to possible spike addition
- **Minimal Interference:** Has low background interference, enhancing the reliability of the results.

The disadvantages of alpha spectrometry are as follows:

- **Complex Sample Preparation:** Requires extensive and meticulous sample preparation to isolate uranium from other materials.
- **Time-Consuming:** The process is often time-consuming, including both the preparation and measurement phases.
- **Specialized Equipment and Training:** Requires specialized equipment and trained personnel to operate and interpret results accurately.
- **Potential for Contamination:** High sensitivity means that even small amounts of contamination can affect results, necessitating strict cleanliness and control protocols.

**LSC:** When using LSC, an aqueous solution containing alpha-emitting nuclides is mixed homogeneously with a cocktail containing an organic solvent (e.g. diisopropylnaphthalene in Hisafe III) and an activator that converts radiation energy into photons. While this method requires the separation of alpha-emitting nuclides from samples, it does not necessitate thin sample preparations. However, LSC has disadvantages:

- **Yield Correction:** The use of a spike for yield correction is typically not feasible due to the relatively broad peaks in the spectrum.
- **Resolution of Isotopes:** The peaks of uranium isotopes $^{234}U$ and $^{238}U$ cannot be resolved clearly, reducing its effectiveness for detailed isotopic analysis.

Due to these limitations, LSC is less frequently used in environmental analytical applications compared to alpha spectroscopy (Tosheva, et al. 2003).

**Gamma spectroscopy** has a detection limit that is 100-1000 times higher than that of alpha spectroscopy, making it suitable only for rough estimations and high yield uranium samples (Khattab 2016).

## 1.4 Polonium

Polonium (atomic number 84) is a highly radioactive element with several isotopes, the most notable being polonium-210 ($^{210}Po$). It is known for both its radiotoxicity and chemical toxicity. $^{210}Po$ is an alpha emitter with a short half-life of 138.4 days, making it highly dangerous even in small amounts.

Polonium was discovered by Marie and Pierre Curie in 1898 during their research on the radioactivity of uranium and thorium minerals (Curie, et al. 1898). Initially, it posed challenges due to its small quantities and the difficulty of separating it from bismuth, as it behaves similarly. Through vacuum sublimation, polonium was successfully isolated from Bi. However, due to the scarcity of polonium and incomplete separation of radioactive impurities, its definitive identification was only achieved in 1906 (Curie, et al. 1898). Until 1944, research on polonium was mainly conducted at trace levels, resulting in some erroneous conclusions about its basic chemistry. Nevertheless, later advancements with milligram quantities have greatly improved our understanding of polonium's chemistry (Katz, et al. 1986).

### 1.4.1 Polonium radiotoxicity

Polonium is notorious for its extreme radiotoxicity, posing significant health risks even in small quantities. $^{210}Po$, the most well-known isotope, has an estimated lethal dose (LD50) for humans of around 50 ng (WHO - $^{210}Po$) if ingested or inhaled.

If taken up, $^{210}$Po does not have a specific target organ, but affects all organs, so making it impossible to eliminate it from the human body. The alpha radiation emitted by $^{210}$Po can cause severe damage to living cells and tissues, leading to various health problems, including radiation sickness, organ damage, and an increased risk of cancer. This radiotoxicity is primarily due to the high linear energy transfer (LET) of alpha particles, which deposit a large amount of energy in a small area as they interact with biological tissues (Tafreshi, et al. 2019). It has been famously associated with cases of poisoning, such as the death of former Russian spy Alexander Litvinenko in 2006.

## 1.5 The $^{210}$Po determination methods for environmental monitoring

After chemical separation from matrix elements and other radionuclides, $^{210}$Po together with a spike can only be measured by alpha-spectrometry.

# 2 Materials and methods

## 2.1 Sampling points

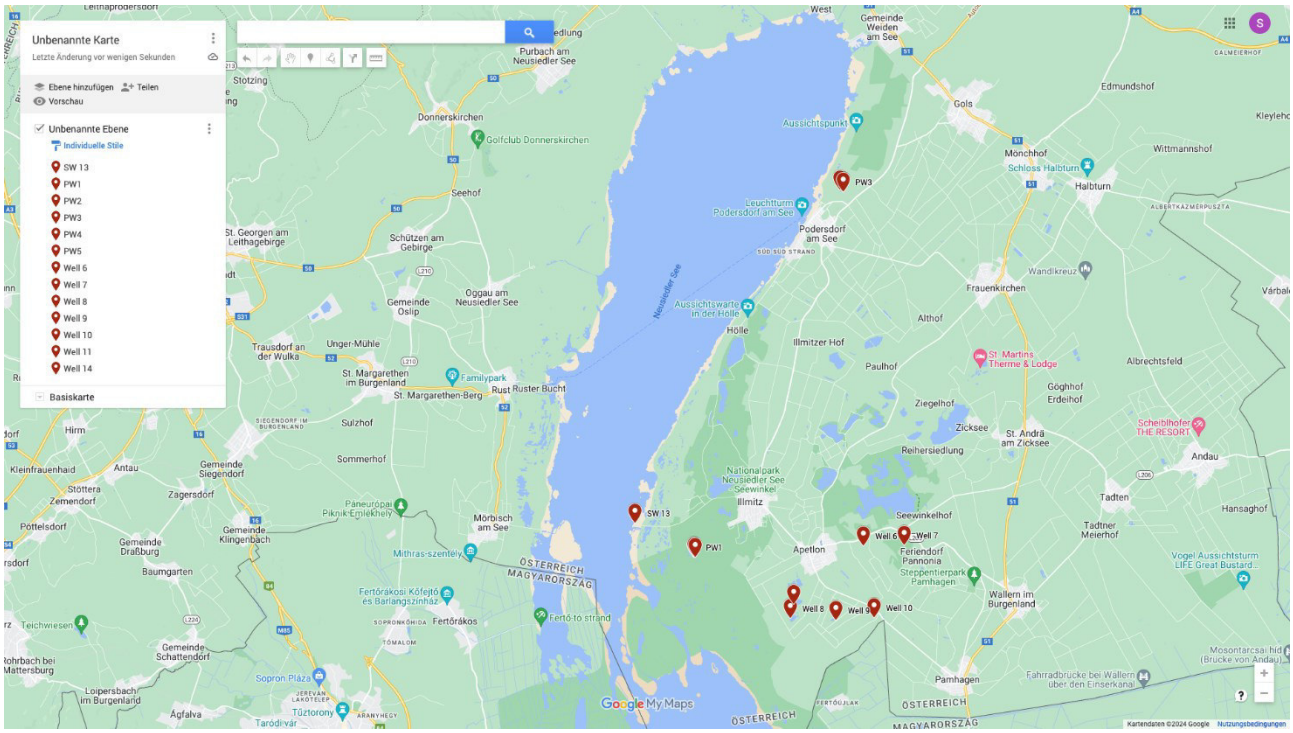
Water samples were collected from various locations in Burgenland from April 2017 to August 2017, as shown in Figure 2. Measurements of temperature, pH, and electrical conductivity were conducted on-site. Picture 1 displays a map of parts of Burgenland with labeled sampling points.

A total of 14 different measuring points, including 5 pore waters, 6 well waters and 3 surface waters, were investigated for uranium and polonium. The 5 pore water samples and 1 surface water sample were taken at the same day and location, but in different bottles, as in the paper by Krachler et al. 2018.

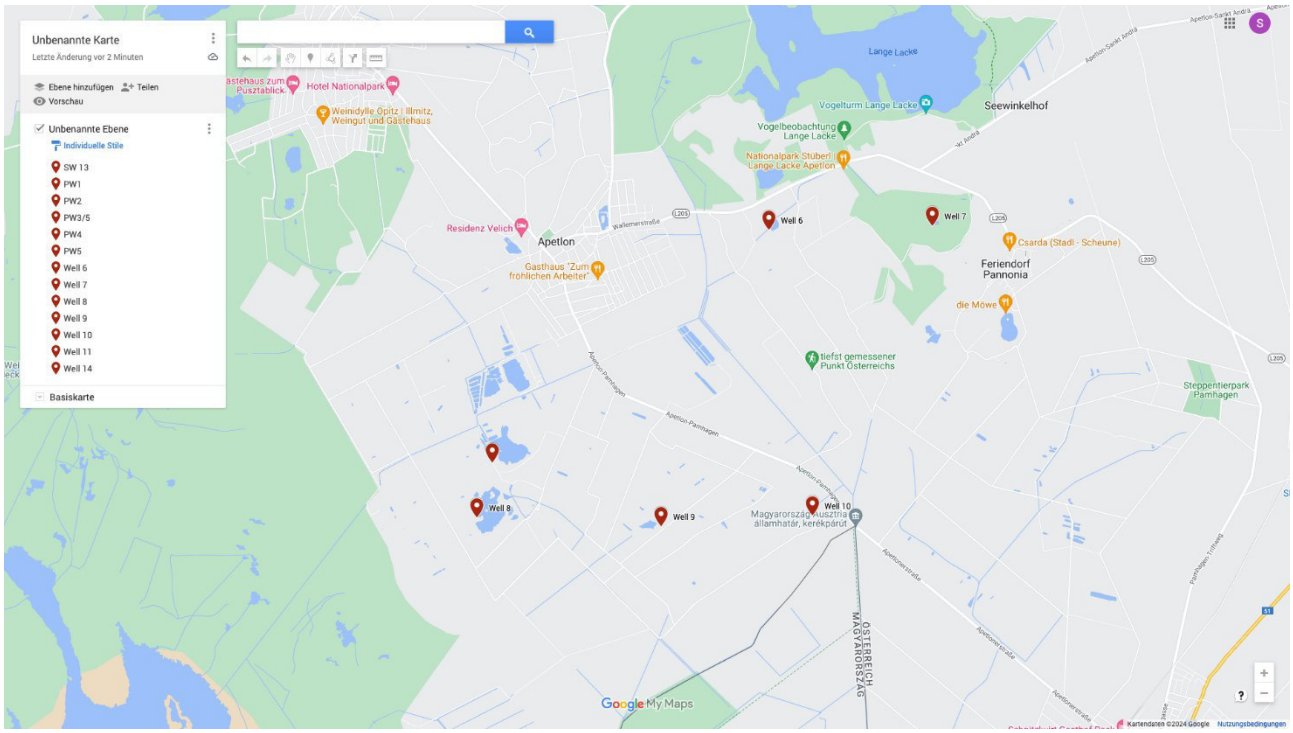
Pore water samples were collected using a vacuum pore water collector, as depicted in picture 5. Table 6 provides details for each sample, including sample names, sampling dates, locations, and measured values (water temperature, pH, electrical conductivity).

To account for potential contamination from fertilizers, samples collected from areas without fertilized agricultural activities were marked with an asterisk "*".

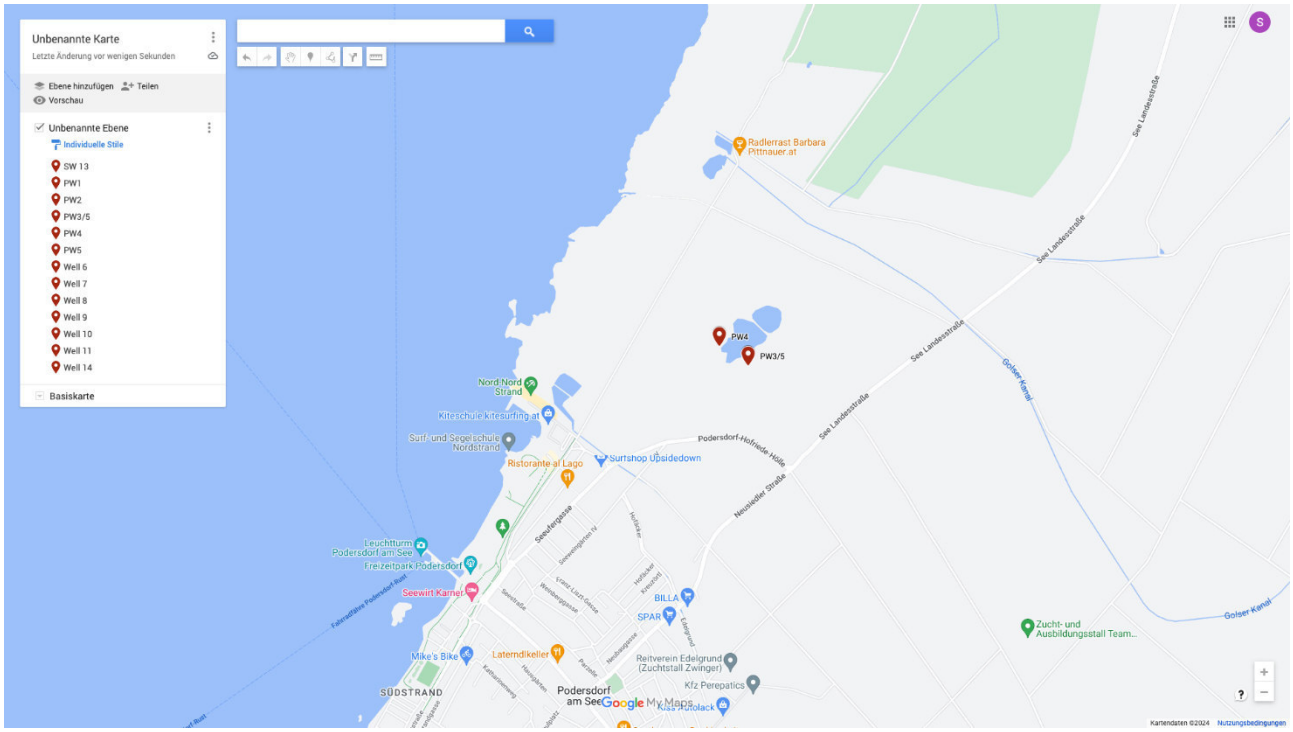
These water samples were provided by ao. Univ. Mag. Regina Krachler and Dr. Mag. Rudolf Krachler and were stored in dark and cooled conditions between 4 - 12°C before analysis. The map picture 1 shows the 13 sample locations in the Seewinkel area. Map picture from 2 to 4 are the close-ups of the locations.



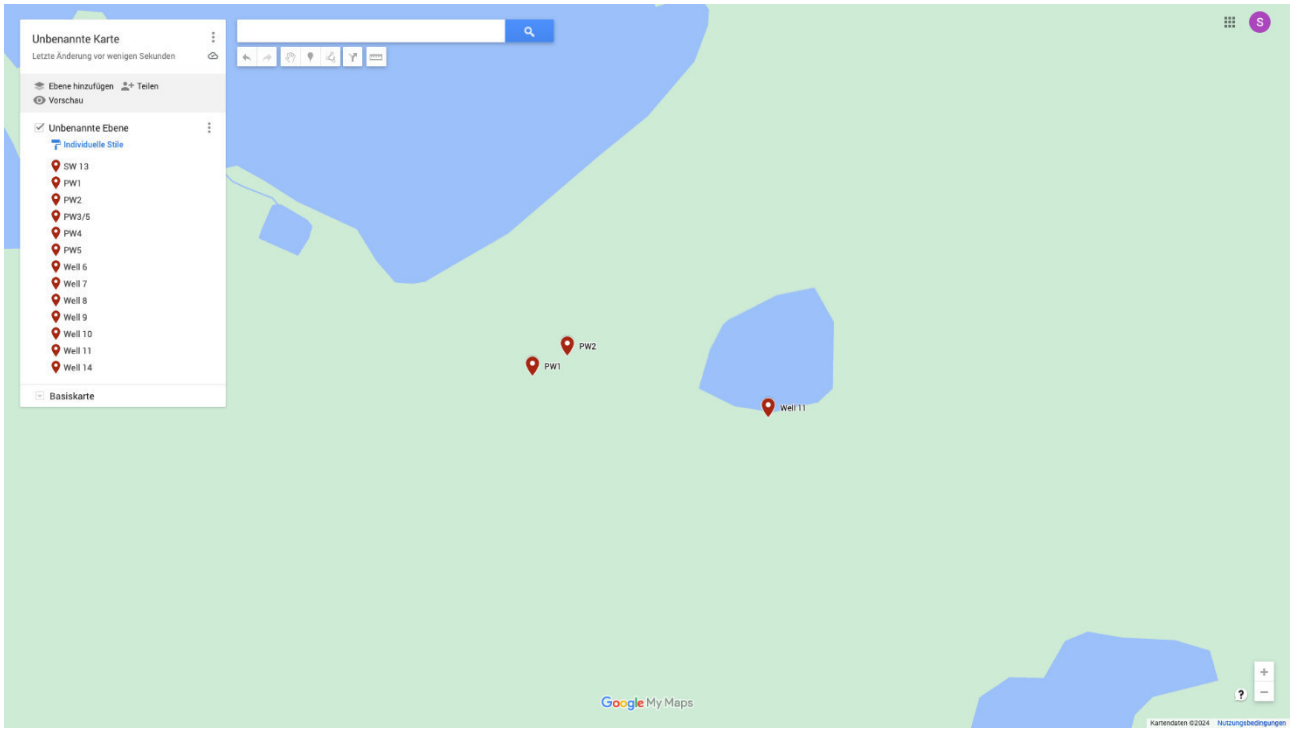

*Picture 1: Picture 1: locations of the sampling*




*Picture 2: close-up of the locations around Apetlon*




*Picture 3: close-up of the locations near Parndorf*




*Picture 4: close-up for the locations of the samples near Herrnsee*

*Picture 5: Vacuum pore water collector*

*Table 6: Water samples details and measured values*

| Name | Label | Date | Position | Temp. (°C) | el. cond. (mS/cm) | pH |
|---|---|---|---|---|---|---|
| Herrnsee Porenwasser 1 (80 cm Tiefe) | 1*PW | 11.04.17 | Elevation 115m N 47°44'35.1" E 16°46'15.0" | 14.2 | 21.0 | 7.39 |
| Herrnsee Porenwasser 2 (80 cm Tiefe) | 2*PW | 11.04.17 | Elevation 115m N 47°44'35.3" E 16°46'15.5" | 14.2 | 30.0 | 7.28 |
| Legerilacke Süd 2 Porenwasser (80 cm Tiefe) | 3PW | 01.04.17 | Elevation 117m N 47°52'07.0" E 16°50'51.3" | 20.6 | 65.6 | 7.35 |
| Legerilacke Süd-West Porenwasser (80 cm Tiefe) | 4PW | 08.04.17 | Elevation 117m N 47°52'10.0" E 16°50'44.7" | 12.0 | 64.1 | 7.20 |
| Legerilacke Süd 2 Porenwasser (117 cm Tiefe) | 5PW | 08.07.17 | Elevation 117m N 47°52'07.0" E 16°50'51.3" | 31.2 | 64.1 | 7.71 |
| Moschadolacke Brunnenwasser (aus 5m Tiefe) | 6Well | 12.07.17 | Elevation 116m N 47°44'48.75" E 16°51'27.64" | 25.5 | 3.49 | 7.37 |
| Götschlacke Brunnenwasser (aus 5m Tiefe) | 7Well | 12.07.17 | Elevation 116m N 47°44'50" E 16°52'43" | 26.0 | 1.851 | 7.04 |
| Apetloner Meierhoflacke Brunnenwasser (aus 5m Tiefe) | 8Well | 12.07.17 | Elevation 116m N 47°43'19.6" E 16°49'12.9" | 13.6 | 10.29 | 7.53 |
| *Dorflacke Brunnenwasser (aus 5m Tiefe) | 9*Well | 12.07.17 | Elevation 116m N 47°43'16.9" E 16°50'37.7" | 25.5 | 9.80 | 8.45 |
| *Arbesthaulacke Brunnenwasser (aus 5m Tiefe) | 10*Well | 21.07.17 | Elevation 116m N 47°43'20.3" E 16°51'47.8" | 14.7 | 2.62 | 6.86 |
| *Herrnsee Oberfläschenwasser | 11SW | 11.04.17 | Elevation 116m N 47°44'34.7" E 16°46'18.4" | 14.7 | 14.0 | 8.99 |
| *Gipsbergwerk Seegrotte Hinterbrühl Quelle „Altes Boot“ | 12*Well | 05.08.17 | | 9.0 | 3.24 | 7.01 |
| Neusiedlersee Seebad Oberflächenwasser Imllitz | 13SW | 31.08.17 | | 25.0 | 2.42 | 8.67 |
| Mitterweißsee Brunnenwasser (aus 5m Tiefe) | 14Well | 21.07.17 | Elevation 116m N 47°43'36.6" E 16°49'20.0" | 13.0 | 7.84 | 7.15 |

**Note:** * indicates samples collected from areas without fertilized agricultural activities.

## 2.2 Chemicals/Materials/Analytical Instruments

- 40% HF (Sigma-Aldrich)
- 0,58 M HF (980 ml H2O + 20 ml 48% HF)
- 0,5 mg/ml Neodym solution: 58 mg $Nd_2O_3$ in 1 M HCl
- $NdF_3$ solution: 10 ml 0,5 mg/ml Neodym solution + 455 ml 1 M HCl + 40 ml 48% HF
- 15% $TiCl_3$ (Sigma-Aldrich)
- HCl (Sigma-Aldrich)
- $HNO_3$ (Sigma-Aldrich)
- 8M HCl
- Dowex 1x2 $Cl^-$ (100-200 mesh)
- $H_2O_2$
- Cu-planchettes
- 2M HCl

- Si surface barrier detector (PIPS Model 7401, Canberra™) for alpha counting
- Cations determination on Flame Atomic Absorption Spectroscopy on Perkin Elmer Analyst
- Alkalinity determination on iodine/iodate electrodes from SCHOTT Instruments and a ProLap 2000 pH meter (Schott Instruments)

## 2.3 Uranium determination

All samples were collected between April 2017 and August 2017 from various locations in the so-called Seewinkel east of Lake Neusiedl. To prevent adsorption of uranium on the bottle walls, the water samples were filled into 1.5 L PET bottles, and when arriving at the laboratory, the samples were acidified with $HNO_3$ to get a sample concentration of 10 ml $HNO_3$ per L of water.

For analysis, 500 ml of the acidified sample was filtered using a Sartorius filter with a pore size of 5 - 8 µm, and 20 µl of $^{232}U$ (corresponding to 35.4 mBq) was added as a spike to the filtered sample. The yield and the activity of the isotopes were calculated based on the amount of spike recovered during the measurement. In table 7 the energy and half-life of uranium isotopes of interest are summarized.

*Table 7: Energy and half-life of uranium isotopes*

| Isotope | Energy in MeV | Half-life in yr |
|---|---|---|
| $^{232}U$ | 5.324 | 70.0 |
| $^{234}U$ | 4.773 | $2.455*10^5$ |
| $^{238}U$ | 4.195 | $4.468*10^9$ |

The sample was gently evaporated to dryness using a hot plate. Subsequently, it was evaporated three times with 10 mL of concentrated HCl each time to remove nitrates. The remaining residue was dissolved in 80 - 90 ml of 8M HCl. Insoluble particles were separated using a black band filter.

To condition Dowex 1x2 $Cl^-$ (100 - 200 mesh), it was soaked in distilled water for at least 3 hours, then slurried, filtered off, and taken up in 8M HCl (first use 12 hours afterwards). The sample was applied to the column (1 cm diameter), which was filled with Dowex (4 - 5 cm). Prior to elution, the column was rinsed with 50 mL of 8M HCl to remove any Th and Ca that could interfere with alpha spectroscopy. The passed through sample and washing solutions were collected for further polonium determinations.

The elution of uranium was conducted using 80 ml of 0.1 M HCl (the complex $UO_2Cl_4^{2-}$ disintegrates on the column). The eluate was evaporated to dryness on the hot plate. The residue was then dissolved with 3x (5 ml of concentrated $HNO_3$ and 2 ml of $H_2O_2$ (30%)) to destroy any remaining organic material from the resin. The residue was taken up in 2 mL of 1M HCl and transferred to a plastic test tube. The beaker was rinsed twice with 1 ml of 1M HCl and these solutions were added to the sample in the plastic test tube.

### 2.3.1 Microprecipitation

The solution was mixed with 100 µL of $Nd^{3+}$ solution. Dropwise, $TiCl_3$ was added until a violet color formed confirming the reduction of U(VI) to U(IV). After the addition of 0.5 ml of 40% HF as a precipitant, the solution was shaken and allowed to stand for 30 minutes.

After one minute in an ultrasonic bath, the sample solution was filtered through a membrane filter (Cellulose Nitrate Membrane Filters, Whatman™, 0.1 µm) previously prepared by filtering 4 ml of $NdF_3$ solution. The (invisible) $NdF_3$ precipitate (with the co-precipitated U(IV)) was first washed with 2 mL of 0.58M HF, then once more with 2 mL of distilled water. The sample on the filter was then sucked dry and fixed on a metal sample holder with a snap

ring, keeping it dust-proof until the measurement. The measurement was conducted using a Si surface barrier detector (PIPS Model 7401, Canberra™).

## 2.4 $^{210}$Po determination

The washing solution from the column is spiked with 10 µL of $^{209}$Po (corresponding to 36.5 mBq). The solution is then evaporated and vaporized three times with concentrated HCl. The resulting precipitate is dissolved in 60 mL of 2 M HCl and heated to 80-90°C on a hot plate with a magnetic stirrer. A Cu planchette, briefly etched with 2 M HCl, is added to this solution. To facilitate spontaneous deposition of Po on the Cu planchette, the solution, along with the Cu planchette, is stirred for approximately 2 hours on the magnetic stirrer at 80°C.

Subsequently, the plate is removed, rinsed with distilled water and dried. In table 8 the energy and half-life of $^{209}$Po and $^{210}$Po are summarized.

*Table 8: Energy and half-life of $^{209}$Po and $^{210}$Po isotopes*

| Isotope | Energy in MeV | Half-life |
|---|---|---|
| $^{209}$Po | 4.90 | 102 a |
| $^{210}$Po | 5.3 | 138 d |

## 2.5 Determination of additional water parameters

### 2.5.1 Determination of salinity with Flame Atomic Absorption Spectroscopy (F-AAS):

The flame atomic absorption measurements (F-AAS) were conducted using a Perkin Elmer Analyst. The original samples were filtered. A dilution series of the samples (1:10, 1:100, 1:1000, 1:10000) was prepared with 2% HNO3. Different concentrations of standards were used to calibrate the device. The concentration ranges of the standards are given in Table 11.

For calibration, the standards were measured starting with the lowest concentration. A polynomial curve was fitted through the origin ($R^2 > 0.9999$). The measurements were carried out at a wavelength indicated in Table 9 below.

*Table 9: Wavelength of ions*

| Element | Kalium | Sodium | Calcium | Magnesium |
|---|---|---|---|---|
| Wavelength (nm) | 766.5 | 589 | 422.7 | 285.2 |
| Measurement range (mg/L) | 0,25-2 | 0,25-1 | 0,5-2,5 | 1-10 |

### 2.5.2 Alkalinity

The acid-binding capacity of the carbonate/carbonic acid/bicarbonate system was determined by titration. 25 ml of the diluted sample were titrated with 0.1 M HCl (Factor: 0.9985). The titration curve was monitored using a iodine/iodate electrodes from SCHOTT Instruments and a ProLap 2000 pH meter (Schott Instruments)

Alkalinity, particularly in the form of bicarbonate and carbonate ions in water, plays a critical role in determining the behavior of uranium in aqueous environments (Hennig, et al. 2008; Bachmaf, et al. 2008).

Alkalinity tends to increase the pH of water. The solubility of uranium compounds generally increases in alkaline conditions due to the stability of these carbonate complexes. In acidic or neutral environments, uranium compounds may precipitate, reducing mobility (Bachmaf, et al. 2008).

### 2.5.3 Electrical conductivity of water samples

Measuring the electrical conductivity (EC) of a water sample is a straightforward process and involves using a conductivity meter or EC meter. The conductivity of aqueous solutions is influenced by the concentration of dissolved substances, the ionic conductivity, and the mobility of the ions present. Water temperature also plays a role in affecting its conductivity (Kumar, et al. 2018).

### 2.5.4 pH influence

Measuring the pH of a water sample is a simple process and can be done using a pH meter or pH test strips.

The correlation between pH and the solubility of uranium is a key aspect in environmental science, geochemistry, and nuclear waste management (Hennig, et al. 2008 and Bachmaf, et al 2008).

# 3 Results and discussion

Calculation of sample activity

$$A(^{238}U) = \frac{counts(^{238}U)}{counts(^{232}U)} * A(^{232}U)$$

*Equation 1: Activity (mBq) of $^{238}U$ (analog calculation of $^{234}U$ activity)*

A($^{238}$U): Activity of $^{238}$U in the sample (mBq/per discharged volume (500 mL)). A($^{232}$U): added Activity of $^{232}$U (mBq). Counts ($^{238}$U) & Counts ($^{232}$U): Net counts in the respective peak areas.

**Measurement uncertainty σ of the activity $^{238}$U:**

calculated following error propagation by Gauss

$$\sigma^2(A\left(^{238}U\right)) = \left(\frac{A\left(^{232}U\right)}{counts\left(^{232}U\right)}\right)^2 * counts\left(^{238}U\right) + \left(\frac{counts\left(^{238}U\right)}{(counts\left(^{232}U\right))^2} * A\left(^{232}U\right)\right)^2 * counts\left(^{232}U\right)$$

*Equation 2: Calculated following error propagation by Gauss (analog calculation for $^{234}U$)*

A($^{232}$U): added activity of $^{232}$U (mBq). Counts ($^{238}$U) & counts ($^{232}$U): Net counts in the respective peak areas.

The measurement uncertainty σ of the activity $^{238}$U is calculated using Gauss's error propagation law (see appendix), which involves the partial derivatives of the $^{238}$U activity with respect to each variable involved in the measurement (counts ($^{238}$U) and counts ($^{232}$U)) as well as the counting uncertainties of $^{238}$U and $^{232}$U, respectively.

According to the Gaussian distribution, there is a 68.3% probability that the result of a repeated measurement lies within the range of first result ± one standard deviation σ.

**Uncertainty of the activity ratio $^{234}U/^{238}U$ (Gauss):**

$$\sigma = \frac{\text{counts}(^{234}\text{U})}{\text{counts}(^{238}\text{U})} * \sqrt{\frac{1}{\text{counts}(^{234}\text{U})} + \frac{1}{\text{counts}(^{238}\text{U})}}$$

*Equation 3: Uncertainty of the activity ratio $^{234}U/^{238}U$*

Counts ($^{238}$U) & Counts ($^{234}$U): Counts in the respective peak areas.

**Chemical yield calculation**

$$\text{Y} = \frac{\text{counts}(^{232}\text{U})}{\text{t} * \varepsilon_{\text{det}} * A(^{232}\text{U})} * \text{F}$$

*Equation 4: Chemical yield in %*

Y: yield (%)

Counts($^{232}$U): net counts in the respective peak area

$\varepsilon_{\text{det}}$: measurement efficiency of the detector (approx. 0.3, see appendix)

t: duration of measurement (ksec)

A($^{232}$U): added activity of spike (mBq)

F: factor (100)

**Mass calculation**

$$A(^{238}\text{U}) = \frac{m}{M} * N_A * \frac{ln2}{\tau}$$

*Equation 5: Relationship between activity and mass*

A($^{238}$U): activity of $^{238}$U in the sample (Bq)

m: mass (g)

M: molar mass of $^{238}$U (g/mol)

$N_A$: Avogadro's number ($6.022 \cdot 10^{23}$ mol$^{-1}$)

τ = half-life of $^{238}$U (s)

The conversion factor for $^{238}$U refers to its specific activity, which is approximately 12.45 mBq/µg (or 12450 Bq/gram). This means that every gram of $^{238}$U has an activity of 12450 Bq.

In natural uranium, radioactive equilibrium exists between $^{238}$U and $^{234}$U, as $^{234}$U is a decay product of $^{238}$U. In this equilibrium state, both isotopes decay at the same rate, meaning their activities (number of decays per second) are equal.

**Mass Ratio of $^{234}U$ to $^{238}U$:**

Since $^{238}U$ and $^{234}U$ are in radioactive equilibrium, the mass ratio between $^{234}U$ and $^{238}U$ can be calculated using the half-lives of the two isotopes:

$$\frac{M(^{234}\mathrm{U})}{M(^{238}\mathrm{U})} = \frac{\lambda(^{238}\mathrm{U})}{\lambda(^{234}\mathrm{U})} = \frac{\tau(^{234}\mathrm{U})}{\tau(^{238}\mathrm{U})}$$

*Equation 6: Mass ratio of $^{234}U$ to $^{238}U$*

With the half-lives from table 7 the ratio becomes:

$$\frac{M(^{234}\mathrm{U})}{M(^{238}\mathrm{U})} = \frac{2.455 * 10^5}{4.468 * 10^9} \cong 0.0000549$$

This means that having a sample containing 1 µg of $^{238}U$, only an insignificant mass of $5.49\times10^{-5}$ µg $^{234}U$ are present, although both isotopes exhibit the same activity.

So far, all activity calculations have been based on the investigated volume (0.5 L), so to get the activity concentration of the samples one has to divide by the volume (in L). For the mass concentration determination, the amount was converted into µg/L. The volume, measurement times, the detector used and its efficiency, as well as other measured values, were listed in the appendix raw data (table 15 and 16).

**Uncertainty of mass**

$$\sigma(m) = \frac{\sigma(A(^{238}\mathrm{U}))}{A(^{238}\mathrm{U})} * m$$

*Equation 7: Uncertainty of mass (µg/L)*

$\sigma$(m): mass uncertainty (µg)
$\sigma(A(^{238}U))$: activity uncertainty of $^{238}U$ (mBq/L)
m: mass of the $^{238}U$ isotope (µg/L)
$A(^{238}U)$: activity of the $^{238}U$ isotope (mBq/L)

In table 10 all results of $^{234}U$ and $^{238}U$ activity concentrations, as well as their activity ratios are summarized. Also, the uranium mass concentrations and the yield of the chemical procedure are shown. Figure 2 shows the results uranium concentration vs activity ration.

*Table 10: Uranium activity, concentrations, activity ratio and chemical yield*

| Name | A conc. $^{234}U$ mBq/L | A conc. $^{238}U$ mBq/L | Activity ratio $^{234}U/^{238}U$ | Uranium conc. (µg/L) | Yield (%) |
|---|---|---|---|---|---|
| 1* (PW) | 701 ± 24 | 634 ± 22 | 1.11 ± 0.02 | 51 ± 2 | 82 ± 4 |
| 2* (PW) | 1526 ± 51 | 1385 ± 47 | 1.10 ± 0.01 | 111 ± 4 | 87 ± 4 |
| 3 (PW) | 7685 ± 575 | 7296 ± 546 | 1.05 ± 0.01 | 587 ± 44 | 4 ± 0.4 |
| 4 (PW) | 8153 ± 148 | 7374 ± 134 | 1.11 ± 0.002 | 593 ± 11 | 73 ± 2 |
| 5 (PW) | 9727 ± 364 | 9975 ± 373 | 0.980 ± 0.004 | 802 ± 30 | 23 ± 1 |
| 6 (Well) | 48 ± 2 | 71 ± 2 | 0.68 ± 0.02 | 5.7 ± 0.2 | 61 ± 3 |
| 7 (Well) | 21 ± 1 | 42 ± 2 | 0.50 ± 0.02 | 3.4 ± 0.1 | 73 ± 4 |
| 8 (Well) | 70 ± 3 | 74 ± 3 | 0.95 ± 0.03 | 5.9 ± 0.2 | 58 ± 3 |
| 9* (Well) | 540 ± 24 | 484 ± 22 | 1.11 ± 0.02 | 39 ± 2 | 15 ± 1 |
| 10* (Well) | 41 ± 2 | 56 ± 2 | 0.74 ± 0.03 | 4.5 ± 0.2 | 64 ± 3 |
| 11* (SW) | 944 ± 20 | 873 ± 18 | 1.08 ± 0.01 | 70.2 ± 2 | 62 ± 3 |
| 12* (Well) | 93 ± 3 | 22 ± 2 | 1.68 ± 0.05 | 4.4 ± 0.2 | 50 ± 1 |
| 13 (SW) | 42 ± 1 | 40 ± 2 | 1.05 ± 0.04 | 3.2 ± 0.1 | 44 ± 2 |
| 14 (Well) | 31 ± 1 | 29 ± 1 | 1.05 ± 0.05 | 2.4 ± 0.2 | 50 ± 2 |

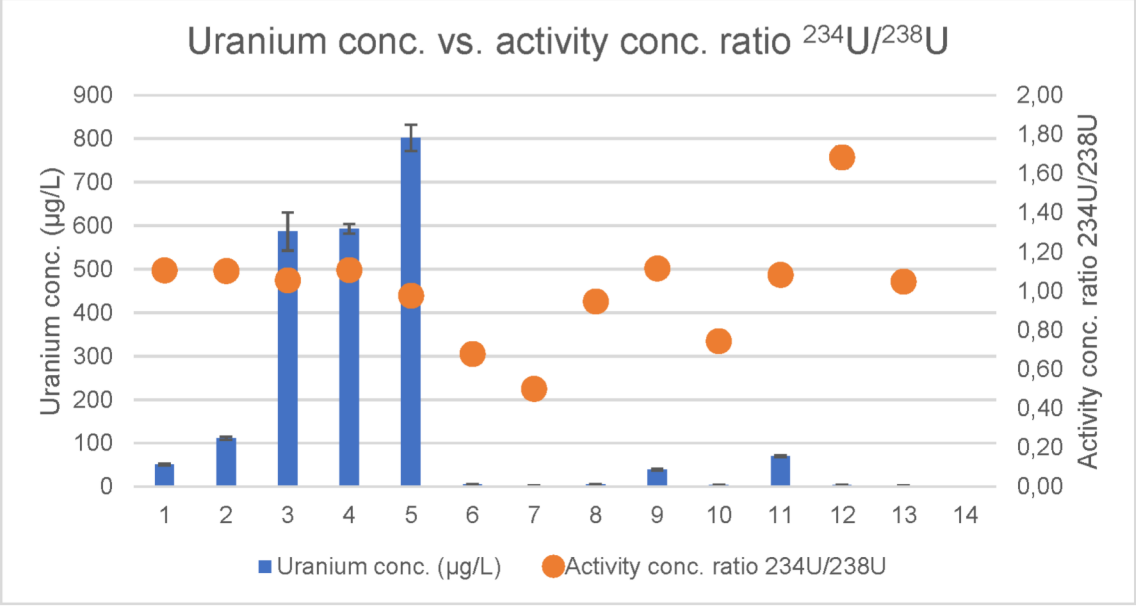



*Figure 2: Uranium concentration (bars) and $^{234}U/^{238}U$ activity ratio (dots)*

Uranium concentrations in pore waters ranged from 51 - 802 µg/L, with the maximum concentration detected in the sample 5 (PW) (Legerilacke Porenwasser). In contrast, uranium levels in the surface waters were lower between 3.2 - 4.4 µg/L, remaining under

the permissible drinking water limit of 15 µg/L. Sample 11* (surface water Herrnsee) stood out with significantly elevated uranium levels reaching up to 70 µg/L. The ratios of $^{234}U/^{238}U$ activities for pore waters span from 0.980 ± 0.004 to 1.11 ± 0.02.

The concentration of uranium in well waters was found from 2.4 - 39 µg/L, with the maximum concentration in the sample 9*(Well) (Dorflacke Brunnenwasser). The ratios of $^{234}U/^{238}U$ activities span from 0.50 ± 0.02 to 1.11 ± 0.02 in well water samples from the Seewinkel region. Only sample 12* (well in Seegrotte, Hinterbrühl) in the Wienerwald region has a clearly higher ratio of 1.68 ± 0.05.

By comparing the uranium concentrations for Legerilacke Porenwasser and Herrnsee Porenwasser und Oberflächenwasser with those reported in paper Krachler et al. 2018, it becomes evident that results are reasonably comparable (6 samples from the paper of Krachler et al. (2018) and from this thesis were taken in series from the same sampling points), as can be seen in Figure 3 and in the table 11.

*Table 11: Comparison with the result of Krachler et al. 2018 paper*

| **Name** | **Activity ratio $^{234}U/^{238}U$** | **Uranium conc. (µg/L)** | **Activity ratio $^{234}U/^{238}U$ (Krachler)** | **Uranium conc. (µg/L) (Krachler)** |
|---|---|---|---|---|
| 1* (PW) (Herrnsee) | 1.11 ± 0.02 | 51 ± 2 | 1.01 ± 0.01 | 91 ± 3 |
| 2* (PW) (Herrnsee) | 1.10 ± 0.01 | 111 ± 4 | 1.09 ± 0.01 | 123 ± 4 |
| 11* (SW) (Herrnsee) | 1.08 ± 0.01 | 70.2 ± 2 | 1.07 ± 0.01 | 69 ± 2 |
| 3 (PW) (Legerilacke) | 1.05 ± 0.01 | 587 ± 44 | 0.91 ± 0.01 | 725 ± 37 |
| 4 (PW) (Legerilacke) | 1.11 ± 0.002 | 593 ± 11 | 1.09 ± 0.01 | 672 ± 37 |
| 5 (PW) (Legerilacke) | 0.98 ± 0.004 | 802 ± 30 | 1.07 ± 0.01 | 853 ± 45 |

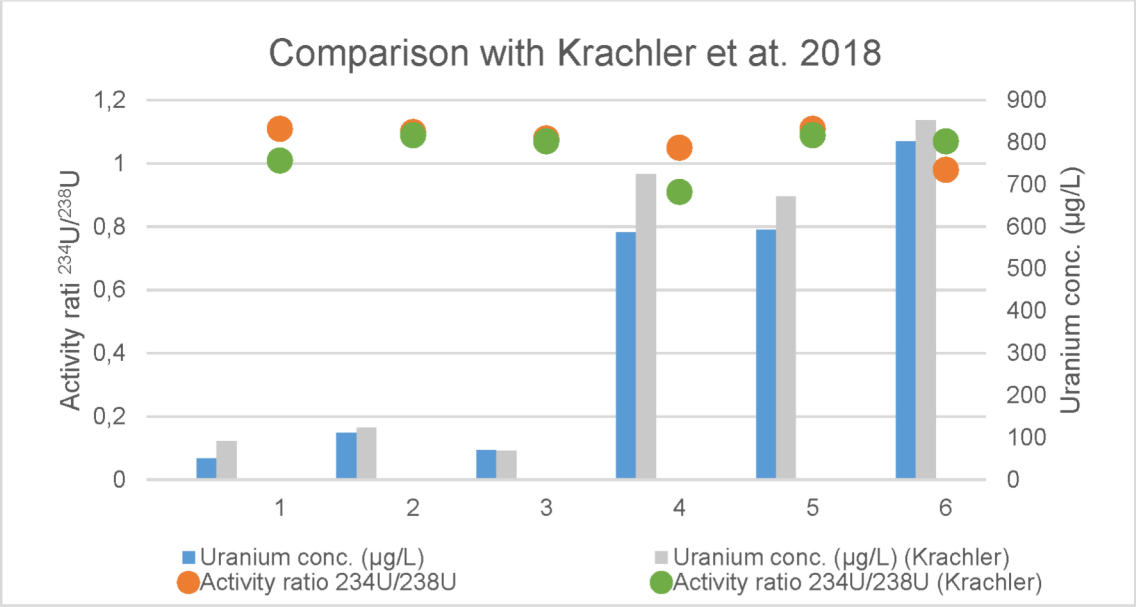



*Figure 3: Comparison of uranium conc. and activity ratios found in this thesis and in Krachler et al. 2018*

In comparing activity ratios and uranium concentrations from the same sampling points (collected on the same date), the activity ratios show close agreement between the two datasets. The uranium concentrations differ slightly but are in comparable range.

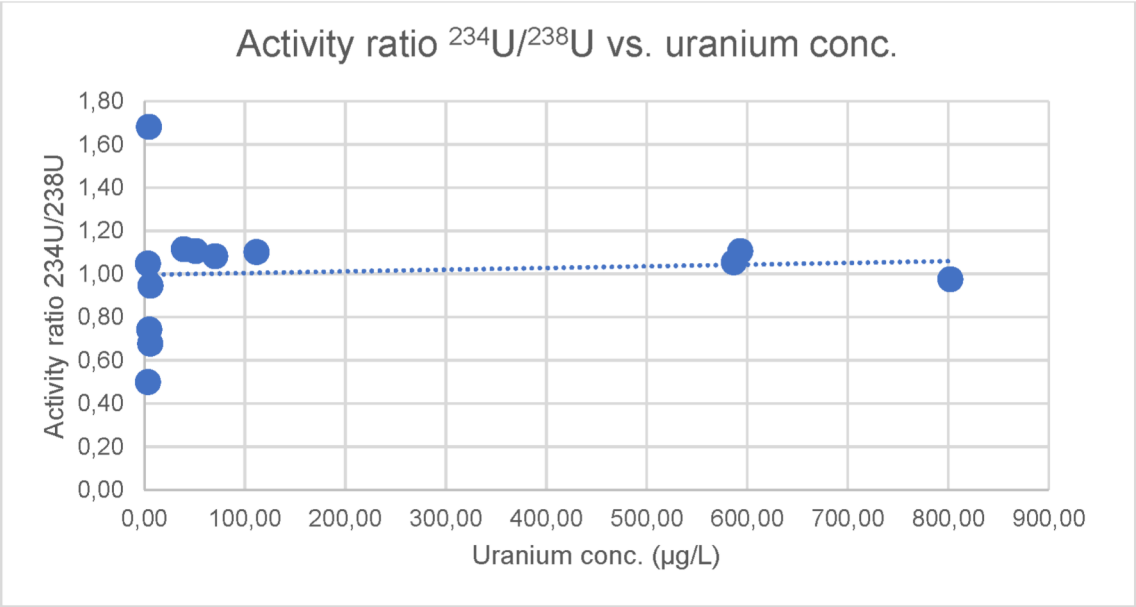



*Figure 4: $^{234}U/^{238}U$ activity ratio vs. uranium conc. (µg/L). The curve has been obtained by curve fitting with linear regression.*

The Figure 4 illustrates that the $^{234}U/^{238}U$ activity ratio remains largely unaffected by uranium concentration. The ratios range from 0.98 ± 0.004 to 1.11 ± 0.02 in waters with high uranium content and 0.50 ± 0.02 to 1.68 ± 0.05 in waters with lower concentrations. These values encompass the range of fertilizer-derived uranium ratios (1.00 ± 0.05) (Zielinski, et al. 2000).

However, the porewater samples, with their extremely high uranium concentrations, clearly fall outside the potential contamination range associated with fertilizers as noted by Krachler et al. (2018).

No correlation is observed between the uranium content of water samples and their proximity to fertilized agricultural lands. For instance, samples 1*(PW), 2*(PW) and 11*(SW) are from the area Herrnsee, which is unaffected by agriculture and display relatively high uranium levels not just in pore water but also in surface water (11*(SW) 70 µg/L).

In contrast, the well water samples are located amidst fertilized fields and surrounded by agricultural activity, show a notably low uranium content between 2.35 - 5.68 µg/L, except for sample 9*(Well) from the Dorflacke, which show a uranium concentration of 29 µg/L. This sample is also from an area, which is unaffected by agriculture.

Electrical conductivity (EC) and salinity are closely connected, as EC measures the water's ability to conduct electricity, which is directly related to the concentration of dissolved ions (salts). As salinity increases, more ions are available to carry electrical charges, resulting in higher EC.

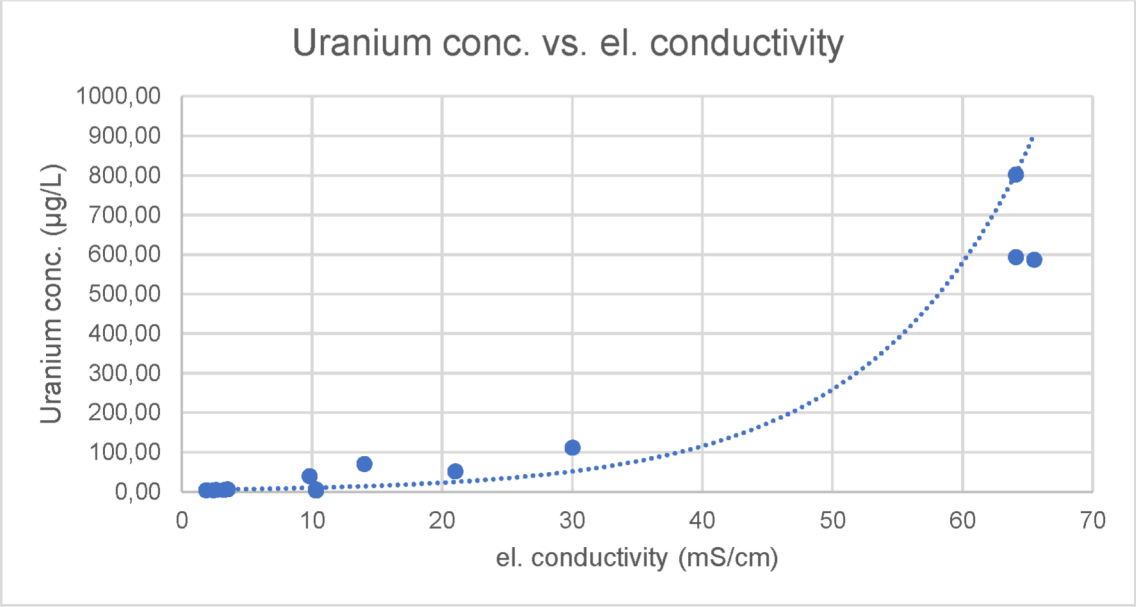



*Figure 5: Uranium concentration µg/L vs. spec. electrical conductivity (mS/cm)*

The analysis of the relationship between electrical conductivity and uranium concentration, as shown in Figure 5, indicates that pore water samples exhibited the highest electrical conductivity values, ranging from 21 - 64.1 mS/cm. Notably, all three pore water samples 3(PW), 4(PW), and 5(PW) from Legerilacke recorded an electrical conductivity of 64.1

mS/cm, which corresponded with the highest uranium concentrations, measured between 587 - 802 µg/L.

The measurements and results for chloride and sulfate were done and provided by Prof. Krachler. In the frame of this thesis only the well waters were investigated. In table 12 the results of all salinity determination are summarized (sample data transferred from Krachler et al. (2018) are marked with *(RK)*.

*Table 12: Results of salinity*

| **Name** | **$SO_4^{2-}$ (g/L)** | **$Cl^-$ (g/L)** | **$Na^+$ (g/L)** | **$K^+$ (g/L)** | **$Mg^{2+}$ (g/L)** | **$Ca^{2+}$ (g/L)** | **$HCO_3^-$ (g/L)** | **U conc. (µg/L)** |
|---|---|---|---|---|---|---|---|---|
| 1* (PW) (*RK)* | 10.09 | 1.88 | 6.30 | 0.08 | 0.61 | 0.14 | 1.88 | 51 ± 2 |
| 2*(PW) (*RK)* | 15.85 | 2.45 | 11.61 | 0.12 | 1.70 | 0.18 | 2.33 | 111 ± 4 |
| 3(PW) (*RK)* | 37.35 | 8.79 | 20.59 | 0.23 | 1.11 | 0.18 | 1.76 | 587 ± 44 |
| 4(PW) (*RK)* | 40.14 | 8.58 | 21.20 | 0.08 | 3.30. | 0.50 | 1.47 | 593 ± 11 |
| 5(PW) (*RK)* | 30.81 | 8.05 | 21.23 | 0.23 | 1.17 | 0.24 | 1.79 | 802 ± 30 |
| 11*(SW) (*RK)* | 4.90 | 1.38 | 3.40 | 0.08 | 0.43 | 0.02 | 2.49 | 70.2 ± 2 |
| 6 (Well) | 0.30 | 0.15 | 0.16 | 0.09 | 0.73 | 0.13 | 1.70 | 5.7 ± 0.2 |
| 7 (Well) | 0.16 | 0.07 | 0.06 | 0.07 | 0.40 | 0.03 | 0.78 | 3.4 ± 0.1 |
| 8 (Well) | 1.18 | 0.95 | 0.52 | 0.04 | 1.11 | 0.16 | 3.07 | 5.9 ± 0.2 |
| 9* (Well) | 1.04 | 0.78 | 0.52 | 0.20 | 1.21 | 0.16 | 3.93 | 39 ± 2 |
| 10* (Well) | 0.14 | 0.17 | 0.10 | 0.07 | 0.03 | 0.12 | 1.30 | 4.5 ± 0.2 |
| 14 (Well) | 0.88 | 0.65 | 0.36 | 0.07 | 0.66 | 0.09 | 2.29 | 2.4 ± 0.2 |

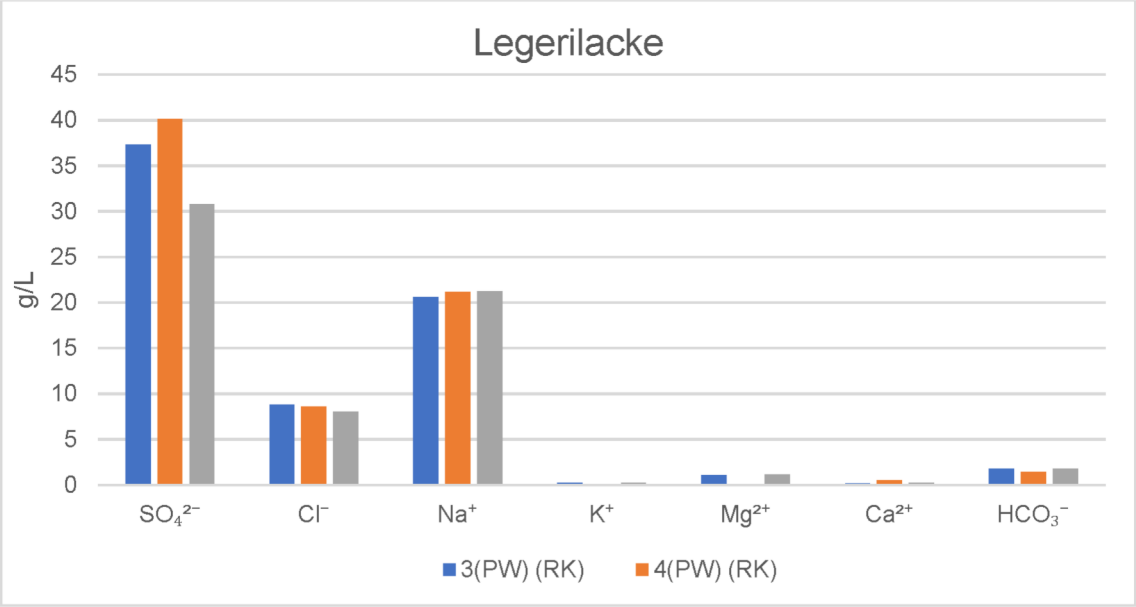



*Figure 6: Ion concentrations (g/L) in Legerilacke PW samples*

The Legerilacke sample PW3 - 5 (see Figure 6) is also known as a so-called sulfate lake (Krachler, et al. 2012). Sulfate is the dominant anion in all three samples. Also, chloride and sodium are high compared to other samples.

The observation in the samples, where the highest uranium concentrations (587 - 802 µg/L) coincide with the highest sulfate concentrations (31 - 40 g/L), is consistent with the findings of Krachler et al. (2018). This indicates that sulfate plays a significant role in the solubility and mobility of uranium by formatting of uranyl-sulfate complexes in these waters.

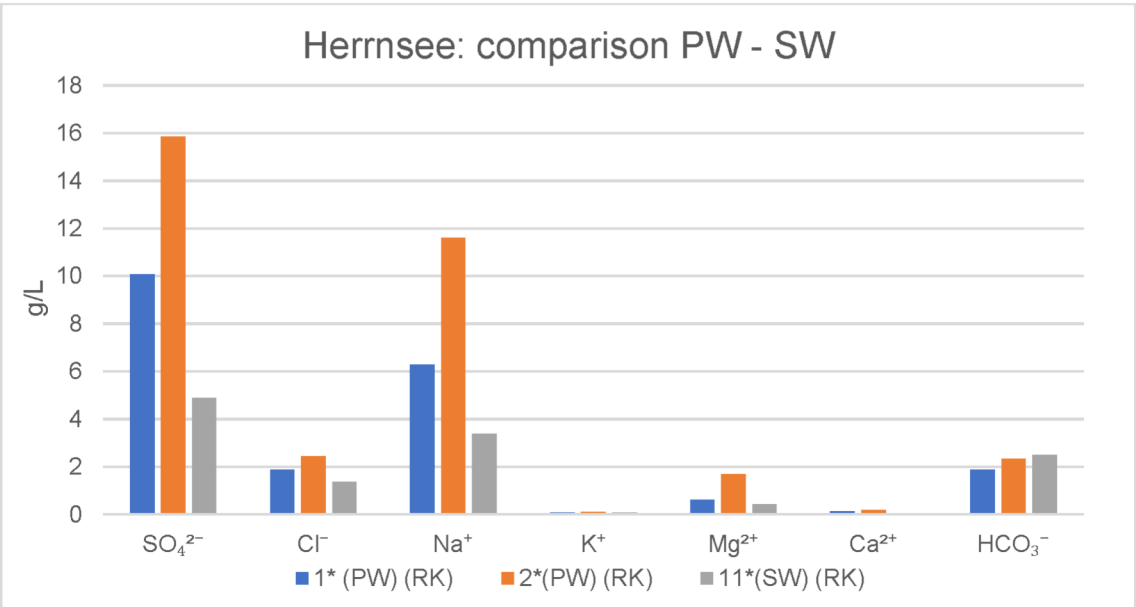



*Figure 7: Ion concentrations (g/L) in Herrnsee PW and SW samples*

Herrnsee (see Figure 7), also referred to as Schwarzlacke (Krachler, et al. 2012), exhibits relatively high sulfate and sodium content in sample 2*(PW). Surface water 11*(SW) pH values were alkaline, recorded at 8.99, while nearly neutral pH levels, averaging 7.47, were measured in the pore water 1*(PW) and 2*(PW) at 80 cm deep. The pH also depends on the salinity.

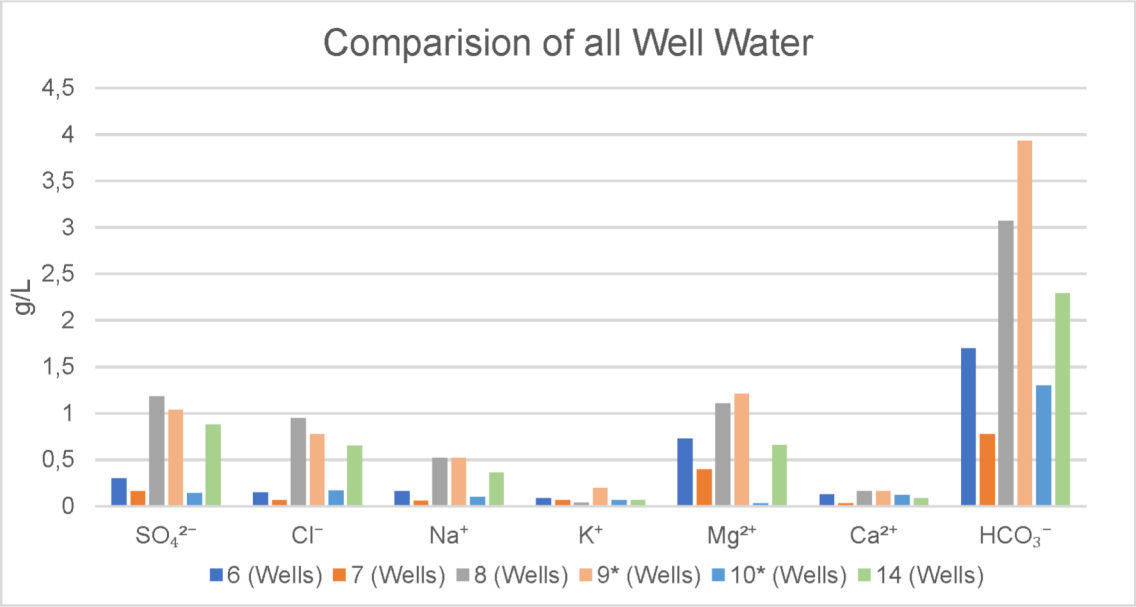



*Figure 8: Ion concentrations (g/L) in well water samples*

The Figure 8 represents the concentrations of major ions in g/L in well water samples, providing a comparative basis for their chemical contribution to water characteristics

The samples 8 (Well) (Apetloner Meierhoflacke Brunnenwasser), 9*(Well) (Dorflacke Brunnenwasser) and 14 (Well) (Mitterweißsee Brunnenwasser) show higher levels in sulfate. The chloride and sodium concentrations are moderately elevated. Magnesium and calcium are indicating harder water. These 3 samples exhibit particularly high concentrations of most ions.

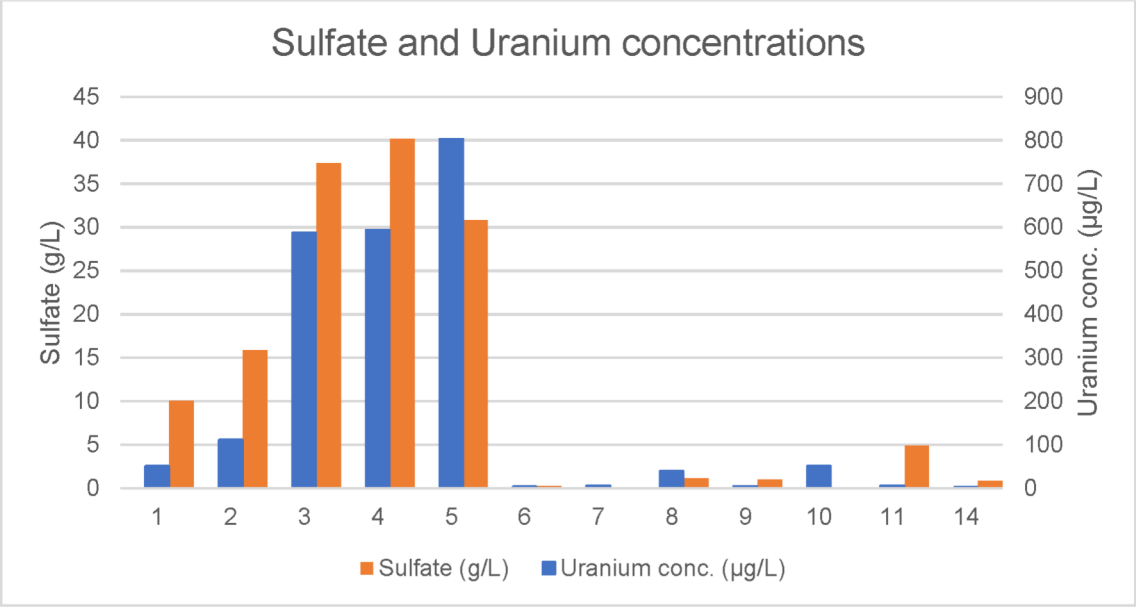



*Figure 9: Uranium concentrations (blue) and sulfate concentrations (orange)*

In Figure 9 uranium (blue) and sulfate (orange) concentrations are shown for all investigated samples. The correlation between elevated uranium levels and higher sulfate levels is clearly visible.

Figure 10 shows that sampling depth does not influence uranium concentration. Well water samples (Well) taken from a depth of 500 cm show lower uranium concentrations compared to pore water samples (PW) taken from a depth of 80 cm. This could be explained by considering the high salinity and el. conductivity in pore waters (PW).

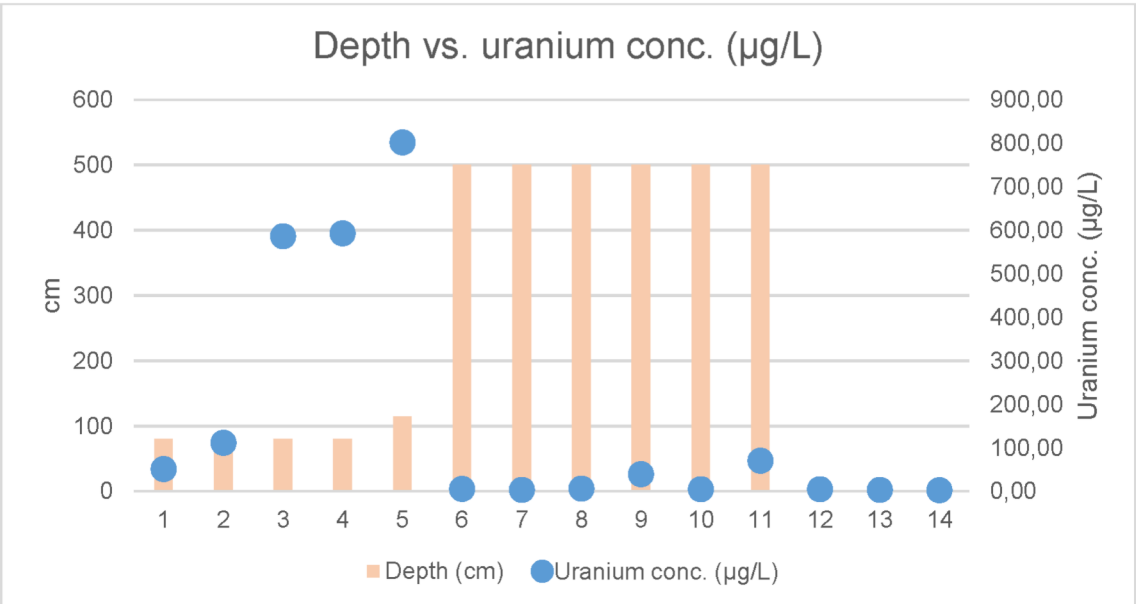



*Figure 10: Depth vs uranium concentrations of all samples*

Figure 11 shows an example Figure with the gran function used to determine the acid-binding capacity. Subsequently, a list of the calculated gran values (see Equation 8) was compiled in the table 13.

$$G = V_{titrant} * 10^{-pH}$$

*Equation 8: Gran function*

$V_{titrant}$ = Volume of the Titrant (mL)

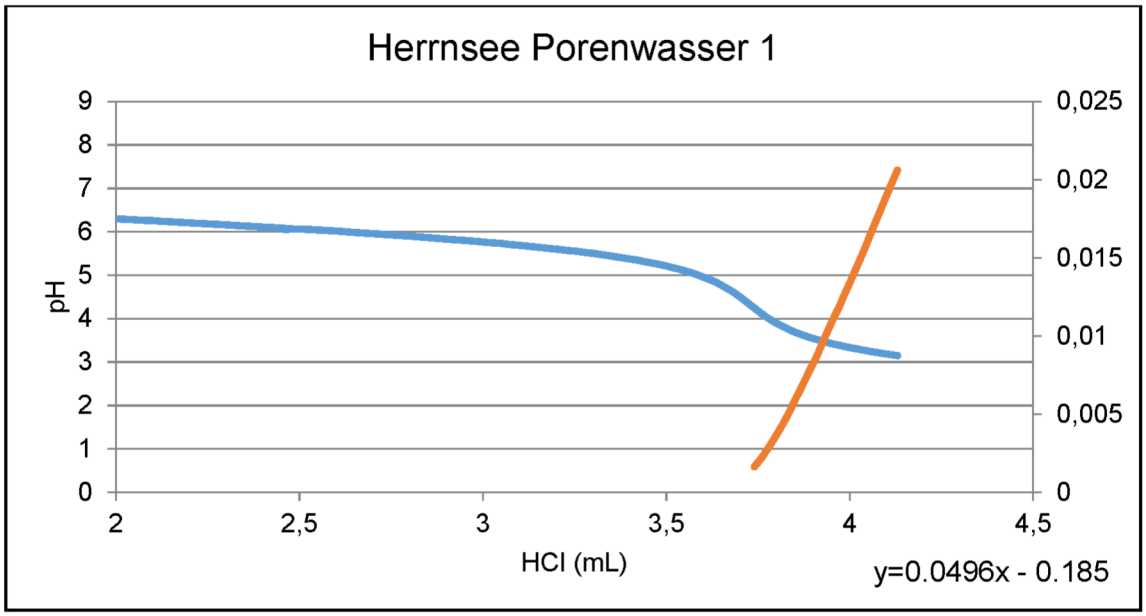



*Figure 11: Plotting of gran function of sample 1* (PW)*

*Table 13: Acid-binding capacity*

| Label | 1. Measurement (mL) | 2. Measurement (mL) | Average (mL) | Dilution | Alkalinity (g/L) |
|---|---|---|---|---|---|
| 1* (PW) | 3.729 | 3.997 | 3.863 | 1:2 | 1.88 |
| 2* (PW) | 3.146 | 3.217 | 3.182 | 1:3 | 2.33 |
| 3 (PW) | 3.591 | 3.649 | 3.620 | 1:2 | 1.76 |
| 4 (PW) | 3.058 | 2.970 | 3.014 | 1:2 | 1.47 |
| 5 (PW) | 3.654 | 3.665 | 3.660 | 1:2 | 1.79 |
| 6 (Well) | 0.695 | 0.700 | 0.698 | 1:10 | 1.70 |
| 7 (Well) | 0.321 | 0.322 | 0.322 | 1:10 | 0.78 |
| 8 (Well) | 6.2711 | 6.314 | 6.293 | 1:2 | 3.07 |
| 9* (Well) | 1.626 | 1.601 | 1.614 | 1:10 | 3.93 |
| 10* (Well) | 5.339 | 5.326 | 5.333 | 1:1 | 1.30 |
| 11* (SW) | 10.191 | 10.279 | 10.235 | 1:1 | 2.49 |
| 12* (SW) | 2.590 | 2.754 | 2.672 | 1:1 | 0.65 |
| 13 (SW) | 3.211 | 3.121 | 3.166 | 1:1 | 0.77 |
| 14 (Well) | 9.248 | 9.534 | 9.391 | 1:1 | 2.29 |

Alkalinity provides a buffering capacity that stabilizes the pH of water. The alkalinity measured in g/L, indicating the water's capacity to neutralize acids, predominantly contributed by bicarbonate ($HCO_3^-$) along with smaller amounts of carbonate ($CO_3^{2-}$) and hydroxides ($OH^-$). In water, uranium primarily exists as the uranyl ion ($UO_2^{2+}$). Carbonate ions ($CO_3^{2-}$) react with uranyl ions to form complex anions such as uranyl carbonate ($[UO_2(CO_3)_3]^{4-}$). These complexes are highly soluble in water and increase the mobility of uranium in the environment.

The alkalinity was measured between 0.65 - 3.93 g/L in the samples. Samples 12* (SW) (Gipsbergwerk Seegrotte), 13 (SW) (Neusiedlersee Seebad) and 7 (Wells) (Götschlacke Brunnenwassser) had the lowest alkalinity (<1 g/L).

All 5 pore water samples showed an alkalinity between 1.47 - 2.33 g/L. The measured alkalinity values for Sample 2* (PW) (Herrnsee Porenwasser 2) and Sample 11* (SW) (Herrnsee Oberflächenwasser) are 2.33 g/L and 2.49 g/L, respectively. These relatively close values suggest that the porewater and surface water in Herrnsee might share similar chemical compositions, particularly in terms of bicarbonate content.

The similar alkalinity levels in both porewater and surface water indicate that there may be significant interaction or exchange between the porewater and surface water. This could occur through processes like seepage, mixing, or infiltration.

The alkalinity for 8 (Wells) (Apetloner Meierhoflacke Brunnenwasser) and 9* (Wells) (Dorflacke Brunnenwasser) are 3.07 g/L and 3.93 g/L, respectively, indicating the hardness of the waters.

Sample 9*(Wells) (Dorflacke Brunnenwasser) shows remarkably high uranium concentration 40 µg/L which could indicate specific geochemical conditions favoring the mobilization and accumulation of uranium in this well.

It was noted that the pH level of surface waters samples 11*(SW) (Herrnsee Oberflächenwasser) is alkaline. This sample exhibits a high uranium concentration 70 µg/L while simultaneously having relatively low specific electrical conductance 14 mS/cm. This unique pattern can be attributed to the alkaline pH of Herrnsee surface water (pH = 8.99) combined with a substantial presence of $HCO_3^-$ 2.49 g/L. This suggests that in this environment, uranyl-carbonate complexes, rather than uranyl-sulfate complexes, are likely facilitating the transport and accumulation of uranium. Consequently, it appears that both carbonate and sulfate serve as effective transport mediums for uranium (VI) in saline conditions.

The Gipsbergwerk Seegrotte sample 12*(SW) is the only sample not from Burgenland but from Lower Austria from a gypsum mine. The sample displays relatively low alkalinity of 0.65 g/L and electrical conductivity of 3.24 mS/cm, uranium is only detectable in moderate amounts of 4.42 µg/L in this sample. This does not come unexpected, as uranium does not occur in limestone, which is predominant there.

In table 14 are the results of $^{210}$Po summarized. All calculations are done analog to the uranium evaluation. The only exception is the yield determination: here the result must be multiplied by 2, because $^{210}$Po is deposited on both sides of the copper planchettes (and only one side is measured).

$$Y = \frac{counts(^{209}\mathrm{Po})}{t * \varepsilon_{Det} * A(^{209}\mathrm{Po})} * F * 2$$

*Equation 9: Yield determination (%)*

Y: yield (%)

A($^{209}$Po): activity of $^{209}$Po (added)

Counts($^{209}$Po): net counts in the respective peak area

$\varepsilon_{det}$: counting efficiency of the detector (approx. 0.3)

t: measurement time (ksec)

F: factor (100)

*Table 14: $^{210}$Po activity concentration and chemical yield*

| **Name** | **A conc. ($^{210}$Po) mBq/L** | **Yield %** |
|---|---|---|
| 1* (PW) | - | - |
| 2* (PW) | - | - |
| 3 (PW) | - | - |
| 4 (PW) | 0.98 ± 0.04 | 40 ± 2 |
| 5 (PW) | - | - |
| 6 (Well) | - | - |
| 7 (Well) | 0.90 ± 0.04 | 93 ± 4 |
| 8 (Well) | - | - |
| 9* (Well) | 1.77 ± 0.08 | 47 ± 2 |
| 10* (Well) | - | - |
| 11* (SW) | 0.45 ± 0.02 | 116 ± 5 |
| 12* (SW) | 0.62 ± 0.02 | 117 ± 4 |
| 13 (SW) | 0.73 ± 0.03 | 74 ± 4 |
| 14 (Well) | - | - |

In only 6 out of 14 samples the $^{210}$Po activity was above detection limit (0.1 mBq). $^{210}$Po levels ranging from 0.45 - 1.77 mBq/L are very low and do not pose a threat for any living fauna. The samples 11*(SW) Herrnsee and 12*(SW) Gipsbergwerk Seegrotte had a yield above 100%, which could be attributed to pipetting errors.

# 4 Conclusion

The uranium concentration in the studied water samples (pore waters, well waters and surface waters) varied significantly, with pore water samples exhibiting the highest values ranging from 51 - 802 µg/L. The maximum concentrations are found in the Legerilacke samples, correlated with the increased salinity of the pore water and the highest electrical conductivity of 64.1 mS/cm. These elevated salinity levels, driven mainly by sulfate concentrations between 31 - 40 g/L, support the increased solubility and mobility of uranium through the formation of uranyl-sulfate complexes.

In contrast, the surface water sample 13 (SW) from Neusiedlersee exhibited a low uranium concentration (of 3.2 ± 0.1) µg/L, while 11* (SW) from Herrnsee reached 70.2 µg/L. This latter sample displayed alkaline conditions with a pH of 8.99, which, along with a bicarbonate concentration of 2.49 g/L, likely contributed to the formation of uranyl-carbonate complexes, facilitating uranium mobility in an otherwise low-salinity environment. The well water samples exhibited significantly lower uranium concentrations (2.4 - 39 µg/L), with sample 9*(Well) Dorflacke showing the highest value.

The activity ratios of $^{234}U/^{238}U$ ranged from 0.50 ± 0.02 to 1.68 ± 0.05 across all samples in close agreement with the activity ratios reported by Krachler et al. (2018), along with reasonable agreement in the respective uranium concentration values. In summary, the results found in this thesis clearly confirm the findings and interpretations of Krachler et al. (2018).

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## Equation

General equation for Gauss Propagation of the Uncertainty:

$$\sigma_f = \sqrt{\sum_i \left(\frac{\partial f(x)}{\partial x_i}\right)^2 * \sigma_i^2}$$

This is the general formula for propagating uncertainty, which calculates the overall uncertainty in a function f(x) when having multiple variables $x_1$, $x_2$,…, each with their own uncertainty $\sigma_1$, $\sigma_2$,…

- $f(x_1, x_2,\ldots)$ is the function of multiple variables (e.g., counts of isotopes, activity),
- $x_i$ are the variables (e.g., counts of different isotopes),
- $\frac{\partial f}{\partial x_i}$ are the partial derivatives of the function f with respect to each variable $x_i$,
- $\sigma_i$ are the uncertainties in the measured values $x_i$, often related to **Poisson statistics**, which gives $\sigma_i = \pm\sqrt{x_i}$, in this work it is $\sigma_i = \pm\sqrt{counts}$.

# Raw Data

*Table 15: Uranium data*

| Comments | Dosage | Label | Sample | Counts $^{232}U$ | Counts $^{234}U$ | Counts $^{238}U$ | Activity $^{232}U$ (mBq/L) | Activity $^{234}U$ (mBq/L) | Error Activity $^{234}U$ | Activity $^{238}U$ (mBq/L) | Error Activity $^{238}U$ | Activity ratio $^{234}U/^{238}U$ | Error Activity ratio $^{234}U/^{238}U$ | Mass conc. (µg/L) | Mass conc. error (µg/L) | Det | Meas. efficient | Duration of meas. (sec) | Yield (%) | Yield error (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| * non fertilized area | 500ml+20µl | 1 PW | Herrnsee Porenwasser1 | 930 | 9203 | 8327 | 35.4 | 700.62 | 24.11 | 633.93 | 21.92 | 1.11 | 0.0167 | 50.97 | 1.76 | 3 | 0.306 | 105120,49 | 81.67 | 3.98 |
| * non fertilized area | 500ml+20µl | 2 PW | Herrnsee Porenwasser2 | 922 | 19872 | 18040 | 35.4 | 1525.96 | 51.41 | 1385.28 | 46.77 | 1.10 | 0.0113 | 111.38 | 3.76 | 4 | 0.284 | 105074,12 | 87.28 | 4.16 |
| | 500ml+20µl | 3 PW | Legerilacke Süd2 Porenwasser | 180 | 19538 | 18548 | 35.4 | 7684.95 | 575.43 | 7295.55 | 546.41 | 1.05 | 0.0108 | 586.58 | 43.93 | 3 | 0.306 | 416323,66 | 3.99 | 0.42 |
| | 500ml+20µl | 4 PW | Legerilacke Süd-West Porenwasser | 3059 | 352277 | 318581 | 35.4 | 8153.39 | 148.06 | 7373.50 | 133.96 | 1.11 | 0.0027 | 592.85 | 10.77 | 4 | 0.284 | 416364,61 | 73.08 | 1.88 |
| | 500ml+20µl | 5 PW | Probe Legerilacke Porenwasser | 719 | 98781 | 101296 | 35.4 | 9726.97 | 364.07 | 9974.63 | 373.31 | 0.98 | 0.0044 | 801.99 | 30.02 | 5 | 0.336 | 260344,41 | 23.22 | 1.23 |
| | 500ml+20µl | 6 Well | Moschadolacke Brunnenwasser | 1945 | 1315 | 1941 | 35.4 | 47.87 | 1.71 | 70.65 | 2.27 | 0.68 | 0.0242 | 5.68 | 0.18 | 6 | 0.345 | 260370,73 | 61.17 | 2.94 |
| | 500ml+20µl | 7 Well | Götschlacke Brunnenwasser | 2030 | 604 | 1211 | 35.4 | 21.07 | 0.98 | 42.24 | 1.53 | 0.50 | 0.0248 | 3.40 | 0.12 | 3 | 0.306 | 256639,3 | 73.02 | 4.30 |
| | 500ml+20µl | 8 Well | Apetloner Meierhoflacke Brunnenwasser | 1486 | 1463 | 1548 | 35.4 | 69.70 | 2.57 | 73.75 | 2.68 | 0.95 | 0.0345 | 5.93 | 0.22 | 4 | 0.284 | 256622 | 57.60 | 2.98 |
| * non fertilized area | 500ml+20µl | 9 Well | Dorflacke Brunnenwasser | 552 | 4209 | 3776 | 35.4 | 539.85 | 24.44 | 484.31 | 22.07 | 1.11 | 0.02 | 38.94 | 1.77 | 3 | 0.306 | 346000 | 14.73 | 0.95 |
| * non fertilized area | 500ml+20µl | 10 Well | Arbesthaulacke Brunnenwasser | 2012 | 1177 | 1585 | 35.4 | 41.42 | 1.52 | 55.77 | 1.87 | 0.74 | 0.0286 | 4.48 | 0.15 | 6 | 0.345 | 256585,73 | 64.21 | 3.19 |
| * non fertilized area | 500ml+20µl | 11 SW | Herrnsee Oberflächenwasser | 2422 | 32295 | 29861 | 35.4 | 944.05 | 19.89 | 872.90 | 18.44 | 1.08 | 0.0087 | 70.18 | 1.48 | 3 | 0.306 | 448423,31 | 49.86 | 3.47 |
| * non fertilized area | 500ml+20µl | 12 Well | Gipsbergwerk Seegrotte | 1964 | 2566 | 1526 | 35.4 | 92.50 | 2.77 | 55.01 | 1.88 | 1.68 | 0.0544 | 4.42 | 0.15 | 4 | 0.284 | 448438,23 | 43.56 | 1.49 |
| | 500ml+20µl | 13 SW | Neusiedlersee Seebad | 2682 | 1574 | 1502 | 35.4 | 41.55 | 1.32 | 39.65 | 1.28 | 1.05 | 0.0378 | 3.19 | 0.10 | 5 | 0.336 | 448445,35 | 50.28 | 1.98 |
| | 500ml+20µl | 14 Well | Mitterweißsee Brunnenwasser | 2169 | 941 | 894 | 35.4 | 30.72 | 1.20 | 29.18 | 1.16 | 1.05 | 0.05 | 2.35 | 0.09 | 4 | 0.284 | 346000 | 62.35 | 2.27 |

*Table 16: Polonium data*

| Comments | Dosage | Label | Sample | Counts $^{209}Po$ | Counts $^{210}Po$ | Activity $^{209}Po$ | Calc. Activity $^{209}Po$ | Activity $^{210}Po$ | Erro of Activity $^{210}Po$ | Mass conc. (µg/L) | Mass conc. error (µg/L) | Det | Measurement efficient | Duration of measurement (sec) | Yield (%) | Yield error (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| * non fertilized area | 500ml+20µl | 1 PW | Herrnsee Porenwasser1 | - | - | 36.5 | - | - | - | - | - | - | - | - | - | - |
| * non fertilized area | 500ml+20µl | 2 PW | Herrnsee Porenwasser2 | - | - | 36.5 | - | - | - | - | - | - | - | - | - | - |
| | 500ml+20µl | 3 PW | Legerilacke Süd2 Porenwasser | - | - | 36.5 | - | - | - | - | - | - | - | - | - | - |
| | 500ml+20µl | 4 PW | Legerilacke Osüd-West Porenwasser | 1061 | 29 | 36.5 | 35.7 | 0.97577757 | 0.044745182 | - | - | 4 | 0.284 | 500000 | 41.85899712 | 1.919483 |
| | 500ml+20µl | 5 PW | Probe Legerilacke Porenwasser | - | - | 36.5 | 35.7 | - | - | - | - | - | - | - | - | - |
| | 500ml+20µl | 6 Well | Moschadolacke Brunnenwasser | 1150 | - | 36.5 | 35.7 | - | - | - | - | 3 | 0.306 | 260282.33 | - | - |
| | 500ml+20µl | 7 Well | Götschlacke Brunnenwasser | 1224 | 31 | 36.5 | 35.7 | 0.90416667 | 0.037908784 | - | - | 4 | 0.284 | 260322.48 | 92.74984325 | 3.8887009 |
| | 500ml+20µl | 8 Well | Apetloner Meierhoflacke Brunnenwasser | 1775 | - | 36.5 | 35.7 | - | - | - | - | 3 | 0.306 | 441445.17 | - | - |
| * non fertilized area | 500ml+20µl | 9 Well | Dorflacke Brunnenwasser | 967 | 48 | 36.5 | 35.7 | 1.77207859 | 0.075250927 | - | - | 5 | 0.336 | 346000 | 46.59860090 | 1.9787993 |
| * non fertilized area | 500ml+20µl | 10 Well | Arbesthaulacke Brunnenwasser | 723 | - | 36.5 | 35.7 | - | - | - | - | 3 | 0.306 | 240957.31 | - | - |
| * non fertilized area | 500ml+20µl | 11 SW | Herrnsee Oberflächenwasser | 1423 | 18 | 36.5 | 35.7 | 0.45158117 | 0.020676844 | - | - | 4 | 0.284 | 240964.7 | 116.49168149 | 5.3338814 |
| * non fertilized area | 500ml+20µl | 12 Well | Gipsbergwerk Seegrotte | 1720 | 30 | 36.5 | 35.7 | 0.62267442 | 0.022218711 | - | - | 5 | 0.336 | 245752.95 | 116.69498951 | 4.1639935 |
| | 500ml+20µl | 13 SW | Neusiedlersee Seebad | 1126 | 23 | 36.5 | 35.7 | 0.72921847 | 0.034717113 | - | - | 6 | 0.345 | 245777.72 | 74.39411195 | 3.5418038 |
| | 500ml+20µl | 14 Well | Mitterweißsee Brunnenwasser | - | - | 36.5 | 35.7 | - | - | - | - | - | - | - | - | - |