Balancing Natural Radionuclides in Drinking Water Supply

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an investigation in Germany and Canada with respect to geology, radiometry & legislation

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Hiermit versichere ich, die vorliegende Arbeit selbständig und ausschließlich unter Benutzung der angegebenen Hilfsmittel angefertigt zu haben.

Mainz, im Juni 2003

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II. Wisser, S. & Stüber, J. (2001): Radon in Wasserwerken: Ursache möglicher externer Strahlenexposition. Strahlenschutzpraxis - Zeitschrift für den sicheren Umgang mit ionisierender und nichtionisierender Strahlung, 4/01, pp. 46-49, TÜV-Verlag, Köln

III. Wisser, S. (2002): Außergewöhnliche Anreicherung natürlicher Radionuklide in Thermalwasserleitungen. Wasser & Boden, 3/2002, pp. 20-22, Blackwell-Verlag, Berlin

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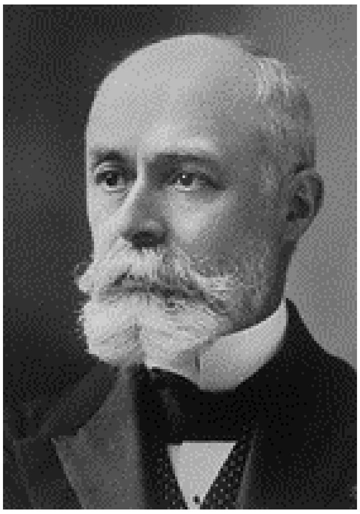
VII. Wisser, S. & Wilken, R.-D. (2003): Determination of Uranium-Isotopes in Ground- and Drinking Waters from Ontario, Canada. Publications du Centre Universitaire Luxembourg (in press)

CONTENT

Preface

In 1903, Antoine H. Becquerel received the Nobel Prize in Physics “in recognition of the extraordinary services he has rendered by his discovery of spontaneous radioactivity”. Becquerel accidentally discovered natural radioactivity in 1896 as he was investigating the fluorescence properties of uranium oxide (UO_2).

On the occasion of his Nobel Lecture in Stockholm he summed up that *“the radioactive substances whose nature is now well established are: uranium, radium and polonium; actinium can be added, although very little information has been published about this last product”.*



Antoine Henri Becquerel (1852-1908)[1]

Presently, more than a century after Becquerel’s discovery, the knowledge about radioactivity has increased exponentially and a large number of natural radioactive isotopes have been revealed. The phenomenon of radioactivity is well understood today and even artificial radionuclides became increasingly important for various purposes in our modern society. However, the pioneers of radiometry were not familiar with the threats arising from exposure to radioactivity and some of them were seriously harmed during the conduct of their experiments. In addition to that, they were also not aware that the occurrence of natural radioisotopes in drinking water could be hazardous to humans.

This thesis is aimed in providing solutions for current problems occurring in water supply with respect to natural radioactivity. The results presented in this study will contribute to the prevention of enhanced levels of natural radioactivity present in potable waters for public consumers.

This dissertation is dedicated in memory of Antoine H. Becquerel for his important discovery of natural radioactivity.

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[1] Picture taken from: *http://www.nobel.se/physics/laureates/1903/becquerel.jpg*

1 Introduction

In June 1992, *Agenda 21* and the *Rio Declaration on Environment and Development* were adopted by 178 states at the United Nations Conference on Environment and Development that was held in Rio de Janeiro, Brazil. Principle 1 of the Rio Declaration had declared that sustainable development belongs to the most important human challenges in the 21st century, as summarized below:

"Human beings are at the centre of concerns for sustainable development. They are entitled to a healthy and productive life in harmony with nature"

Freshwater resources are part of the fundamental component within Agenda 21. It is a major objective of Agenda 21 to provide an adequate supply of good quality drinking water for the entire population of this planet. Due to this reason, the protection of water resources, water quality and aquatic ecosystems is critical for global drinking water supply.

The current legislation by the European Community adopts the main objectives of Agenda 21 and aims at achieving a sustainable development. The *European Water Framework Directive* came into force in December 2000 and focuses at good quality waters in the Community in agreement with Agenda 21. Other water protection directives remain valid even after the adoption of the EC Water Framework Directive.

The *European Drinking Water Directive*, which deals with the quality of drinking water, was passed in 1998. Within this particular directive, the European Community acknowledges the fact that elevated levels of natural radionuclides in drinking waters can be harmful to humans, especially for babies and children. Hence, the levels of some natural radionuclides in potable waters are restricted on the basis of the resulting radiological doses of the consumer. Main radionuclides of concern are isotopes of uranium and radium. As a consequence, a large number of water supply companies in Europe will be obliged to monitor natural radionuclides in their waters and if necessary, to remove those substances from the drinking water.

The mentioned approach is in full compliance with the main objectives of Agenda 21, which is to provide good drinking water quality for the consumers. Member States of the EU were given time to transform the new European Drinking Water Directive into their national law until 25th December 2000. For instance, the new European Directive has been implemented in Germany by the amendment of the *Trinkwasserverordnung* that came to effect on 1st January 2003. The radioactivity parameters of this new ordinance will take effect in December 2003.

Medical and biological research in the past decades discovered that radiation exposure due to the incorporation of natural radionuclides could lead to chronic diseases such as cancer of the kidney, colon, and lung.

This health concern enforces water supply companies to incorporate the new regulations. However, there exist no official instructions for the monitoring of radionuclides in drinking waters yet, although a new limiting value of 0.1 mSv per year (total indicative dose) was set to be in agreement with the European Drinking Water Directive.

The juridical frame in Canada is different from the situation within the European Union. Water suppliers in the Provinces of Canada, such as Ontario, have already to deal with maximum acceptable concentrations for the most important radionuclides present in potable waters. There already exist instructions and recommendations for municipal waterworks to achieve a compliance with the Canadian regulations.

2 Goals of Thesis

In order to follow the new regulations, water supply companies in Europe are in the need of recommendations for the compliance with the new directives. Therefore, the existing problems in determination and assessment of natural radionuclides in water supply will be tackled in this particular study.

This thesis aims at building the first comprehensive catalogue of recommendations for the affected water supply companies in Europe. The implementation of the new regulations must be cost effective and feasible for water suppliers – chiefly with respect to the monitoring of radioisotopes in drinking waters. Innovative and affordable measurement techniques for natural radioisotopes in drinking waters have to be carried out. This is a great challenge because of the expensive and troublesome measurement procedures for natural radionuclides, which are still applied today.

This study is focused on a ground breaking and challenging scientific approach. The main scientific objectives can be summarized as follows:

- first-time balancing of natural radionuclides in the entire pathways of water supply to assess the occurrence of natural radionuclides in drinking waters. It is very ambitious to calculate balances for radionuclides, because possible measurement errors and the statistics of radioactive decay have to be considered.

- utilizing *stock flow analysis* for quantifying substances in the system of water supply. This modern tool has not been implemented yet for assessing natural radionuclides in drinking water supply. Residues from water treatment have to be included in the calculation as well to determine the disposition of long-lived radionuclides. This approach is very sophisticated and has never been tried out before.

- applying innovative measurement procedures for uranium and radium isotopes that could easily be used by water supply companies to satisfy the monitoring requirements of the European Drinking Water Directive. These new methods will be assessed with respect to the new legislation for the very first time.

- relating the levels of natural radioactivity present in the investigated waters to the local geological environment. This is conducted to obtain additional information about the behavior of radioisotopes in the environment.

The desirable locations for the initially balancing of natural radionuclides in water supply could be found in Western and Southern Germany and the Province of Ontario, Canada. Three typical water treatment facilities will be investigated in this particular study.

3 Natural Radionuclides in the Environment

Planet Earth is radioactive and has continuously been since it was formed more than 4.5 billion years ago. In nature, over 80 radionuclides can be found in detectable concentrations (Siehl, 1996) and they can generally be grouped into three categories according to how they were formed:

Primordial – creation during nucleosynthesis, before the Earth was formed
Cosmogenic - formed by cosmic ray interactions in the upper atmosphere
Anthropogenic – artificial radionuclides produced through human processes

The primordial radionuclides which exist today have half-lives that are at least comparable to the age of the Earth. Secondary radionuclides are derived from radioactive decay of the primordial isotopes. Cosmogenic radioisotopes are continuously produced in the Earth's atmosphere due to interactions of stable isotopes and cosmic rays. Some artificial radionuclides remain in the environment, but these isotopes are obviously not natural and as a consequence not of concern in this particular study.

There are three naturally occurring decay series beginning with the long-lived ^{238}U, ^{235}U and ^{232}Th which were already present when the Earth was formed (Table 1). The Neptunium decay series and its members have completely become extinct in the evolution of the Earth. The most significant decay series with regard to human radiation exposure is the ^{238}U series, which contains 8 alpha and 6 beta decays to form stable ^{206}Pb.

Table 1: Properties of the four natural decay series of the actinides (Wahl, 2000)

Name of series	*Initial nuclide*	*Half-life (years)*	*Type of series*	*Stable end-member*
Thorium	^{232}Th	1.405×10^{10}	4n	^{208}Pb
Neptunium	^{237}Np	2.140×10^{6}	4n + 1	^{209}Bi
Uranium	^{238}U	4.470×10^{9}	4n + 2	^{206}Pb
Actinium	^{235}U	7.038×10^{8}	4n + 3	^{207}Pb

The natural decay series of ^{232}Th, ^{238}U and ^{235}U contain 45 natural radioisotopes (Siehl, 1996). The most important radioisotopes of these three decay chains are illustrated in Figure 1 with respect to their individual half-life.

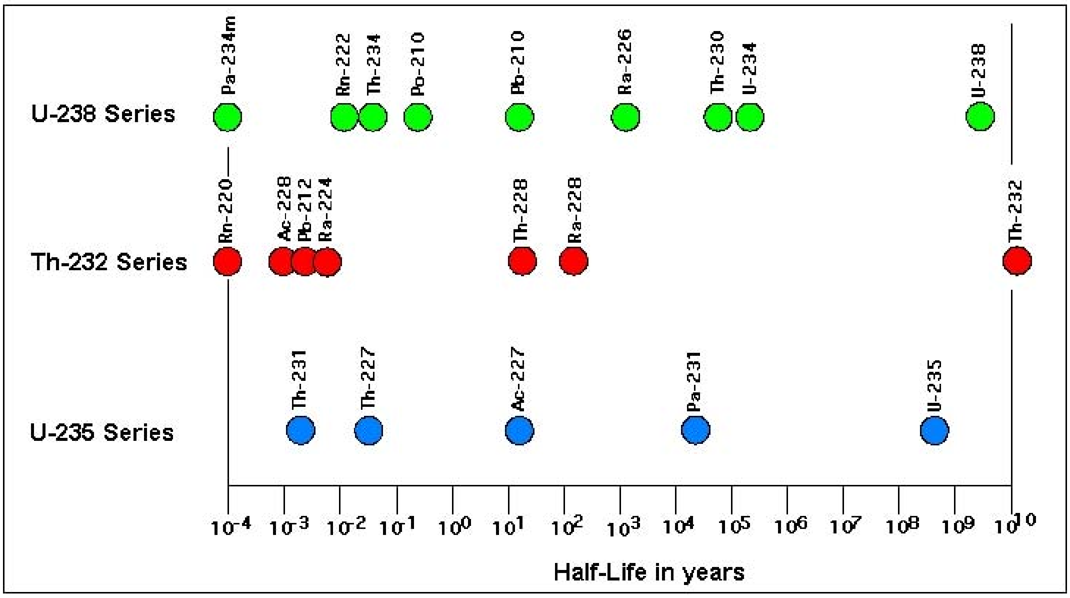


Figure 1: The natural decay series and their most important isotopes

Human radiation exposure is mainly dominated by natural radiation (Figure 2). Radon contributes to more than a half of the annual radiation exposure to humans. Terrestrial radiation and cosmic radiation are other important forms of natural ionizing radiation. The global average of the effective dose attributed to natural radiation has been estimated to be about 2.4 mSv per year (ICRP, 2000).

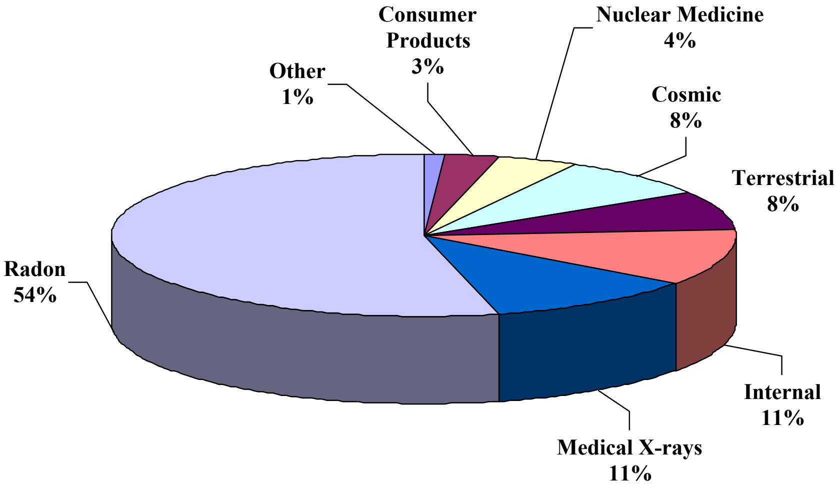


Figure 2: Natural radiation exposure (adopted from UNSCEAR, 2000).

The distribution of natural radioisotopes in waters depends on the occurrence of rocks from which they stem and the processes, which concentrate radionuclides. Hence, it is important know the occurrence of source-rock materials containing elevated levels of radionuclides and to understand the physical and geochemical processes that concentrate radionuclides. For this reason, the following chapters will deal with the geochemical properties of the most important natural radionuclides.

3.1 Geochemistry of Uranium, Thorium and Their Daughters

3.1.1 Properties of Uranium and Thorium

Uranium and thorium belong to the so-called actinides (Z 89-102). The actinides are the heaviest naturally existing elements in the cosmosphere. All the actinides occur in association with varying amounts of their radioactive decay products that are isotopes of radium, radon, polonium and lead. The differences in the chemical and physical properties of an actinide and its daughters may lead to fractionation of the mentioned radionuclides. As a consequence, disequilibria between these radioisotopes are often observed in the natural environment. Uranium-series disequilibria are frequently used in earth sciences for different applications, for example in geochronology, hydrology and planetology.

The actinides and radium are electropositive elements and have a tendency to form strong ion bonds. On the contrary, radon is a noble gas and is inert under environmental conditions. Polonium, bismuth and lead are amphoteric and may form ionic bonds with some covalent character in the environment. The actinides and radium are lithophile elements and stable isotopes of bismuth and lead have chalcophile properties (Gascoyne, 1992).

Uranium (Z=92) is the heaviest naturally occurring element and exists as a silvery-white, ductile and slightly paramagnetic metal, which is pyrophoric when finely divided. It is slightly softer than steel and easily oxidizes and becomes coated with layer of oxide (Bleise et al., 2003). The Earth's continental crust contains uranium in an average concentration of about 2.7 ppm (Wedepohl, 1995). Uranium occurs naturally in the +2, +3, +4, +5 or +6 valence state, but most commonly found in the hexavalent form. In nature, hexavalent uranium is dominantly associated with oxygen as the uranyl ion, UO_2^{2+}. Naturally occurring uranium (U_{nat}) is a mixture of three isotopes as provided in Table 2.

Table 2: Natural uranium isotopes and their properties (Wahl, 2000)

	$T_{1/2}$	α-decay energy, MeV (probability)	Abundance (%)	Specific activity (Bq/g)
^{238}U	4.470 x 10^9 a	4.198 (79.0 %) 4.151 (20.9 %)	99.2745	12,455
^{235}U	7.038 x 10^8 a	4.3987 (55 %) 4.3661 (17 %) 4.2147 (5.7 %) 4.5964 (5.0 %)	0.7200	80,011
^{234}U	2.455 x 10^5 a	4.7746 (71.38 %) 4.7224 (28.42 %)	0.0055	2.31 x 10^8

Thorium (Z=90) consists of six naturally occurring isotopes: ^{232}Th, the parent isotope of a natural decay chain, and the intermediates ^{234}Th, ^{231}Th, ^{230}Th, ^{228}Th and ^{227}Th. When in pure form, thorium is a silvery white metal that is air-stable and retains its luster for several months. When contaminated with the oxide, thorium slowly tarnishes in air, becoming gray and finally black (World Nuclear Association, 2002). Thorium oxide has a melting point of 3,300°C, the highest of all known oxides (webelements.com, 2003). The average thorium content of the Earth's continental crust is about 8.5 ppm (Wedepohl, 1995).

Table 3: Geologically relevant thorium isotopes and their properties (Wahl, 2000)

	Decay series	$T_{1/2}$	α-decay energy, MeV (probability)	Specific activity (Bq/g)
^{232}Th	^{232}Th	1.405 x 10^{10} a	4.0123 (78.2 %) 3.9472 (21.7 %)	4.07 x 10^{3}
^{228}Th	^{232}Th	1.9131 a	5.4232 (72.2 %) 5.3404 (27.2 %) 5.2210 (0.42 %)	3.05 x 10^{13}
^{234}Th	^{238}U	24.10 d	- (β-decay)	8.5 x 10^{14}
^{230}Th	^{238}U	7.538 x 10^{4}	4.6877 (76,6) 4.6205 (23.4)	7.6 x 10^{8}
^{227}Th	^{235}U	18.7 d	6.0380 (24.2) 5.9971 (23.5) 5.7569 (20.4)	1.17 x 10^{15}

3.1.2 Geological Distribution of Uranium and Thorium

Uranium and thorium are lithophile elements and are mostly concentrated in crustal rocks with an average Th/U ratio of approx. 3.5. The consistency of this ratio is due to a general lack of fractionation between the two elements during magmatic processes. Uranium and thorium are incorporated into late crystallizing magmas and residual solution because their large ionic radii preclude them from early crystallizing minerals such as olivine and pyroxene. Thus, uranium and thorium may be enriched especially in acidic igneous rocks (e.g. granites, pegmatites) compared with intermediate, basic, and ultrabasic varieties (Bonotto et al., 2001).

Both elements occur in the 4^+ oxidation state in primary igneous rocks and minerals, but uranium can be oxidized to 5^+, 6^+ valence state in the near-surface environment. The U^{6+} oxidation state is the most stable and forms uranyl complex ions UO_2^{2+}, which play the most important role in uranium transport during weathering. Thorium is transported as insoluble resistant mineral or is adsorbed onto the surface of clay minerals.

Uranium and Thorium are distributed in **igneous rocks** chiefly by three processes (Gascoyne, 1992):

- Direct cation substitution in the silicate lattice of the major rock-forming minerals
- Components of accessory minerals
- Adsorption in lattice defects or onto crystal and grain boundaries

Table 4: Average uranium and thorium content of some minerals in ppm (modified after Raff, 1999)

Mineral	*Uranium (ppm)*	*Thorium (ppm)*		Mineral	*Uranium (ppm)*	*Thorium (ppm)*
Allanite	200	9,100		*Quartz*	1.7	0.5-10
Apatite	65	70		*Feldspar*	2.7	0.5-10
Epidote	43	200		*Biotite*	8.1	0.5-50
Monazite	3000	125,000		*Muscovite*	2-8	-
Titanite	280	510		*Hornblende*	7.9	5-50
Xenotime	300 – 40,000	-		*Pyroxene*	3.6	-
Zircon	1330	560		*Olivine*	0.05	0.02

Due to the similarity in ionic radius of tetravalent uranium and tetravalent thorium, the primary distribution of both elements in igneous rocks is very similar. However, thorium is distributed throughout the entire rock, whereas in felsic rocks uranium is concentrated in the micas and amphiboles. Uranium is more evenly spread through the minerals of mafic rocks (Gascoyne, 1992).

Despite their comparable distribution in igneous rocks (Table 6), thorium and uranium have a completely different geochemical fate. An extensive separation of both elements takes place during several geological processes. The reason behind this is the relatively high mobility of uranium and the extremely low solubility of thorium in water. The leaching of uranium from the host rock is a common process in aqueous environment. On the contrary, thorium mainly remains intact to its origin and does not form secondary ore deposits or enrichments. However, thorium becomes slightly concentrated in heavy sands and other residual deposits.

The most important source of thorium is the mineral monazite (Table 5) that can be found in placer deposits. Some thorium is also recovered from igneous veins and igneous calcium carbonate deposits called carbonatites. It is estimated that the thorium in these deposits comes to a total of approximately 500,000 tons. In addition, some igneous deposits contain smaller concentrations of thorium. The economically extractable world thorium reserves amount to about. 1.2 million tons. Considerable deposits of thorium are found in Australia, Brazil, Canada, Greenland, India, South Africa, and the United States (World Nuclear Association, 2002).

Canada is the world leader when it comes to the production of uranium. In 2001, Canada extracted approx. 14,700 tons of uranium oxide. The mentioned number amounts to almost 35% of the total world production of uranium. The main source for uranium is the igneous mineral pitchblende, but sedimentary deposits are of importance as well. The worldwide recoverable uranium reserves are estimated to be about 3.1 million tons (World Nuclear Association, 2002).

Table 5: Economic sources for uranium and thorium (Matthes, 1996)

Uranium	Scientific term		Thorium	Scientific term
UO_2	Uraninite		$ThSiO_4$	Thorite
UO_2-U_3O_8	Pitchblende		ThO_2	Thorianite
$USiO_4$	Coffinite		$[Ce, Y, La, Th]PO_4$	Monazite

Sediments:

Most clastic sediments contain uranium in the range of 0.4 – 4.0 ppm, while organic-rich black shales and marine phosphates contain uranium concentrations of up to 1200 ppm (Table 6). The extremely low solubility of ThO_2 in natural waters precludes the concentration of thorium in sediments. Most clastic sediments, therefore, contain thorium concentrations similar to the source rocks.

As mentioned earlier, high thorium concentrations may be present in some sands. This is due to the mechanical sorting processes, which concentrate minerals according to their densities. Limestone only possesses uranium contents of 1-2 ppm and only very small concentration of thorium.

In recent sediments, uranium is strongly enriched in certain organic sediments, which are formed from humic substances, such as peat, lignite and coal. Humic substances play an important role in the adsorption of uranium and thorium from water. Higher uranium contents of geological deposits were obtained by repetition of the leaching-reduction-precipitation cycle, rather than from one single depositional event.

Metamorphic rocks

The abundance of uranium and thorium strongly depends on the composition of the initial rocks and the effects of radionuclides' migration during the process of metamorphism. High-grade metamorphic rocks are depleted in uranium and thorium content compared to low-grade metamorphic rocks (Table 6). This is due to a fluid loss with increased metamorphism at high pressure and high temperature conditions (Gascoyne, 1992).

Table 6: U and Th concentration in selected rock types (modified after Gascoyne, 1992)

Origin	Rock type	U (ppm)	Th (ppm)	Th/U ratio
Igneous	Granites Granodiorites Rhyolithes Dacites	2.2 – 6.1	8-33	3.5-6.3
	Gabbros	0.8	3.8	4.3
	Basalts	0.1-1	0.2-5	1-5
	Ultramafics	< 0.015	< 0.05	variable
Metamorphic	Eclogites	0.3-3	0.2-5	2-4.3
	Granulites	4.9	21	4.3
	Gneiss	2.0	5-27	1-30
	Schist	2.5	7.5-19	≥ 3
	Phyllite	1.9	5.5	2.9
Sedimentary	Black shales	3-1250	-	low
	Limestones	~2	0-2.4	< 1
	Manganese nodules	2-8	10-130	~7
	Phosphates	50-300	1-5	< 0.1
	Peat	1-12	1-5	< 1

3.1.2.1 Uranium and Thorium in Ground Waters

The occurrence of thorium in natural waters has been documented as being extremely low. This is due to the low solubility of ThO_2 in water. In nature, thorium exists only as a tetravalent cation and only a few complexed thorium compounds are of any relevance (Langmuir, 1980). These compounds are fluoride, phosphate and sulphide complexes (pH < 7.5) and thorium hydroxide compounds (pH > 7.5). However, Th^{4+} species are considered as almost chemically immobile in the near surface environment. Hence, the sorption on to particulate matter (e.g. colloids) is an important transport mechanism for thorium in aquifers or surface waters. Under aqueous conditions, thorium generally forms colorless solutions and is particularly prone to hydrolysis (Gascoyne, 1992).

Compared with thorium, the solubility of uranium species in water can be considered as excellent - especially under aerobic conditions. However, uranium mobility in the 4^+-oxidation state (uranous complexes) can be regarded as poor, particularly in an anoxic environment. Uranyl complexes [U^{6+}] are far more soluble than uranous complexes [U^{4+}]. The dominating uranium species under oxidizing conditions are dependent on Eh- and pH-conditions, availability of complexing ions, and temperature. In the absence of other complexing ions, UO^{2+}, UO_2OH^+ and $[UO_2]_3[OH]_5^+$ play the most important role in oxidized waters. Their significance is reduced in the presence of comparably low concentrations of CO_2 and pH > 5.

Uranium is predominantly transported in the U^{6+} oxidation state in aerobic waters. In solution, U^{6+} does not simply exist as a hydrated ion but instead as an “oxo ion” of the form UO_2^{n+} (uranyl complexes). The uranyl phosphate complex $UO_2[HPO_4]_2^{2-}$ is the dominating uranium species at pH < 7.5 (Figure 3). If the water does not contain significant amounts of phosphate, uranyl carbonate complexes become increasingly important (Figure 4).

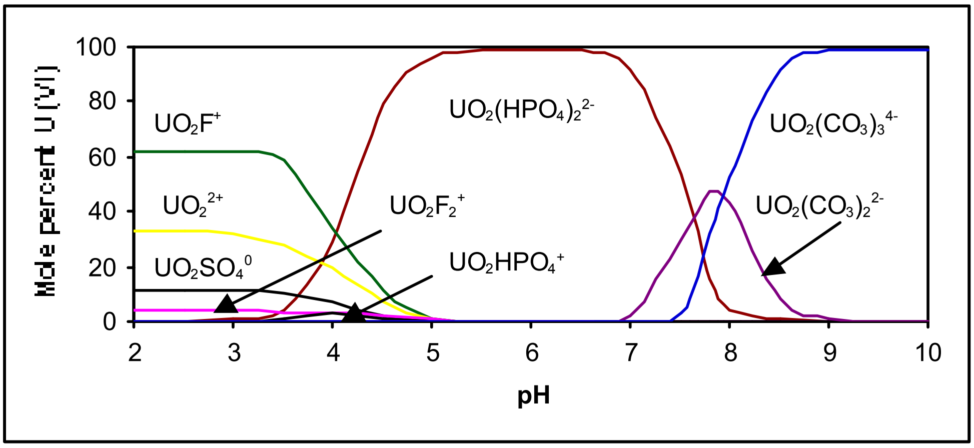


Figure 3: Distribution of uranyl complexes plotted against pH for $\sum U = 10^{-8}$ M, in the presence of other ions ($\sum F = 0.3$ ppm, $\sum Cl = 10$ ppm, $\sum SO_4 = 100$ ppm, $\sum PO_4 = 0.1$ ppm, $\sum SiO_2 = 30$ ppm) at 25°C (after Langmuir, 1978)

Soluble uranyl complexes are formed with ions of carbonate (pH > 7.5), phosphate (pH 4.0 – 7.5), sulphate (pH < 4), fluoride (pH 3-4) and silicate (pH ~ 6). The most important ones are carbonate complexes $UO_2[CO_3]_3^{4-}$ and $UO_2[CO_3]_2^{2-}$ and they are stable over a wide range of pH (4-10), dependent on temperature and also on P_{CO2}. In high carbonate or high bi-carbonate aerobic ground waters, the solubility of uranium may exceed 1g per liter. However, natural waters containing higher uranium concentrations than 100 µg/L are quite rare, and have generally been found only in aquifers containing uranium mineralization (Singh et al., 1995).

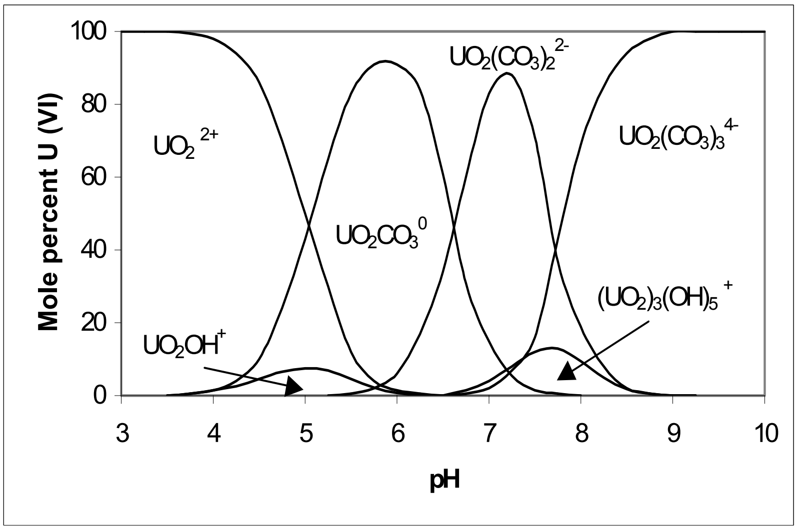


Figure 4: Distribution of uranyl-hydroxy and -carbonate complexes plotted against pH for $P_{CO2} = 10^{-2}$ atm, and $\sum U = 10^{-8}$ M at 25 °C (after Langmuir, 1978)

The most important uranium isotopes in natural waters are ^{238}U and ^{234}U. However, ^{235}U rarely occurs in higher activity concentrations. Characteristic concentrations for ^{238}U and ^{234}U in aquifers range from 10 – 100 mBq/l. ^{238}U and ^{234}U activity concentrations higher than 100 Bq/l have been reported by several authors – especially in areas with uraniferous granitic intrusions, such as in Finland (Salonen, 2002) or Canada (Moss et al., 1983). High levels of uranium in ground waters are often associated with $NaHCO_3$ waters (Dongarra, 1984). This is due to the high availability of carbonate ions that are probably responsible for an effective leaching of uranium and the formation of uranyl carbonate complexes within these aquifers.

Disequilibrium between ^{238}U and ^{234}U in natural waters has been reported to be the rule rather than the exception. The activity ratios for ^{234}U /^{238}U in waters vary from 0.5 – 40 (Gascoyne, 1992). Excess of ^{234}U is predominately caused by radioactive decay within the crystal lattice and particularly by successive alpha-recoil (Sun et al., 1998). The transformation from ^{238}U to ^{234}U involves one alpha and two beta particle emissions. The crystal lattice around parent ^{238}U might be damaged by the ejection of the particles. Therefore, the resulting ^{234}U atom is dislocated and thus more accessible by fluids. On the other hand, the decay of ^{238}U may eject the daughter isotope ^{234}Th into the surrounding media (e.g. water). Due to the relatively short half-life of ^{234}Th ($T_{1/2}$ = 24.1 d), the subsequent decay of ^{234}Th would increase the ^{234}U /^{238}U isotope ratio within the aquifer.

The levels of thorium isotopes in natural waters are known to be extremely low. Representative levels of ^{232}Th, ^{230}Th and ^{228}Th in ground waters range from 1.0 – 10 mBq/l. The activity concentration of thorium in ocean water is negligible. Higher amounts of thorium in aquifers might be present in areas with uraniferous granitic rocks, such as in Western Spain (Fernández et al., 1992) or in the Eastern Desert in Egypt (Dabous et al., 2002).

3.1.2.2 Mobilization and Transport of Uranium and Thorium in Water

An important mechanism for the migration of actinides might be the transport by colloids. The mobility of actinides in the colloidal phase is of increased interest in earth sciences with respect to nuclear waste disposal (Bhattacharyya, 1998). The colloidal phase is defined as particulate matter with a size of ≤ 0.45 µm. In groundwater, colloids may consist of bacteria, precipitates, organic matter, and rock or mineral fragments. Actinides, such as uranium and thorium, may adsorb or precipitate onto these tiny particles. Radionuclides that are irreversibly sorbed may not be subsequently removed by changes in groundwater chemistry, redox or solubility limitations. However, they will migrate with the velocity of the groundwater. Recent investigations have revealed that a large fraction of uranium and thorium may be associated with colloids (Tricca et al., 2001). Other studies discovered that up to 15% of the total uranium and almost 70% of the total thorium content of groundwater may stem from the colloidal phase (Gascoyne, 1992).

Alpha-recoil is another important process for the mobilization of α-decay daughters in ground water. Indeed, it can be assumed that the predominant process for the release of thorium, radium and radon into ground water is as a result of successive alpha-recoil (Sun et al, 1998).

The decay energies of the radionuclides of interest range between 4 and 6 MeV. A large portion of the α-decay energy goes to the α-particle and only a small portion goes to the daughter nuclides as recoil energy (60 – 120 keV). This is due to the equal momentum provided to both particles after decay (Sun et al., 1998). It is generally predicted that the daughter isotopes have a slightly higher activity concentration than their parents in ground water. This process leads to disequilibria between the radionuclides within the three natural decay series.

3.2 Properties of the Daughter Isotopes of Uranium and Thorium

3.2.1 Radium

Radium (Z=88) belongs to the earth-alkaline metals and behaves chemically similar to barium. Since earth-alkaline elements are highly electropositive (2^+ valence state), radium is not prone to hydrolysis over a wide pH-range (Eikenberg, 2001) and is present in solution mainly as ionic species [Ra^{2+}]. Radium is one of the least abundant elements in the Earth's crust. In nature, four radium isotopes originate from the decay of different thorium isotopes (Table 7).

Table 7: Natural radium isotopes and their properties (Wahl, 2000)

Isotope	Decay series	$T_{1/2}$	Mode of decay, decay energy, MeV (probability)	Daughter isotope
^{228}Ra	^{232}Th	5.75 a	β: 0.039 (40 %) β: 0.013 (30 %)	^{228}Ac
^{226}Ra	^{238}U	1600 a	α: 4.784 (94.45 %) α: 4.601 (5.55 %)	^{222}Rn
^{224}Ra	^{232}Th	3.66 d	α: 5.6854 (94.92 %) α: 5.4486 (5.06 %)	^{220}Rn
^{223}Ra	^{235}U	11.43 d	α: 5.7162 (52.6 %) α: 5.6067 (25.7 %)	^{219}Rn

Radium does not form primary minerals in nature, but Ra^{2+} ions may co-precipitate with the following minerally compounds:

- Calcite, $CaCO_3$
- Celestine, $SrCO_3$
- Strontianite, $SrSO_4$
- Barite, $BaSO_4$

Barite might especially contain high amounts of radium due to Ba/Ra substitution if it was formed in uranium-rich environment (Eikenberg, 2001). The distribution of radium isotopes in primary igneous and metamorphic rocks is principally dependent on the occurrence of the predecessor elements uranium and thorium. ^{226}Ra, when fractionated from parent isotope ^{230}Th, is found in hydrothermal precipitates such as barite and in association with lead deposits. Most radium salts are insoluble, particularly the sulphate and carbonate (Gascoyne, 1992).

In general, radium is mobile in anoxic and saline waters, respectively. On the other hand, radium is almost insoluble under aerobic and low mineralized water conditions. If the water chemistry changes from anoxic to aerobic, radium most probably co-precipitates with iron and manganese hydroxides. The predominating radium isotope in ground waters is ^{226}Ra. This particular radionuclide possesses a relatively long half-life (1600 a) and is the most important decay product of ^{238}U. ^{226}Ra forms its own decay chain, including important natural radionuclides, such as ^{222}Rn and ^{210}Po and is a major radioisotope of health concern.

The isotope ^{228}Ra has a significantly shorter half-life (5.7 a) and is only present in higher concentrations if the retention period in the ground water is comparably low. Otherwise, the radioactive decay would decrease the originally existing amount of ^{228}Ra in the water. Both isotopes, ^{228}Ra and ^{226}Ra, are generally found in excess of their parent isotopes (^{232}Th and ^{230}Th). This is mainly attributed to the higher solubility of Ra over Th and the resulting diffusion into the water column from the aquifer material and sediments, respectively.

Generally, low mineralized ground waters contain low radium levels, while elevated concentrations occasionally occur in saline waters. The typical concentrations for ^{228}Ra and ^{226}Ra in aquifers are in the order of 10 mBq/l. Some ground waters from the Jordan-Dead Sea Rift Valley revealed ^{226}Ra activity concentrations of up to 10 Bq/l (Moise et al., 2000). Saline thermal waters from the Bad Kreuznach area, Germany, contain ^{226}Ra levels from 10 to 35 Bq/l and are among the highest radium concentrations in natural waters from Europe (Wisser, 2001).

Other natural radium isotopes (^{224}Ra and ^{223}Ra) have relatively short half-lives in the order of days and are therefore not of a concern in this study. However, it has to be mentioned that ^{224}Ra might be present in potable waters in low concentrations. Only few investigations regarding ^{224}Ra in ground- and drinking waters from Europe have been performed (e.g. Dueñas et al., 1993).

3.2.2 Radon

Radon (Z=86) is probably the most-investigated natural radionuclide in ground and drinking waters worldwide. Radon is a rare noble gas and is the element with the least abundance in the Earth's crust composed of only 6 x 10^{-16} % (Trueb, 1996). As provided in Table 8, naturally occurring radon consists of three isotopes: ^{222}Rn (Radon), ^{220}Rn (Thoron) and ^{219}Rn (Actinon).

Table 8: Natural radon isotopes and their properties (Wahl, 2000)

Isotope	Decay series	$T_{1/2}$	Mode of decay, decay energy, MeV (probability)	Daughter isotope
^{222}Rn	^{238}U	3.82 d	α: 5.4895 (99.92 %) α: 4.968 (0.078 %)	^{218}Po
^{220}Rn	^{232}Th	55.6 s	α: 6.2881 (99.89 %) α: 5.747 (0.114 %)	^{216}Po
^{219}Rn	^{235}U	3.96 s	α: 6.8191 (79.4 %) α: 6.5526 (12.9 %)	^{215}Po

With respect to the very short half-lives of ^{220}Rn and ^{219}Rn, only ^{222}Rn is of interest in drinking water supply. The hydrochemistry of ground water is usually not crucial for radon transport due to radon being an inert noble gas. In fact, the migration of ^{222}Rn in aqueous media is a well-studied phenomenon in the natural environment. A radon atom that originates from radium decay within a grain of rock usually remains there until it decays. However, when radon is created near the surface of the grain, it may recoil into the pore between grains. The quantity of radon that reaches the pores is described by the emanation fraction. For typical soils or bedrock, the emanation fraction might range from 5 % – 50 % (Nazaroff, 1992).

The most important means for radon transport in water are diffusion, convection, and the presence of microbubbles. Várhegyi (1986) discovered the importance of microbubbles for radon migration in waters and introduced a model for the vertical subsurface transport of radon by geogas microbubbles, such as CO_2 and CH_4. Radon has the tendency to “attach” to the microbubbles and move together with them for long vertical distances (Várhegyi, 1992). The geogas microbubbles may originate from decompostation of organic material, chemical reactions, and gas exhalations in volcanic or post-volcanic areas. The presence of microbubbles might explain very long transport distances for radon, which formerly could not be interpreted by diffusion or convection models.

It can be assumed that the major contributor to radon in ground water is the presence of accessible radium at the surfaces of aquifer material (Raff, 1999). However, dissolved radium in ground water does not decisively contribute to the radon concentration. This is confirmed by the fact that ^{222}Rn usually exceeds the ^{226}Ra concentrations of aquifer waters in orders of magnitude. Typical activity concentrations of ^{222}Rn in ground waters usually range from 1 – 200 Bq/l, but higher radon levels up to several kBq/l have been reported from different locations and countries, as provided in Table 9.

Table 9: ^{222}Rn in ground waters from some countries as reported in literature (indicated as maximum levels)

Country	*^{222}Rn (Bq/l)*	*Remarks*	*Source*
Belgium	210	Waters from Ardenne Massif	Zhu, 1997
China	3,735	Groundwaters from Fulian Province	Zhuo et al., 2001
Finland	77,500 32,560	Waters from private drilled wells; Drilled wells in Helsinki region	Salonen, 2002 Asikainen & Kahlos, 1979
Germany	1,165	Former German Democratic Republic	Gans et al., 1987
Jordan	10,000	Jordan-Dead Sea Rift Valley	Moise et al., 2000
Mexico	2,200	Toluca Valley	Segovia et al., 1999
Norway	6,840	Groundwaters from Oslo region	Reimann et al., 1996
Sweden	55,000	Waters from deep drilled wells	Åkerbloom, 1994

The highest radon concentration in ground waters from Europe amounts to 77.5 kBq/l and has been discovered in Finland (Salonen, 1994). The maximum radon level of ground water ever published was determined in a spring-water from Bad Schlema in Eastern Germany (Genser, 1932). The radon level of this water amounted to 182 kBq/l and originated from granitic aquifers within the famous Erzgebirge.

The presence of radon in groundwater can be applied for hydrogeology to determine the right moment of a representative groundwater sampling. This method shortens the sampling time and reduces the costs of sampling (Dehnert et al., 1997). Surface water generally does not contain significant amounts of radon due to the degassing of the volatile noble gas. Thermal and saline waters may contain radon levels in the order of several kBq/l, such as waters from Bad Brambach, Germany, and Jáchymov, Czech Republic (Sächsische Staatsbäder, 2003; Kolar, 1999).

3.2.3 Lead and Polonium

Lead isotopes ($Z = 82$) are generated within all of the three natural decay series, but only ^{210}Pb ($T_{1/2} = 22.3$ a) is sufficiently long-lived to be of interest in drinking water supply. The isotope ^{214}Pb is a short-lived ^{222}Rn decay product with a half-life of only 27 min, which is of importance for the radiometry of radon in secular equilibrium. With exception of nitrate, lead salts are either insoluble or sparingly soluble in water, often associated with partial hydrolysis to monomeric and polymeric hydroxide species (e.g. $PbOH^+$). ^{210}Pb is rapidly removed from water by adsorption onto sinking particles, like thorium, before decaying to ^{210}Bi. Furthermore, lead-isotopes may co-precipitate with iron and manganese oxides or form insoluble lead sulphide in anaerobic waters (Bacon et al., 1980). However, ^{210}Pb is continuously formed in solution by the decay of ^{222}Rn and consequently of interest in drinking water supply.

Only little is known about the chemical properties of polonium (Z = 84) because it has no stable isotope and ^{210}Po is intensely radioactive with a short half-life. Polonium is a metallic main group element. Its aqueous chemistry is likely to be dominated by a tendency to hydrolyze to insoluble species or to form negatively charged complexes in acid medium under oxidizing conditions (e.g. polonate, PoO_3^{2-}).

Typical concentrations of ^{210}Pb and ^{210}Po in ground waters are in the range of 1 – 10 mBq/l. Due to their radiotoxicity, these isotopes are of great importance for radiation protection and drinking water quality (refer to chapter 3.5.4, page 30). Salonen (2002) published extraordinarily high concentrations of ^{210}Pb (21 Bq/l) and ^{210}Po (7.6 Bq/l) in Finnish ground waters. Generally, lead and polonium isotopes are almost immobile under solution. Mobilization of these hazardous isotopes on particulate matter may explain the high levels determined in the aquifers of Finland.

In geology, ^{210}Pb is highly suitable for the dating of young sediments (Eikenberg, 1999) and is most commonly found in disequilibrium with its progenitor ^{210}Po.

3.2.4 Protactinium

Only the isotope ^{231}Pa ($T_{1/2}$ = 3.276 x 10^4 a) has any importance in drinking water supply since the other naturally occurring isotope ^{234m}Pa ($T_{1/2}$ = 1.18 min) is far too short-lived to migrate long distances. ^{231}Pa originates from the decay of ^{231}Th within the ^{235}U decay series and is rapidly removed from water because of its tendency to hydrolyze and to adsorb onto sinking particles (Gascoyne, 1992). This process is one reason for the very low ^{231}Pa levels found in ground- and especially drinking waters. It has to be kept in mind that the actinium decay series is only a minor contributor to natural radioactivity because of the very low content of ^{235}U in natural uranium (approx. 0.72 %). Unfortunately, there are no recent publications concerning ^{231}Pa in ground- and drinking waters.

3.3 Relevant Isotopes in Drinking Water Supply

After the discussion of the main properties of radionuclides from the natural decay series, it becomes obvious that only a few radioisotopes are of any relevance in water supply. These radionuclides have to possess a sufficient half-life to reach the consumer and they must be transportable with aquifer waters. Since the members of the ^{238}U series are quite common in groundwater, radioisotopes of this decay chain are of major concern in water supply. In addition to that, a few radionuclides from the other natural decay series are of importance as well (Figure 5).

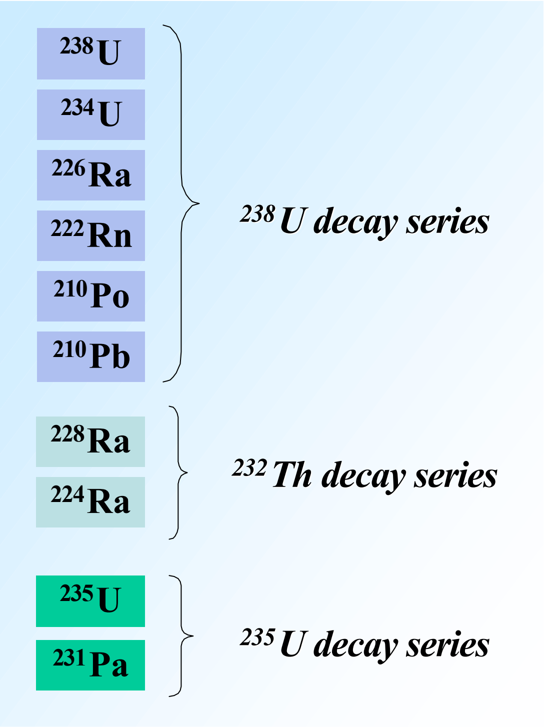


Figure 5: Significant radionuclides in drinking water supply

Only these ten natural radionuclides may occur in potable waters in harmful concentrations. However, these radionuclides are part of a small fraction of the approx. 80 natural radionuclides present in the environment. Nonetheless, the occurrence of these most-widespread radioisotopes in potable waters may lead to serious health impacts to the population (refer to chapter 1.1, page 28).

In summary, only isotopes of uranium, radium and radon are of any relevance in drinking water supply. Additionally, long-lived radon decay products (^{210}Pb and ^{210}Po) and ^{231}Pa may be enriched in potable waters as well.

3.4 Natural Radionuclides in Drinking Waters

The determination of natural radionuclides in drinking waters became increasingly important during the past few years. This is mainly attributed to possible health impacts and new regulations regarding natural radioactivity in the European Union and its Member States. In the present time, data concerning natural radionuclides in potable waters is available from all over the world. The highest concentrations of radon in potable waters were reported from Finland (77.5 kBq/l) and Sweden (55 kBq/l). High levels of natural uranium have been determined in tap waters from Canada, Greece, India and Morocco. Elevated ^{226}Ra concentrations were also found in potable waters from Scandinavia, Hungary and Spain. However, long-lived radon decay products were only determined in a few studies such as from Brazil, Germany and Sweden. Additionally, there is almost no data available regarding ^{228}Ra, ^{224}Ra and ^{231}Pa in drinking waters.

Table 10 *”Maximum levels of natural radionuclides in potable waters from some countries as reported in literature“* provides an overview of accessible data with respect to natural radionuclides in potable waters from different countries. For better comparison purposes, concentrations of the respective radionuclides are presented at their maximum levels. The reason for this is because maximum concentrations may provide a more appropriate value compared to average values when it comes to indicating regions with enhanced radioactivity in drinking water.

The levels of natural radioactivity presented here are without error bars and only represent a compilation of data that were available from the different countries. It is apparent that the concentrations of natural radioisotopes in
Table 10 vary in orders of magnitude. This is chiefly attributed to different geological background and geochemical conditions in waters from the areas of interest.

The table presented below is not complete, because values for some radioisotopes in different countries simply do not exist, possibly due to lack of measurement and thus were not accessible. There are also possibly higher maximum levels of radioisotopes occurring in waters from the mentioned countries, which may be in the process of being published or were not accessible during the conclusion of this thesis.

Table 10: Maximum levels of natural radionuclides in potable waters from some countries as reported in literature

Country	*U nat. µg/l*	^{238}*U Bq/l*	^{234}*U Bq/l*	^{222}*Rn Bq/l*	^{226}*Ra Bq/l*	*Source*	*Remarks*
Austria				757	0.49	Schönhofer, 1992	Waters from Lower Austria;
				18	0.23	Kralik et al., 2003	Bottled mineral waters
Brazil				1,255		Lima et al., 2002	Recife area, Brazil;
				315	0.235	Oliveira et al, 2001	Sao Paulo State
Canada	50					Mao et al., 1995	Saskatchewan;
	4.21					OMEE, 1996	Ontario
Greece	48.9			161		Zouridakis et al., 2002	Migdonia Valley, NE of Thessaloniki
Finland		150	288	77,500	7.5	Salonen, 1994	Waters from private drilled wells
Germany		0.48	0.39			Bünger & Rühle, 1993	Waters from Saxony and Thuringia;
		0.48	0.20	19	0.26	Bünger & Rühle, 1996	Waters from Southern Saxony;
				481	0.16	Gans et al., 1987	Former German Democratic Republic;
				1,600		Rühle, 1994	Federal Republic of Germany
India	113.70					Singh et al., 1995	Waters from Punjab, India
Hungary					3.16	Somlai, J. et al., 2002	Bottled mineral water;
				30		Wisser & Wilken, 2002	Pécs area
Morocco		1.62				Saqan et al., 2001	-
Norway				7,000	3.6	Lind & Strand, 1991	Waters from granitic aquifers
Spain				25,000	4.0	Soto et al., 1988	Cantabria and Arribes del Duero;
		0.00433	0.00290			Herranz et al., 1997	Biscay region;
					0.892	Dueñas et al., 1993	Drinking waters
Sweden				28,000	2.46	Kulich et al., 1988	Waters from deep drilled wells
		2.78	6.88			Kulich et al., 1997	-
Switzerland		0.357		654	0.95	Deflorin & Surbeck, 2003	Canton of Grison
United States of America					0.266	Sidhu & Breithart, 1998	Water Supplies of Michgan;
	1,200					Hakonson-Hayes et al., 2002	Private wells, New Mexico

3.5 Health Effects of Natural Radionuclides in Drinking Water

Exposure to ionizing radiation represents a potential hazard to humans and radioactivity is known to trigger *deterministic* and *stochastic* effects. *Deterministic effects* are those of which generally a threshold level of dose exists. Above the threshold, the severity of the effect is dependent on the radiation dose. The level of the threshold dose is characteristic of the particular health effect but also depends, to a limited extent, on the exposed individual. For instance, deterministic effects include erythrodermia and acute radiation syndrome. On the contrary, *stochastic effects* take the form of radiation-induced health effects, the probability of occurrence is greater for a higher radiation dose and the severity is independent of dose. Stochastic effects may be somatic effects or genetic effects, and generally occur without a threshold level of dose. For example, cancer and leukemia belong to the stochastic effects of ionizing radiation.

Currently, there is an ongoing scientific debate, whether there exists a threshold for health effects of ionizing radiation or not. This debate is the so-called linear-no-threshold controversy (Becker, 2002). Research in molecular biology and epidemiology discovered positive health effects produced by adaptive responses to low-level radiation. In addition to that, LNT fails in the low dose region, grossly over-estimating the cancer risk of low level radiation (Cohen, 1999). Thus, a demise of the linear-no-threshold hypothesis seems to be justified (Pollycove & Feinendegen, 1999). Despite the recent criticism, the LNT model is considered to be appropriate for radiation protection purposes, particularly at workplaces.

The following sections deal with the main health impacts due to the ingestion of natural radionuclides via drinking water.

3.5.1 Health Impacts of Uranium

Although ubiquitous in the natural environment, uranium has no known metabolic function in the human body and is considered to be non-essential (Berlin & Rudell, 1986). As with other heavy metals, uranium has been identified as a nephrotoxic (Zamora et al., 1998). This is due to its chemical properties rather than its radiological characteristics. In fact, the radiotoxicity of uranium metal is regarded to be low and does not present a radiological hazard (Burkart, 1991). This is because of the extremely long half-live of the most abundant uranium isotope ^{238}U ($T_{1/2} = 4.5 \times 10^9$ a). The daily intake of uranium is estimated to be 1-2 µg in food and 1.5 µg in consumed drinking water. The average human body (70 kg) contains approx. 56 µg of uranium, more than 50 % of this amount is accumulated in the skeleton (Bleise et al., 2003). It has been calculated that 90 % of the ingested uranium is excreted in urine within 24 hours after intake (Priest, 2001). The remaining fraction is likely to be excreted within the subsequent weeks after uptake and only a small portion is accumulated in the skeleton, tissues and organs. High levels of uranium intake (> 70-100 µg/kg body wt) will lead to a temporarily accumulation of uranium in the kidneys and produce chemical damage to the proximal renal tubes. At further increased levels of intake, studies indicate that damage might also occur in renal glomeruli. On the other hand, these effects seem to be transitory and fully reversible (Priest, 2001). It can be summed up that the only chemical toxic effect due to the ingestion of uranium via drinking water is reversible damage to the kidney.

A recently published case-cohort study in Finland had the objective to assess the effect of natural uranium and other radionuclides in drinking water on risk of leukemia. The median activity concentration of uranium in the studied well waters was 80 mBq/l for the leukemia cases and 60 mBq/l for the reference group, with radon concentrations at 80 and 130 Bq/l, respectively, and ^{226}Ra concentrations at 10 mBq/l for both groups. The results do not indicate that there is an increased risk of leukemia from ingestion of natural uranium or other radionuclides through drinking water at these exposure levels (Auvinen et al., 2002).

The current WHO guideline value for uranium in drinking water is 2 µg/l and was considered to protect the public against possible renal effects (WHO, 1998). The WHO is presently preparing the 3rd edition of its Guidelines for Drinking Water Quality. This represents a major update of the 2nd edition of the Guidelines. In the draft of the new Guidelines, WHO amended its provisional guideline value for uranium in drinking water from 2 µg/l to 9 µg/l. The update is based on a modification of the allocation of the tolerable daily intake (TDI) to drinking water from 10% to 50%. Several countries, such as Canada, set chemical guidelines for uranium consumption in the order of 20 µg/l. These guidelines and limits seem to be comparably low with respect to the high levels of uranium in some potable waters from Scandinavia (several hundred µg/l). It has to be taken into account, that there is yet no indication that the local population is negatively affected by the ingestion of natural uranium via drinking water (Frengstad et al., 2000).

3.5.2 Health Impacts of Radium

Radium is one of the most hazardous elements with respect to internal radiation exposure and is known to be carcinogenic (U.S. EPA, 1996). As an alkaline-earth metal, radium may substitute calcium and strontium in human bone cells and it remains intact and thus causing radiation damages by emitting α-particles. Chronic human exposure to ^{226}Ra is associated with occurrence of bone sarcomas and the so-called head carcinomas. However, these diseases only occurred in people who received skeletal doses exceeding 10 Gy. Fortunately, no excess leukemia or other tumors due to ingested radium were found up to now (Priest et al., 2001).

The β-particle-emitting isotope ^{228}Ra is only linked with bone cancer. Nevertheless, current dose conversion factors for ^{228}Ra indicate the possible negative health effects of this radionuclide. The dose conversion factors for ^{228}Ra are more than 10 times higher than for ^{238}U, ^{234}U or ^{224}Ra, respectively. Exposure to high levels of radium causes several adverse health effects such as benign bone growth, osteoporosis, kidney & liver disease, anemia and immunological depression (Sidhu, 1998).

3.5.3 Health Impacts of Radon

Despite its ubiquitous occurrence, radon in drinking water does not present a major health concern, even at high levels of ingestion. Radon is an inert noble gas and does not form any compounds in the human body. However, ingestion of radon from drinking water could possibly pose a direct health risk through irradiation of sensitive cells in the gastrointestinal tract and in the organs, after an absorption into the bloodstream. Thus, there is a small risk of stomach cancer arising from ingested radon. Actually, ingested radon is quickly removed from the bloodstream with a half-time in the order of minutes (Health Canada, 1995).

An age and gender averaged cancer death risk from lifetime exposure to radon in potable water has been calculated to be 0.2×10^{-8} per Bq/m^3 (NRC, 1999). This extremely small risk is mainly attributed to stomach cancer. In spite of this, only approx. 0.15 percent of the stomach cancer cases in the USA are caused by ingested radon in drinking water (Environmental Health, 1999). Furthermore, the risk from ingested radon could be as low as zero, if the linear, no-threshold hypothesis is unfounded (NRC, 1999). In spite of this, radon in tap waters might contribute to the airborne radon concentration in buildings. The inhalation of radon and its short-lived decay products is believed to be a major contributor to the development of lung cancer (Mc Laughlin, 2001; NRC, 1999). Hence, the levels of radon in tap waters should be restricted to avoid an increase of airborne radon levels in dwellings.

3.5.4 Health Impacts of Lead and Polonium

Among the radon progeny, the two relatively long-lived isotopes ^{210}Pb and ^{210}Po are of health concern due to their radiotoxicity. Ingested ^{210}Pb can be easily incorporated in the human skeleton because lead substitutes the calcium in apatite, which is a major constituent of human bones. The decaying ^{210}Pb might negatively affect the red bone marrow. Additionally, ^{210}Pb has a half-life of 22.3 years and remains fixed in the human skeleton and produces additional ^{210}Po by its decay.

The biochemical behavior of polonium has been investigated extensively in laboratory animals (Leggett et al., 2001). It is very likely that ingested polonium persists in the human body and decays by the emission of high energetic α-particles (5.3 MeV). Since the half-life of ^{210}Po is only 138 days, there is an intensive decay within the human body. It has been estimated that the dose due to ingestion of ^{210}Po is about 7% of the natural internal radiation dose (Bulman et al., 1995). ^{210}Po is believed to be the most radiotoxic α-particle emitter in the ^{238}U-decay chain (EPA, 1996).

In fact, ^{210}Pb is considered to be the most hazardous natural radionuclide present in potable waters. This assumption is proven by the fact that the current dose conversion factor for ^{210}Pb is the highest for all natural radioisotopes present in drinking waters (refer to Table 13, page 42).

4 Basics of Radioactive Decay

Radioactive decay is the spontaneous transition of an atomic nucleus into a different nuclide by the emission of particles or photons. The decay of a radioactive nuclide is a random process and is subject to the laws of statistics.

4.1 Decay Law

The decay rate or activity of a radioisotope source is described by a simple linear differential equation, the so-called decay law, where the number of decaying atoms (N) per unit time is proportional to the number of atoms that persisted decay at the moment t (Lieser, 1991):

(eq. 1) $$A(t) = \frac{dN}{dt} = -\lambda \cdot \mathrm{N}\ (\mathrm{t})$$

with A(t) = activity (decays per unit time) and λ = decay constant

Integration of the decay law with respect to time provides the following equation (Lieser, 1991):

(eq. 2) $$\mathrm{N(t)} = \mathrm{N}_0 \cdot \mathrm{e}^{-\lambda t}$$

This exponential expression may be useful for correcting the radioactive decay if short-lived radionuclides are investigated (e.g. ^{222}Rn, ^{224}Ra, ^{210}Po). The decay constant is dependent on the half-life of the respective radionuclide and can be calculated from the following equation:

(eq. 3) $$\lambda = \frac{\ln 2}{T_{1/2}}$$

Statistically, λ refers to the probability of the number of nuclei that will undergo radioactive transformation in time t and is characteristic for each radioactive isotope.

The standard SI-unit of *activity* is the Becquerel (Bq), defined as one disintegration per second.

(eq. 4) $$\mathrm{A} = \lambda * \mathrm{N}$$

The *specific activity* of a radioactive source is defined as the activity per unit mass of the radioisotope sample.

4.2 Half-life

The half-life ($T_{1/2}$) for the decay of a radioactive nuclide is the length of time it takes for exactly one-half of the radioactive nuclei in the sample to decay. Consequently, after one half-life 50 % of the initially present atoms will remain. Substituting $T_{1/2}$ into the radioactive decay law and setting the result equals to $N_o/2$ will establish the relationship between the half-life and the decay constant (Lieser, 1991).

$$T_{1/2} = 0.69315/\lambda \qquad \text{(eq. 5)}$$

The half-lives of natural radioisotopes vary from some microseconds to billions of years.

4.3 Modes of Radioactive Decay

Several modes of decay have been investigated since the discovery of radioactivity. The following section deals with the types of radioactive transitions, which occur within the three natural decay chains. Other natural modes of decay, such as spontaneous fission, have negligible importance with respect to radioactivity present in drinking waters and are not of concern in this particular study. A common feature in all modes of decay is that they release ionizing radiation, i.e. the energy of the released particles or photons is sufficiently high enough to remove electrons from atoms and molecules, respectively.

4.3.1 Alpha-Decay

Alpha decay is usually restricted to elements with mass numbers higher than 170 and atomic numbers greater than 70. These heavy isotopes have excess protons and decay by emission of α-radiation. The α-particle is identical to a ^{4}He nucleus consisting of 2 neutrons and 2 protons. Alpha decay reduces the number of nucleons by 4 mass units and decreases the atomic number by 2 units. For example, alpha decay of ^{238}U produces ^{234}Th as the daughter isotope:

$$^{238}_{92}U \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He} + 4.198\ \mathrm{MeV} \qquad \text{(eq. 6)}$$

The health effects of α-particles are dependent on the exposure path. Alpha-radiation was recognized to be the most hazardous type of radiation when incorporated in the human body. This is due to the high mass and the high energy of α-particles. However, external exposure is of minor health concern than internal exposure, because α-particles are not able to penetrate through the outer layers of the human skin.

4.3.2 Beta-Decay

Electron emission (β^-) occurs when the ratio of neutrons to protons in the nucleus is too high. This process decreases the number of neutrons by one and increases the number of protons by one. Since the number of protons in the nucleus determines the element, electron emission leads to the formation of a different element. For instance, ^{40}K decays to ^{40}Ca by the emission of an electron:

$$\text{(eq. 7)} \qquad {}^{40}_{19}\mathrm{K} \rightarrow {}^{40}_{20}\mathrm{Ca} + {}^{0}_{-1}\mathrm{e}$$

Another mode of beta decay is electron capture. The nucleus captures an electron from an inner orbital of the electron cloud and decreases the ratio of neutrons to protons by this process. ^{40}K is not only a characteristic electron emitting radionuclide; it may also decay to ^{40}Ar by electron capture.

$$\text{(eq. 8)} \qquad {}^{40}_{19}\mathrm{K} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{40}_{18}\mathrm{Ar} + h\nu$$

A third form of beta decay is the so-called positron emission (β^+). This process does not occur in nature and is consequently not of interest in this study.

4.3.3 Gamma-Emission

The daughter nuclides produced by α-decay and especially by *ß*-decay are often obtained in an excited energy state. The energy associated with this excited state is released when the nucleus emits a photon of high energy. Most frequently, the γ-ray is emitted within 10^{-12} seconds after a particle emission. In some cases, gamma decay is delayed, and a meta-stable radionuclide is formed. For example, the meta-stable ^{241m}Pa nuclide has a half-life of only 11.7 minutes. Since electromagnetic radiation does not carry charge or mass, the product of γ-ray emission by ^{241m}Pa is the isotope ^{241}Pa.

$$\text{(eq. 9)} \qquad {}^{241\mathrm{m}}_{91}\mathrm{Pa} \rightarrow {}^{241}_{91}\mathrm{Pa} + \gamma$$

4.4 Natural Radionuclides and Geochronology

The discovery of radioactivity had a profound effect on geology. Radioactivity not only causes heat generation in rocks but also provides an accurate method of measuring the ages of rocks and minerals (Faure, 1986). The occurrence of natural radioisotopes is applicable for determining the age of geological formations and the Earth itself.

Knowledge of the half-life of present radionuclides is useful for calculating the age of natural materials, such as rocks, fossils and organic matter. Some examples of isotope systems currently used in geochronology for dating geological formations are compiled in Table 11.

Table 11: Isotope systems as used in geochronology (data taken from Faure, 1986 and Wahl, 2000)

Parent	Daughter	$T_{1/2}$	Useful Range	Type of material
^{238}U	^{206}Pb	4.47×10^9 a	10 Ma – 4.6 Ga	e.g. zircon, monazite, sphene, apatite
^{235}U	^{207}Pb	7.03×10^8 a		
^{232}Th	^{208}Pb	14×10^9 a		
^{40}K	^{40}Ar	1.28×10^9 a	10 Ka – 4.6 Ga	K-bearing minerals
^{87}Rb	^{87}Sr	4.88×10^{10} a	10 Ma – 4.6 Ga	e.g. mica, K-feldspar, clay minerals
^{147}Sm	^{143}Nd	1.06×10^{11} a	100 Ma - 4.6 Ga	Igneous and metamorphic rocks and minerals
^{14}C	^{14}N	5,730 a	100 – 70 Ka	Organic matter

The principal difficulty of radiometric dating lies in precision when measuring very small amounts of isotopes. Several factors can cause dates based directly on radiometric methods to be incorrect. For example, if the daughter isotopes have partly escaped from the investigated rock, the age of the rock would be underestimated.

Where feasible, two or more radiometric dating procedures are used on the same piece of material to confirm previous results.

5 Statistics of Radioactive Decay

The decay of radioactive matter is a random process and is subject to the laws of statistics. As a consequence, the number of decay events per unit time is variable. Counting statistics provides the means to describe the average behavior of all nuclear decays in a certain sample and is used to express the probability of obtaining a given count within a certain confidence limit. However, the exact time for an individual atom transformation cannot be predicted; each single atom will decay spontaneously and unaffected by any external influences such as temperature or pressure (Lieser, 1991).

By applying counting statistics, the validity of a single count determination as being representative of the true count rate may be determined (Knoll, 2000). However, it is impossible to perform a measurement of radioactive isotopes that is completely free of errors, or uncertainties. Every single determination is influenced by many uncertainties, which can never be entirely eliminated, so the true value for any quantity is always unknown (Skoog et al., 1996).

It can be distinguished between at least two types of measurement errors, termed systematic errors and random errors. There are three major forms of *systematic errors*:

1. *instrument errors*, caused by imperfections and instabilities in the instrumentation
2. *method errors*, arising from imperfect chemical or physical behavior of analytical systems (e.g. fluctuations in air-pressure, temperature, humidity)
3. *personal errors*, resulting from personal limitations or inattention of the staff

Random errors are mainly due to the statistical nature of radioactive decay and can be evaluated by methods of statistics, in contrast to systematical errors. In general, random errors affect the precision of measurements while systematic errors influence the accuracy of measurements (Skoog et al., 1996).

5.1 Statistical Models for the Distribution of the Count Rate

The mean of a theoretical probability distribution is usually of interest in statistical processes. Under certain conditions, the distribution functions for measurement replicates can be predicted. For further consideration, the probability of a single event is p, and the probability of a non-event is $q = 1 - p$ and the probability of an event is a constant for all trials. In the following section, the three main models for the distribution of statistical data will be introduced.

5.1.1 Binomial Distribution

The Binomial Distribution is the most general model of statistical distributions and is widely applicable in natural sciences but rarely used in nuclear applications (Knoll, 2000). The binomial distribution applies to any process with two possible results. Since the probability of a single event is *p*, the probability of *n* events in *N* trials is obtained from the binomial expansion. The probability of the event is described by the following equation:

(eq. 10) $$p_n = \frac{N!}{n!(N - n)!} p^n (1-p)^{N-n}$$

The mean (x) and the variance (σ^2) are:

$$x = Np \text{ and } \sigma^2 = Npq$$

Unfortunately, the binomial distribution is difficult to handle with respect to radioactive decay, where the number of nuclei is always very large (Knoll, 2000).

5.1.2 Poisson Distribution

The Poisson distribution serves as a direct mathematical simplification compared to the binomial distribution but with the exception that the probability of an event has to be small ($p \ll 1$):

(eq. 11) $$p(n) = \frac{(pN)^n e^{-pN}}{n!}$$

variance is equal to the mean, σ^2=x.

The Poisson distribution is applicable if the counting time is smaller than the half-life of the respective radioisotope, or when the detection efficiency is relatively small (Knoll, 2000).

5.1.3 Gaussian Distribution

A further simplification of the Poisson distribution - under the precondition that the mean value of the distribution is larger than 20 - leads to the Gaussian distribution:

(eq. 12) $$p(n) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(n-\sigma)^2}{2\sigma^2}\right]$$

The Poisson distribution and the Gaussian distribution are approximately the same for any situation in which more than a few counts during the performance of measurements are accumulated (Knoll, 2000). In a Gaussian distribution, the mean, median and the mode (most frequent value) are all the same because this distribution is symmetrical.

The application of Gaussian distribution leads to confidence intervals, which are very important for counting measurements. A given result of a radioactivity measurement without indicated confidence interval can be considered to be inappropriate and wrong, because it is impossible to obtain the true count rate of a radioactive sample. As mentioned earlier, it is only achievable to determine a representative value for the true count rate within a certain limit of confidence.

Confidence intervals:

It can be calculated that 68.3% of the area under a Gaussian curve lies within one standard deviation (± 1σ) of the mean x. Consequently, the probability of an observed value falling within ±1σ is about 68%. This term is the so-called confidence limit. In continuation, approx. 95% of all data is within ± 2σ of the mean and 99.7% are within 3σ (Figure 6).

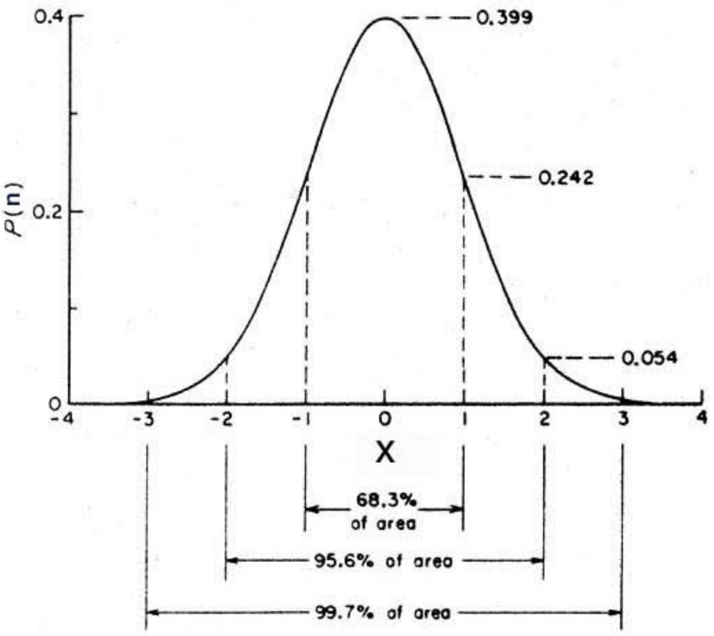


Figure 6: Gaussian Distribution

The predicted standard deviation in a Gaussian distribution can be calculated from a simple equation:

(eq. 13) $$\sigma = \sqrt{n}$$

The standard deviation of the mean value is an adequate indicator if the sample count rates are large compared to the background radiation and must be modified if counter background is not negligible (e.g. in gamma radiation measurements). The variance is simply the square of the standard deviation (Papula, 2001).

For practical purposes, only Gaussian distribution was applied for this study. It can be assumed that a normal distribution was applicable in all of the performed measurements because the calculated mean of the statistical distribution was always higher than 20. It has to be noted that the three presented distributions become identical for processes with a small individual probability *p* but with a sufficient number of “trials” so that the expected mean number of success is comparably large (Knoll, 2000).

In radiometry, high confidence limit is desirable when performing experimental work. Thus, all the results obtained in the radioactivity measurements for this study are always presented at a 96% confidence interval (2σ): ***count rate* ± *2.0*$\sqrt{n}$ *.***

5.2 Statistical Tests

A statistical test provides means for making quantitative decisions about a process. The intent is to determine whether there is enough evidence to reject a hypothesis about the process (Papula, 2001). There exists a large number of statistical tests for different applications and purposes. In the following section, two frequently used statistical tests with respect to radioactivity measurements will be introduced.

5.2.1 T-Test

When radiological measurements are performed, it is often of interest to determine whether concentrations vary between different locations or intervals of time. To investigate this, a so-called t-test can be applied. Groups are considered significantly different if the 95% confidence interval for their averages does not overlap (t-test with $\alpha = 0.05$). Thus, the t-test assesses whether the means of two groups are *statistically* different from each other or not. Moreover, the t-test corrects for the uncertainty of the sample standard deviation (σ) caused by taking a small number of samples (Papula, 2001).

5.2.2 Q-Test

One of the crucial problems encountered in radiometry is the question, whether a questionable result can be rejected or not. The q-test is used to determine if there is a statistical basis for removing a result from a set of data.

In this widely-used test, the absolute value of the difference between the questionable result χ_q and its nearest neighbor χ_n is divided by the spread (*w*) of the entire set to give the quantity Q_{exp} (Skoog et al., 1996):

$$\text{(eq. 14)} \qquad Q_{exp} = \left|\chi_q - \chi_n\right| / w$$

This ratio is then compared with rejection values Q_{crit} available in literature. If Q_{exp} is greater than Q_{crit}, the questionable result can be rejected with the indicated degree of confidence.

6 Legislation in Europe and Canada

6.1 European Union (EU)

According to the main objectives of the United Nations Agenda 21, the European Community passed the European Water Framework Directive, which came into force in December 2000. This regulation focuses on the quality of waters in the Member States in agreement with a sustainable development. The regulation dealing with drinking water quality is the European Drinking Water Directive, which was passed in 1998. This regulation is called "Tapwater Directive" because the point of water use is the point of compliance with the quality standards. Member States have a deadline until 25th December 2003 to ensure that the drinking water quality complies with the new quality standards.

The ***Council Directive 98/83 on the quality of water intended for human consumption*** entered into force in December 1998 to restricts the levels of tritium to 100 Bq/l and limits the total indicative dose (TID) caused by radionuclides present in drinking waters to 0.1 mSv per year. However, the TID excludes ^{3}H, ^{40}K, radon and radon decay products. Due to this limitation, the main radionuclides of concern are minimized to be uranium- and radium-isotopes. The TID has to be calculated from the radionuclide concentrations and the dose coefficients for adults and children as stated in Annex III, Table A of European Council Directive 96/29/EURATOM. Table 12 supplies the reference concentrations for some uranium and radium isotopes, where each radionuclide is treated as if they are the only radioisotopes present in drinking water.

Table 12: Reference concentration for radioactivity in drinking water

Radionuclides	**Reference concentration Adults (> 17 a)**	**Reference concentration young children (2 -7 a)**	**Reference concentration babies (< 1 a)**
^{238}U	3.0 Bq/l	7.3 Bq/l	5.35 Bq/l
^{234}U	2.8 Bq/l	6.7 Bq/l	4.90 Bq/l
^{228}Ra	0.2 Bq/l	0.2 Bq/l	0.06 Bq/l
^{226}Ra	0.5 Bq/l	1.0 Bq/l	0.40 Bq/l
Water consumption	730 l/a	170 l/a	55 l/a

When more than one radionuclide is detected, compliance with the TID shall be determined using the equation given below:

$$\sum_{i=1}^{n} \frac{A_i}{RC_i} \leq 1 \qquad \text{(eq. 15)}$$

The observed concentrations of each radionuclide present in drinking water (A_i) have to be divided by the respective reference concentration (RC_i) and then summed up. Once the relationship is satisfied, the Member State is then allowed to renounce further investigations if the TID is less than the parametric indicator value of 0.1 mSv per year.

For practical purposes, Member States of the EU may use screening methods for gross-alpha activity and gross-beta activity to monitor the parametric indicator value for TID. If the gross-alpha and the gross beta activities were less than 0.1 Bq/l and 1.0 Bq/l respectively, the Member State may assume that the TID is less than the parametric value of 0.1 mSv per year and therefore no further radiological investigation is needed. This also applies vice versa, if gross-alpha or gross-beta activity exceed their corresponding indicator value, analysis for specific radionuclides must be conducted.

The maximum acceptable concentration of radon and radon progeny in drinking water is not regulated through the European Drinking Water Directive. However, the European Commission 2001 gave a "*recommendation on the protection of the public against exposure to radon in drinking water supplies*". Above a radon concentration of 100 Bq/l, Member States are recommended to set a reference level for radon. For concentrations in excess of 1,000 Bq/l remedial action is considered to be justified on radiological protection grounds (2001/928/Euratom). The proposal provides reference concentrations for the radiotoxic radon decay products ^{210}Pb (0.2 Bq/l) and ^{210}Po (0.1 Bq/l). It should be taken into account that these recommendations are without any obligation for the Member States of the EU.

6.2 Legislation in Germany

Meanwhile, the Directive 98/83/EC has been implemented in German law. The German legislator has fulfilled exactly the most important obligations of the European Drinking Water Directive.

The amended *Trinkwasserverordnung* came into effect on 1st January 2003. However, the radioactivity parameters of the Trinkwasserverordnung will only be enforced on 1st December 2003. According to the Directive 98/83/EC, the maximum acceptable total indicative dose (TID) caused by radionuclides in drinking water has been set to 0.1 mSv per year, excluding ^{3}H, ^{40}K, radon and radon decay products. In addition to that, the maximum acceptable concentration of ^{3}H has been reduced to 100 Bq/l. The TID has to be calculated after the dose conversion factors laid down in the Directive 96/29/EURATOM. Up until now, there exist no official regulations or recommendations for the detection and assessment of radionuclides in drinking waters. Nevertheless, it is very likely that German water suppliers will be permitted to use screening methods for the determination of gross-alpha and gross-beta activity to ensure the abidance of the total indicative dose (0.1 mSv/year). If the maximum acceptable levels for gross-alpha (0.1 Bq/l) or gross-beta activity (1.0 Bq/l) are exceeded, analysis for specific radionuclides must be performed (Aurand & Rühle, 2002).

6.3 Canada

The basic regulation for Canadian drinking waters is provided by the *Guidelines for Canadian Drinking Water Quality*. The Federal-Provincial Subcommittee on Drinking Water develops the Guidelines, which apply to drinking waters from all private and municipal water sources (Health Canada, 1996). In agreement with the United Nations Agenda 21, the Guidelines for Canadian Drinking Water Quality have been updated and include guidelines for radiological parameters as well. In addition, several Canadian Provinces have established their own Drinking Water Standards with maximum acceptable concentrations for certain parameters adopted from the Health Canada Guidelines. Moreover, regulations for several other parameters have been established, which were not included in the *Guidelines for Canadian Drinking Water Quality*.

In the Province of Ontario, a stringent new regulation has been introduced recently for the improvement of water quality. The *Drinking Water Systems Regulation* (O. Reg. 170/03) entered force on June 01, 2003. The Ontario government has passed this particular drinking water regulation under the *Safe Drinking Water Act*. The *Drinking Water Systems Regulation* will replace the *Drinking Water Protection Regulation for Larger Waterworks* (O. Reg. 459/00) and the *Drinking Water Protection Regulation for Smaller Waterworks Serving Designated Facilities* (O. Reg. 505/01). Tough standards for the protection of potable waters continue to apply, with regular sampling and testing requirements for drinking water. The testing for bacteria and chemical parameters has to be performed by accredited laboratories only. Furthermore, minimum standards for water treatment, public reporting and tough penalties for non-compliance will take effect.

The new regulation defines eight categories of drinking water systems, including the following:

- *municipal systems*, including smaller municipal systems serving less than 100 residences
- *private residential systems* (not on municipal systems) serving six or more residences for 10 or more months of the year (e.g. apartment complexes and mobile home parks)
- *seasonal waterworks* capable of supplying drinking water to the public at a rate of 2.9 liters per second (such as campgrounds, hotels, resorts)
- *private non-residential systems* that serve drinking water to the public (resorts, restaurants)

However, the quality of drinking waters from private wells is not regulated by any restricted guidelines, as long as the well waters are not used as mentioned above. Hence, the vast majority of private well waters in Ontario are not regularly monitored. Owners of individual water supplies are not obliged to analyze their waters with respect to natural radioactivity.

In addition to the Drinking Water System Regulation, supporting regulations have been enacted, such as the *Ontario Drinking-Water Quality Standards Regulation* (O. Reg. 169/03), which deals with the standards that are to be used for water testing. Schedule 3 of this particular regulation contains the radiological standards for potable waters in Ontario. In Schedule 3 of O. Reg. 169/03, radiological standards were established as maximum acceptable concentrations (MAC) for the most important natural and artificial radionuclides. These MAC levels for radionuclides in drinking water have been derived based on a committed effective dose of 0.1 mSv from one year's consumption of drinking water. This approach is in agreement with the International Commission on Radiological Protection (ICRP), of Publication 26. It has to be kept in mind that the effective dose of 0.1 mSv/a represents less than 5% of the average annual dose attributed to natural background radiation.

The MACs of radionuclides in public water supplies are calculated by dose conversion factors for adults. This is done so by assuming an annual water intake of 730 liters and a maximum committed effective dose of 0.1 mSv/year.

$$\text{(eq. 16)} \qquad \text{MAC (Bq/L)} = \frac{1 \text{ x } 10^{-4} \text{ (Sv/year)}}{730 \text{ (L/year) x DCF (Sv/Bq)}}$$

When two or more radionuclides are found in drinking water, the following relationship should be satisfied:

$$\text{(eq. 17)} \qquad \frac{C_1}{MAC_1} + \frac{C_2}{MAC_2} + ... + \frac{C_i}{MAC_i} \leq 1$$

where C_i and MAC_i are the observed and maximum acceptable concentrations, respectively, for each contributing radioisotope.

Table 13: MAC levels for some natural radionuclides in Ontario's Drinking-Water Quality Standards Regulation

Parameter	***Dose conversion factor (adults)***	***MAC (Bq/l)***
^{238}U	3.6 x 10^{-8}	4.0
^{235}U	3.8 x 10^{-8}	4.0
^{234}U	3.9 x 10^{-8}	4.0
^{228}Ra	2.7 x 10^{-7}	0.5
^{226}Ra	2.2 x 10^{-7}	0.6
^{210}Pb	1.3 x 10^{-6}	0.1
^{210}Po	6.2 x 10^{-7}	0.2

There also exists a chemical guideline of 20 µg/l for natural uranium, which had been established in July 2002 (O. Reg. 213/02). The activity concentration of natural uranium corresponding to this regulation is approximately 0.5 Bq/l.

A maximum acceptable concentration for radon in drinking water has not yet been established in Canada. Thus, radon belongs to the parameters without any guidelines in Canada, in contrast to the “Recommendations of the European Commission on the protection of the public against the exposure to radon in drinking water”. The Canadian Authorities had stated that no experimental or epidemiological data has linked ingested radon with health impacts in humans, and it has generally been concluded that the risk from ingestion is insignificant compared to the risk from inhalation. Due to this conclusion, no MAC for radon in drinking water has been set (Health Canada, 1995).

It can be summarized that the presented radiological parameters are obligatory for smaller and larger waterworks and water distribution facilities. However, they are not binding for private residential systems that are not on municipal systems, do not serve six or more residences for 10 or more months of the year and do not serve drinking water to the public.

7 Removal of Natural Radionuclides from Potable Waters

Ground and surface waters are the most common sources for the production of drinking water. Ground waters may contain significant amounts of natural radionuclides, while surface waters generally do not carry enhanced levels of natural radioactivity. However, different methods are applied for the treatment of ground waters, especially for the removal of iron, manganese and toxic pollutants. If the levels of natural radionuclides in raw waters are elevated, suitable treatment processes have to be applied or the already existing facilities have to be optimized for removing radionuclides.

Natural radionuclides can be effectively removed from drinking water. There are diverse treatment methods used for the different natural radionuclides. However, these removal processes concentrate the radioactivity, thus a proper disposal of contaminated residues has to be ensured. The EU-Project TENAWA accomplished a collection of important data for the removal of radionuclides from drinking water. Raff (1999) provided another important source regarding the elimination of radionuclides from potable waters.

Artificial radionuclides, such as ^{137}Cs, ^{89}Sr and ^{131}I, might be of interest in drinking water supply, especially after nuclear accident events. A removal of these isotopes from drinking water is feasible, but is not of interest in this study. The following section deals exclusively with the removal of the most common natural radionuclides from drinking water (isotopes of U, Ra, Rn, Po and Pb).

7.1 Removal Processes

In general, removal processes for natural radionuclides are dependent on the physical and chemical characteristics of the respective radionuclide. For example, radon as an inert noble gas has a completely different behavior during water treatment than heavy metals, such as uranium and lead. Widespread removal processes include aeration, filtration, flocculation and lime softening. Sophisticated techniques such as reverse osmosis and nanofiltration are highly suitable for radionuclide removal from waters, but these methods are very costly and only applicable for smaller units (Raff & Wilken, 1999).

The removal efficiency is primarily influenced by the following factors:

- Physical and chemical properties of the radionuclides
- Hydrochemistry of the water
- Water treatment equipment
- Process conditions and their variations

7.1.1 Aeration

Aeration is a common treatment method used for the physical de-acidification of raw water. The effect of this method is based on the increase of pH due to the degassing of CO_2 during aeration. Furthermore, other volatile gases, such as H_2S, are also stripped out off the water. On the other hand, aeration is actually considered as the primary treatment method for eliminating radon from water. Aeration removes radon and CO_2 quite similarly and the water quality does not change significantly (Salonen et al., 2000). Some aerators are extremely efficient and can be applied in smaller waterworks as well. This is due to the relatively high Henry's law constant of radon (Raff, 1999):

$$\mathbf{K_{Rn} = 25.8 \times 10^{-3}\ mol\ l^{-1}\ atm^{-1}}\ \text{(20°C; 1 atm pressure)}$$

Generally, two different principles can be used for aeration:

- water released to air (e.g. spraying of raw water into a water tank)
- air released to water (e.g. bubbling air through a water tank at high pressures)

Usually, commercial aeration systems utilize a combination of both principles. However, aeration equipment is far too expensive for an application in private homes. The removal of other natural radionuclides by aeration is not practicable (TENAWA, 2000).

→ **removal of**: **Rn** at high efficiencies (> 90%)

Another possible method for radon removal from contaminated waters is heat treatment (Abulfaraj & Mamoon, 1995). Radon elimination by this method is due to the decreasing radon solubility at increasing water temperatures. However, water treatment by heating is obviously not feasible for waterworks because of the high-energy demand and the possible degassing of radon into the indoor air of buildings.

7.1.2 Filtration

Filtration is probably the most common water treatment process in the world. It can be distinguished between single and multiple layer filtrations, in dependence of the composition of the filter. Filtration separates solid particles by running water through a porous medium. Either gravity or a pressure differential is applied across the filtration medium to drive the filtration process (Grombach et al., 2000). Thus, only radionuclides adsorbed onto particles can be easily removed by filtration. Dissolved compounds of radionuclides and colloids will probably not get retained by sand filtration. The combination of flocculation and sand filtration increases the removal efficiencies for natural radionuclides. In open filtration processes, dissolved radon will partly escape from the water and may accumulate in the indoor air of buildings.

→ **removal of:** *solid particles containing* ***U, Ra, Po, Pb*** *& degassing of* ***Rn***

7.1.3 Ion Exchange / Water Softening

Ion exchange is a common method to remove toxic ions from polluted water in an exchange with relatively harmless ions (H^+, Na^+, OH^-) provided by the ion exchange material. In addition to that, ion exchange is highly suitable for eliminating water hardness, caused by Ca^{2+} and Mg^{2+}. Water softening is a typical and important treatment method for groundwater. The following equation indicates the stoichiometry of the process (S = surface):

$$\text{(eq. 18)} \qquad (S^{2-})\left\langle \frac{Na^+}{Na^+} \right\rangle + Ca^{2+} + 2\,HCO_3^- \leftrightarrow (\mathrm{S}^{2-})\left\langle \mathrm{Ca}^{2+} \right\rangle + 2\,Na + 2\,HCO_3^-$$

Modern ion exchange units consist of synthetic organic materials (such as resins) containing ionic functional groups to which exchangeable ions are attached (Figure 7). The exchange reaction is reversible and dependent on the concentration of contaminants. Ion exchange resins can usually be recycled for use by pouring a concentrated regeneration solution into the system (Grombach et al., 2000). However, the regeneration step leads to the production of liquid waste, which must be treated separately, especially if it contains high amounts of natural radioactivity.

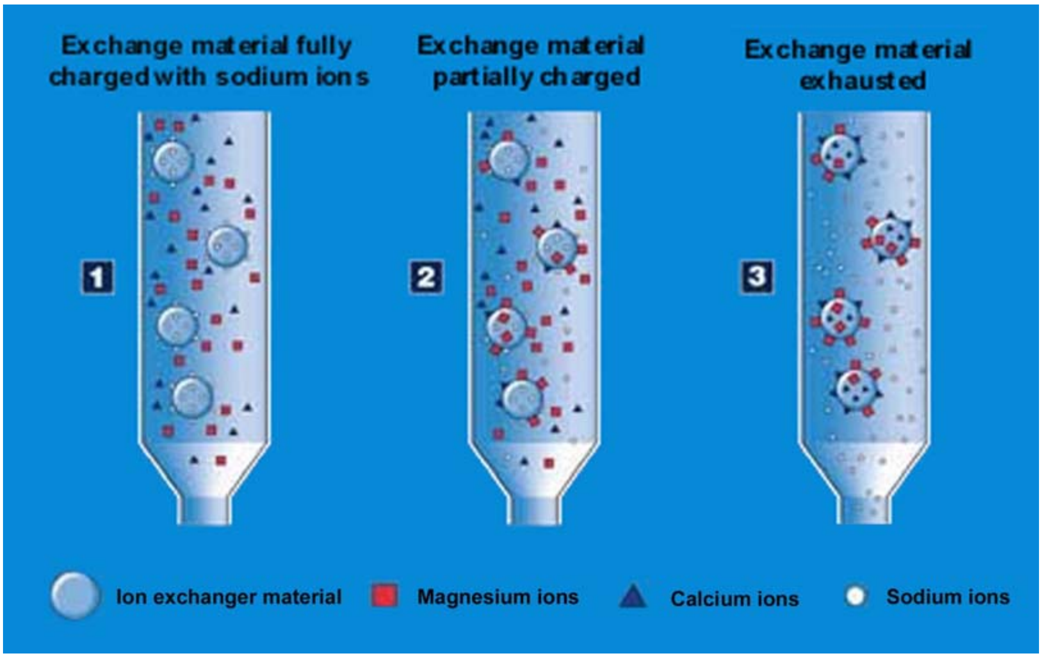


Figure 7: The ion exchange process

This method is suitable for smaller water treatment facilities and can be used particularly for the elimination of uranium and radium. An anion resin is suitable for the removal of ^{210}Pb and ^{210}Po, because it is very likely that these radionuclides are present in water as anionic particles, which are adsorbed and filtered by the exchanger beds (Vaaramaa et al, 2000). A pre-treatment of the water is necessary, when iron and manganese or suspended matter is present (Raff, 1999).

→ **removal of**: dissolved **U, Ra, Po, Pb** at high efficiencies (> 90%)

Unfortunately, this exceptional method is very costly and the disposal of contaminated waste could be problematic.

7.1.4 Lime Softening

The classical method for removing water hardness is lime softening. In this water treatment process, the pH of the raw water is raised adequately to precipitate calcium carbonate and magnesium hydroxide. The pH during water softening needs to be close to 10. Lime milk is added to the water to remove the bicarbonate hardness caused by Ca and Mg. The simplified formula of the reaction for precipitating calcium-carbonate from water is provided by the following equation:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\,CaCO_3 \downarrow + 2\,H_2O \qquad \text{(eq. 19)}$$

Since the chemical properties of radium are closely related to calcium, it is quantitatively co-precipitated with calcium during the process of lime-softening. Other natural radionuclides are not sufficiently removed from water by this treatment method.

→ **removal of**: dissolved **Ra** at high efficiencies (> 90%)

The produced sludge may contain significant amounts of radium and has to be disposed with care.

7.1.5 Granulated Activated Carbon

Water treatment systems based on **G**ranulated **A**ctivated **C**arbon (GAC) are highly efficient for removing pollutants from waters, including dissolved radon. GAC is produced from several raw materials such as charcoal, peat or coconut. Treatment of the raw material with steam, CO_2 or air at temperatures between 700 and 1,000 °C ensure the „activation“ of granulated activated carbon (Grombach et al., 2000).

Several studies have proven the efficiency of GAC, and radon removal rates of almost 100% have been reported (Turtiainen, 2000). The reason for the high removal yield of GAC is the extremely high internal surface of activated carbon, which leads to an effective adsorption of dissolved compounds. Typical activated carbons used for water treatment have internal surfaces of up to 1,200 m^2 per gram (Grombach et al., 2000).

Batch experiments performed during the TENAWA project indicate high but not uniform efficiencies for the removal of uranium, radium, lead and polonium by GAC filtration. Furthermore, adsorption of uranium and radium is strongly dependent on the carbon type.

The most important parameters affecting the removal efficiency of GAC (TENAWA, 2000):

- Physical & chemical water quality (particularly pH, Temp., Fe and Mn)
- granular size
- adsorption velocity / contact time
- dissolved organic carbon (DOC) in water

GAC filters are affordable and can be used for the treatment of private well waters, smaller and larger water treatment facilities. It has to be kept in mind, that disposal of used-up GAC could be problematic. Enhanced radiation doses have been detected in the vicinity of GAC filter systems. Maximum dose rates on the filter surfaces of up to 100 µSv/h have been reported (TENAWA, 2000). A regeneration of used GAC filters is not feasible in waterworks, because adsorbed radionuclides can only be removed with strong solvents, such as hydrochloric acid (Wisser & Bott, 2003).

→ **removal of**: ^{222}**Rn** and ^{220}**Rn** at high efficiencies (> 95%)
→ **removal of**: dissolved **U, Ra, Po, Pb**

7.1.6 Flocculation / Precipitation

The combination of precipitation/flocculation and sedimentation is an established method particularly for the treatment of surface waters. This technology works by precipitating heavy metals along with artificially generated flakes. Typical removal of radionuclides utilizes precipitation with hydroxides, carbonates, or sulphides. Generally, the precipitating agent is added to water in a mixing tank along with flocculating agents, such as various iron- and aluminum salts (Grombach et al., 2000). This mixture is transferred to a flocculation chamber that agglomerates particles, which are subsequently separated from the liquid phase in a sedimentation chamber. Other physical processes, such as filtration, may follow in further water treatment steps (Grombach et al., 2000).

Uranium and polonium can be removed efficiently in the coagulation-flocculation process. A recently concluded study in Sweden had reported removal capacity for U, Th, Pu and Po greater than 85%. However, Ra, Sr and Cs passed through the treatment process with almost unchanged activity concentration (Gäfvert et al., 2002).

The entire process has to be optimized with respect to pH and total alkali content. The best yield for uranium removal has been observed at pH 10.6 – 11.4. The addition of Mg could especially increase the uranium elimination yield (Lee & Bondietti, 1983).

→ **removal of**: dissolved **U, Po** at high efficiencies (> 90%)
→ **removal of**: dissolved **Ra, Pb** at low efficiencies (< 30%)

7.1.7 Reverse Osmosis

Osmosis is a natural process defined as the passage of water from a dilute solution through a semi-permeable membrane to a more concentrated solution. During osmosis, particles pass from areas of low concentration to areas of high concentration as allowed by the pore size of the membrane. The solution of higher concentration will be diluted by lower concentrated water and the osmotic pressure will decrease until the system is balanced (Raff, 1999).

Reverse osmosis is the artificial reversal of this natural process. In this water treatment method, water under pressure is placed against a special membrane. The membrane allows water molecules to pass through but hinders the passage of other contaminants including radionuclides.

This method is highly suitable for the removal of radium and uranium from polluted water. The effectiveness of this treatment process is rather independent on other water constituents, but the required pressure is proportional to the total ion content (Raff, 1999). Radium removal yields of up to 98% have been reported and the removal efficiency for uranium is even higher (Huikuri et al., 1998). This is mainly attributed to the size of uranium complexes. However, reverse osmosis is very costly and a pre-treatment of the water seems to be necessary – particularly when suspended solids are present.

→ **removal of**: dissolved **U** and **Ra** at high efficiencies (> 98%)

7.1.8 Nanofiltration

Nanofiltration is a membrane liquid separation technology that is positioned between reverse osmosis (RO) and ultrafiltration. Nanofiltration combines removal of uncharged components on nanoscale with charge effects between solution and the membrane (Van der Bruggen et al., 2003). Nanofiltration, like reverse osmosis, is affected by the charge of the particles being rejected. Thus, particles with larger charges are more likely to be rejected.

Nanofiltration is particularly applied where the high salt rejection of reverse osmosis is not necessary. Nanofiltration membranes are mainly used for the separation of multi-valent ions and uncharged organic molecules, which have molecular weights between 200 and 1000 Dalton (Dias et al., 1999).

The most important uranium complexes in natural waters (uranyl carbonate & uranyl phosphate) are efficiently rejected by nanofiltration (Raff, 1999). This is mainly due to the relatively heavy molecular weights of uranyl complexes. Additionally, other water contaminants, such as bacteria and viruses are partly removed from water by simple sieve effects (Van der Bruggen et al. 2003).

→ **removal of**: dissolved **U** at high efficiencies (> 95%)

7.1.9 Greensand Filtration

Greensand is a naturally occurring sediment containing a high percentage of the mineral glauconite ($(K, Na)(Fe^{3+}, Al, Mg)_2(Si,Al)_4O_{10}(OH)_2$). Glauconite is a phyllo-silicate, which forms in shallow-water marine sedimentary environments in modern oceans (Chafetz & Reid, 2000).

An oxidizing water filter, mainly composed of manganese greensand can be applied for the removal of iron, manganese, and hydrogen sulfide. In addition, it eliminates dissolved radium at high efficiencies (Mott et al., 1993). Contaminants are removed through filtering and by oxidizing chemical reactions. Soluble iron and manganese are oxidized and precipitated by contact with higher oxides on the greensand granules.

The major disadvantage is that the filter bed has to be regenerated by injecting $KMnO_4$ into it. Furthermore, conventional greensand treatment for the removal of iron and manganese from groundwater is not quite appropriate for waters with a high content of iron and manganese (Lessard et al., 2000). On the other hand, the costs for removing Ra from water by greensand-filtration are minimal, especially in comparison to ion exchange and reverse osmosis (Qureshi & Nelson, 2003).

→ **removal of**: dissolved **Ra** at high efficiencies (> 90%)

7.1.10 Disposal of Waste from Water Treatment

The disposal of radioactive waste arising from water treatment processes is quite problematic. Liquid and solid wastes from waterworks may contain high amounts of natural radionuclides, especially uranium and radium isotopes. GAC-filtration and ion exchange predominantly produce solid wastes, whereas iron and manganese removal, lime-softening, and flocculation generate liquid residues. For instance, an investigation of 80 waterworks in Germany revealed ^{226}Ra levels in filter sludge from water purification of up to several Bq/g (Haberer, 1999).

Unfortunately, there is no comprehensive regulation within the European Union with respect to the disposal of radioactive wastes from water treatment yet. The Basic Safety Standards (BSS) laid down in the in the **Council Directive 96/29/EURATOM** defines practices, which involve a risk from ionizing radiation in cases where natural radionuclides are used in respect to their radioactive, fissile or fertile properties. Wastes from water treatment are obviously not used due to the previously mentioned properties. Thus, their production, processing and handling cannot be considered as a practice and exemption levels are not applicable.

Nevertheless, Member States of the EU may implement regulations for the disposal of wastes from water treatment in their national law. In Germany, the amended Strahlenschutzverordnung entered force on 1st August 2001. Wastes from water treatment are not explicitly included in Annex XII (§§ 97-102), where the considerable residues are listed. However, § 102 of the Strahlenschutzverordnung regulates the monitoring of residues, which could significantly increase the radiation exposure of individuals. The competent authorities have to instruct how a proper disposal of these residues can be guaranteed.

There are different possibilities for the disposal of wastes from water treatment in dependence of the amount of radioactivity and legislation in the Member States:

- *Delivery to municipal dumps*
- *Discharge into communal sewers*
- *Disposal in the environment*
- *Discharge to private waste water systems*

Water suppliers are recommended to contact the competent authorities concerning the disposal of their wastes until the European Union or the respective Member State has passed comprehensive regulations.

In Canada, the Canadian Nuclear Safety Commission (CNSC) regulates the use and disposal of radioisotopes. However, there is no regulation concerning the disposal of radioactive wastes from drinking water treatment.

7.2 Summary of Applicable Radionuclide Removal Methods

Modern water treatment technology is appropriate for the elimination of natural radioisotopes present in drinking waters. There exist methods for an application in private homes, smaller and larger waterworks. Several studies on the different treatment techniques have been concluded in the past decade, and even innovative methods such as reverse osmosis and nanofiltration have been introduced. An important point is the proper disposal of radioactive waste from water treatment. However, in the European Union and in Canada, regulations have not yet been issued with regards to this problem.

Table 14 *“Maximum removal efficiencies for radionuclides during water treatment processes”* provides a compilation of the current treatment methods for removing natural radionuclides from potable waters. The removal efficiencies are presented as maximum values as reported in literature. To achieve a maximum removal yield, the entire water treatment system has to be working under ideal conditions.

Table 14: Maximum removal efficiencies for radionuclides during water treatment processes

	Water treatment processes								
	Aeration	***Flocculation & Filtration***	***Activated Carbon***	***Nano-filtration***	***Reverse osmosis***	***Ion Exchange***	***Lime Softening***	***Greensand***	***Source***
Uranium		98 %				99 %			Lee & Bondietti, 1983
			95 %	95 %		99 %			Raff, 1999
					99 %				Huikuri et al., 1998
					99 %	100 %	99 %		AWWA, 1993
Radium						97 %	96 %		Brinck et al., 1978
						95 %	95 %		Sorg & Logdson, 1980
								98 %	Mott et al., 1993
					98 %				Sorg et al., 1980
					99 %				Huikuri et al., 1998
Radon & Thoron	99 %		> 99 %						Raff, 1999
			99.8 %						Lowry & Lowry, 1987
Polonium						97 %			TENAWA, 2000
Lead						93 %			TENAWA, 2000

8 Experimental Part

8.1 Analytical Quality Assurance

Analytical quality assurance (AQA) is a very important step in the world of quality management and quality control. The main objective of quality assurance is to achieve reliability and quality of results during analytical measurements. This is of great importance, since harmful contaminants could be undetected in water supply, if the measurements are not performed properly. The loss of confidence might put the future existence of a particular laboratory at risk. That is why most analytical laboratories and research facilities apply elements of quality management today.

Quality in the analytical practice can be summarized as everything that meets the specific needs of the customer, attracts the confidence of the customer and all others who make use of the results (Prichard et al., 1995). These principles are already observed and applied in the research fields of the ESWE-Institute and the ESWE-Laboratory. These institutions have an enormous experience and knowledge when it comes to AQA.

The following definitions are of importance for quality management (Prichard et al., 1995)

- ***Quality:*** *degree to which a set of inherent characteristics fulfils requirements*
- ***Quality assurance:*** *part of quality management focused on providing confidence that quality requirements will be fulfilled*
- ***Quality management system (QMS):*** *management system to direct and control an organization with regard to quality*
- ***Self-assessment:*** *a comprehensive and systematic review of the organization's activities and results referenced against the quality management system or a model of excellence*
- ***Standard operation procedure (SOP)****: working instructions for the staff, which should be properly authorized, documented and available to the staff when carrying out the work*
- ***Good Laboratory Practice (GLP)****: set of principles governing the organization and operation of toxicology studies for food, chemical or pharmaceutical development, which were first introduced by the OECD. Compliance with the principles of GLP allows the validity of the results of tests or experiments to be accepted between organizations and countries*
- ***Good laboratory practice (glp)****: term used to describe how scientists should go about their day-to-day work. It includes safety, tidiness, cleanliness, care and organization. An analyst who has these qualities and uses them is more likely to get the right results*

Several elements of quality management were applied and carried out for this thesis to ensure accuracy and precision of radionuclide determination. In addition to that, possible errors of measurements were estimated and confidence limits for every single measurement have been calculated. It has to be kept in mind that AQA is only applicable for reduction and handling of systematical errors, because random errors in this work are mainly due to the statistical nature of radioactivity.

These elements of quality control have been applied during the performance of this study:

I. Utilization of the internal quality management system of ESWE-Institute by applying standard operation procedures (SOP)
II. Taking part in inter-laboratory studies organized by the *Bundesamt für Strahlenschutz* to achieve good analytical quality in Germany
III. Quality Control Charts for the used instrumentation
IV. Participation in analytical inter-comparison workshops with other laboratories
V. Regular calibration of instrumentations with external and internal standards
VI. Internal comparison of the instrumentation by using different analytical principles
VII. Spiking of aqueous samples with tracers, such as ^{232}U
VIII. Proper methodology for recording of results

The new developed analytical methods for radionuclide determination described in section 8.4 are in the process of being included in the quality management system of the ESWE-Institute. Detailed SOP´s already exist, they only have to be verified and assessed by an auditor.

8.2 Detection of Radioactive Isotopes

Measurement systems for radioactive isotopes are primarily based on the interaction between ionizing radiation and matter. Presently, three categories of radiation detection systems are mainly used for radionuclide determination:

- **Semiconductor detectors** (α- and γ-spectrometry)
- **Scintillation counters** (α- and β-measurements)
- **Proportional counters** (α- and β-measurement)

Counting techniques are still highly applicable for the determination of radioisotopes with half-lives of less than a few thousand years (Eikenberg, 2000). However, inductively coupled plasma mass spectrometry is the current state-of-art instrumentation for measuring multiple elements at trace level. The reason for this is because of the high sensitivity of the instrument. Unfortunately, this outstanding method is only applicable for stable isotopes or long-lived primordial isotopes, such as ^{232}Th and ^{238}U.

An innovative method for the determination of the alpha-emitters ^{238}U, ^{234}U, ^{226}Ra and ^{210}Po by using selectively radionuclide-adsorbing discs was applied and optimized for this particular study. The following sections provide details of the applied measurement techniques and present a brief summary of the advantages and disadvantages of the respective counting method.

8.2.1 Semiconductor Detectors

The use of solid detection medium is of great advantage for the detection of high-energy electrons, heavy particles and γ-rays. In the first place, detector dimension can be kept smaller due to the high density of semiconductors. In addition to that, a superior energy resolution can be achieved by using a solid semiconductor detector. There are different semiconductor materials available today, such as silicon and germanium. The fundamental information carriers are electron-hole pairs created in the crystal lattice by primary or secondary charged particles along their path to the detector (Knoll, 2000). The movement of electron-hole pairs through the crystal generates the basic electrical signal from the detector.

Since the intensity of the electric pulse is proportional to the energy of the penetrating particle, semiconductor detectors contribute full energy information. Multi-channel analyzers (MCA) provide the energy resolution and the primary analog signal is transformed into digital units by use of an analog-digital-converter.

Compared with other counting techniques, semiconductor detectors possess advantages, such as excellent energy resolution, good stability, excellent timing characteristics and simplicity of operation (Knoll, 2000).

8.2.1.1 Alpha-Spectrometry

Alpha-spectrometry is an extremely useful and sensitive method for the detection of α-emitting radionuclides in a variety of materials. One of the main reasons for the sensibility of this method is the very low background. High-purity silica surface barrier detectors have become the detectors of choice for the measurement of α-particles. The relatively small size of a silicon detector might be a limitation, especially when a large surface area is required. Modern α-spectrometers are equipped with vacuum chambers to achieve a high-energy resolution of 20-30 keV. The obtained α-spectrum can easily be analyzed by using simple region of interest (ROI) settings. In addition, the energy resolution is generally sufficient to separate the peaks of the most important natural radionuclides present in waters.

Alpha-spectrometry was applied in this study for the detection of ^{238,234}U, ^{226}Ra and ^{210}Po. Unfortunately, extended measurement times (2-3 days) are necessary to achieve low detection limits in the range of several mBq/l. The α-measurements presented in this study have been performed with a modern SARAD α-spectrometer that consists of four independently operating detectors, including four vacuum chambers. This system was particularly developed for low-level α-spectrometry of planar discs with a diameter of 25 mm.

8.2.1.2 Gamma-Spectrometry

High-purity germanium (HPGe) detectors are preferably used for complex γ-ray spectrometry. This is due to the lower melting point of germanium compared with silicon, which makes the exclusion of impurities in the refining process much easier (Knoll, 2000). Additionally, the extremely high density of germanium (5.33 g/cm^3) leads to a higher adsorption probability for γ-rays (Knoll, 2000). Another advantage of gamma-spectrometry is the relatively low self-absorption of γ-rays within the sample, which results in a simple sample preparation. However, the counting efficiency of HPGe detectors is comparably low and the occurring γ-background radiation might be problematic when trying to achieve low detection limits.

These three effects of radiation interactions with matter are fundamental of γ-spectrometry:

- **Photo effect** (detector-atom absorbs the energy of the incident photon entirely)
- **Compton effect** (incident photons are scattered by electrons of the detector)
- **Pair production** (positron-electron pair is created by the incident photon)

The operation of germanium detectors at room temperature conditions is impossible. This is because of the thermally induced leakage current that would occur at room temperature. Hence, germanium detectors must be cooled with liquid nitrogen to reduce the leakage current to the point that the associated noise does not spoil their excellent energy resolution (Knoll, 2000). Usually, the temperature is reduced to –196°C by using an insulated vessel in which liquid nitrogen is kept in thermal connection with the detector. Figure 8 provides an example for the excellent energy resolution of an HPGe detector.

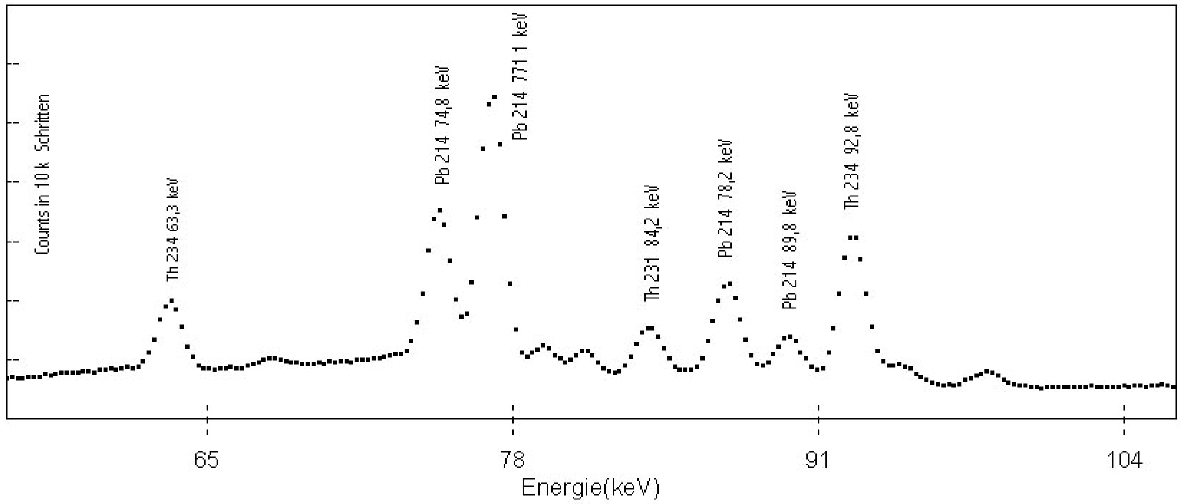


Figure 8: Gamma-Spectrum of a sample containing natural radionuclides

The γ-measurements for this study were performed using a Canberra HPGe (p-type) detector to determine natural radioisotopes in water samples and residues from water treatment, respectively.

8.2.2 Liquid Scintillation Counting

The liquid scintillation method is one of the oldest and most useful method for detection and spectroscopy of ionizing radiations (Knoll, 2000). It is mainly utilized for the detection of low-energetic β-emitting radioisotopes, such as ^{3}H and ^{14}C, but α-emitting radioisotopes can also be detected with high efficiencies. The approach involves dissolving the sample to be counted directly into the liquid scintillator. Problems relating to sample self-adsorption or beta-backscattering from the detector are completely avoided (Knoll, 2000). The scintillation technique is based on the phenomenon of fluorescence and detects photons produced by the scintillator material. These light flashes are caused by exited states of the scintillator molecules after the absorption of energy from radioactive decay. The photons are converted in electrical pulses by a photo multiplier tube (PMT) and can be analyzed by electronical equipment. The liquid scintillation cocktail is composed of a primary and a secondary scintillator - that are able to transform the decay energy to light flashes - and an organic solvent (e.g. toluene) as carrier substance. Thus, the scintillator molecules can be regarded as the actual radiation detector in a liquid scintillation counter.

Modern liquid scintillation counters are able to distinguish between the different types of radiation and even between the different energies of the same type of radiation. The discrimination between α- and β-radiation in water samples is applicable for determining gross-alpha and gross-beta activity concentrations. One major disadvantage of liquid scintillation counters is their relatively poor energy resolution. Furthermore, quench effects may reduce the counting efficiency and background radiation might negatively affect the measurement. On the other hand, the counting efficiency for α- and β–particles can potentially be close to 100% in unquenched samples (Knoll, 2000). Liquid scintillation counting was applied in this study to determine ^{222}Rn, gross-alpha and gross-beta activities of water samples.

The LSC instrumentation used in this study for ^{222}Rn determination was a Canberra Packard TRI CARB 1900 CA. Gross-Alpha and Gross-Beta in water samples were determined with a Triathler Multilabel Tester (Hidex Oy, Finland) via α/β-separation.

8.2.3 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) provides a rapid and sensitive technique for determining long-lived radionuclides and stable isotopes. The principal use of the ICP-MS is that of a mass spectrometer – to detect the mass of elements according to their mass to charge ratio (m/z).

In the case of ICP-MS, the mass spectrometer utilizes inductively coupled plasma as the source of ionization. The plasma is generated by interaction of intense magnetic field along with a tangential flow of gas through the torch. Analytes in liquid form have to be converted into smaller particles and this is achieved by using a *nebulizer* and a *spray chamber*. The nebulizer is responsible for converting liquid samples into aerosol droplets. The aerosol droplets will then be separated by their size using the spray chamber where the smaller droplets would make their way to the plasma and the larger droplets would continue to the exit tube. The method of detection in this case is a very sophisticated one. Provided below is a schematic of a common ICP-MS which owns a quadrupole mass analyser:

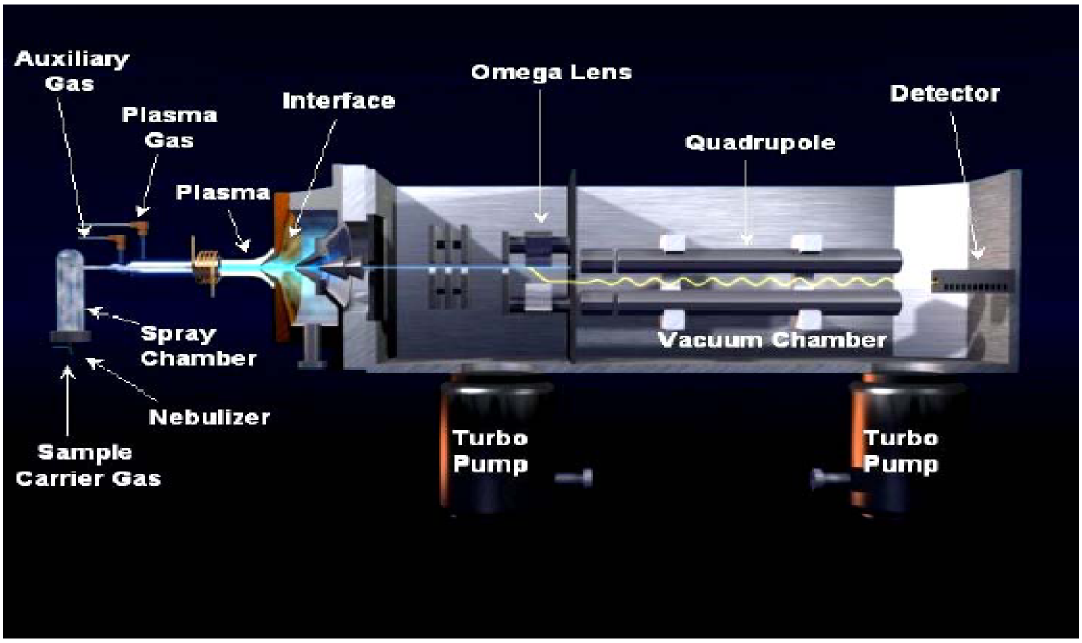


Figure 9: Schematic of an ICP-MS with a quadrupole mass detector

As the analytes enter the plasma, they are stripped off to their ionic form. This is only possible due to the high temperature of the plasma, which goes up to approximately 6,000 – 10,000 K (Ponce de Léon et al., 2002). An important region in the ICP-MS is the ion transport system that consists of the *interface region* and the *ion lens system*. The transport system ensures the delivery of the extracted ions from the plasma to the detector. The operation of this particular system is crucial because it sits between the plasma and the mass spectrometer where pressure difference exists. As a matter a fact, the ions have to be delivered from the *high temperature – atmospheric pressure* plasma to the mass spectrometer, which operates in *high vacuum condition* (10^{-5} *Torr) at room temperature*. While passing through the interface region, the ions get focused with two types of cones, which are the sample cone and the skimmer cone, and they operate at a pressure of about 1-3 torr and 10^{-3} – 10^{-4} torr, respectively. With the existence of the interface region, the ions are able to experience gradual decrease in pressure. Finally, the ions will enter the ion lens system that is situated in the front part of the mass spectrometer. This lens allows extraction of positive ions and focuses the ion beam directly into the mass spectrometer.

There are different types of mass separation devices, which can be used in the mass spectrometer. The most common ICP mass spectrometers are quadrupole-based instruments (ICP-QMS), which allow isotope ratio measurements with a precision for short-term isotope ration measurements from 0.1 % to 0.5 % relative standard deviation (Becker & Dietze, 2000). The quadrupole consists of four parallel conducting rods of which controlled potentials are applied to. This enables only ions of specific masses / charges to go through. The positively charged ions will be attracted to the negatively charged dynode of the detector and the number of ions is displayed as count per second (cps).

However, a quadrupole mass analyzer has its limitation when it comes to resolving power. Due to this reason, development of a high-resolution system based on *double focusing* has taken place. Instead of using a quadrupole mass analyzer, an instrument typical of this system utilizes two analyzers, which consists of an electro-magnet and electrostatic analyzer. The electro-magnet works by creating a magnetic field, which is dispersive with respect to ion energy and mass. These two devices are the ones that allow the double focusing to take place and consequently providing a high-resolution system (Thermo Finnigan, 2001).

Element2 by Thermo Finnigan is an ICP-MS of this very particular system, and was used to analyze water samples, which were taken in Ontario, Canada. An example of a mass spectrum of ^{238}U can be seen as this sample given below:

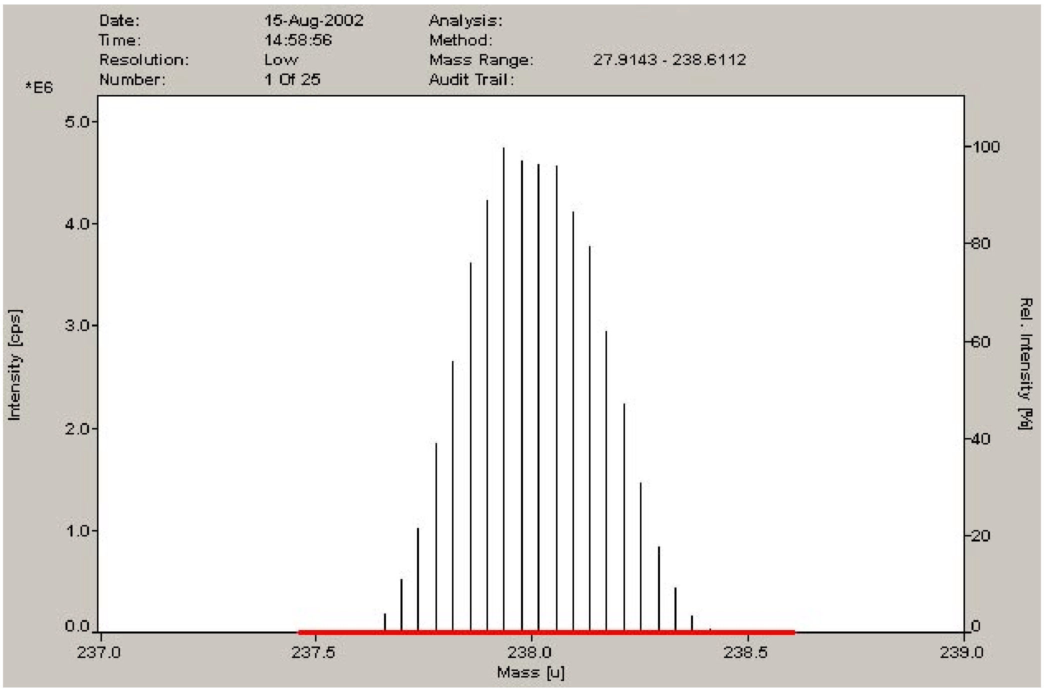


Figure 10: Mass spectrum of ^{238}U from a tap water sample

The known LLD of the used ICP-MS instrumentation for the determination of uranium isotopes is 0.1 ng/l.

The mass concentration of 1,000 ppt (1,0 μg/l) corresponds to an activity concentration of 12.5 mBq/l for ^{238}U and 25.4 mBq/l for natural uranium. Unfortunately, it was not possible to determine the concentrations of ^{234}U in the drinking water samples by ICP-MS. This is due to the half-life of ^{234}U ($T_{1/2} = 2.45 \times 10^5$ a), which is approx. 20,000 times shorter than the half-life of ^{238}U. If both isotopes existed in the same activity-concentration in a water sample, the number of atoms of ^{234}U would be 20,000 times lower than of ^{238}U. Thus, at environmental levels, as measured in this study, the number of atoms of ^{234}U is below detection limit for a high-performance ICP-MS. Obviously, it is possible to optimize the method for lower uranium levels but the decision was made to determine the ^{234}U activity-concentrations of specific samples by alpha-spectrometry.

Major advantages of ICP-MS are the small sample sizes, high sample throughputs, and short measurement times with only few sample preparation steps (Shen et al., 2002). Not only that, ICP-MS offers efficient and sensitive multi-elemental analysis in trace or ultra-trace levels. (Becker & Dietze, 2000). However, the instrument itself is rather costly and it requires high maintenance. High sample matrix concentration may interfere with the determination of low levels of uranium, but solid-phase extraction may overcome these problems (Unsworth et al., 2001).

8.3 Overview of the Measured Radionuclides with Detection Limits

All of the above introduced measurement techniques have been utilized for radionuclide determination in this study. Table 15 provides an overview of the measured radionuclides with respect to the applied measurement techniques and presents the lower limits of detection (LLD) for the respective radionuclides.

Table 15: Measurement techniques applied in this study for the detection of natural radioisotopes

	Half-Life	Mode of Detection	Sample sources	LLD
^{238}U	4.470 x 10^9 a	α-spectroscopy ICP-MS	Uranium-extracting planar discs Untreated water samples	5 mBq/l 1.5 µBq/l
^{234}U	2.455 x 10^5 a	α-spectroscopy	Uranium-extracting planar discs	5 mBq/l
^{228}Ra (via ^{228}Ac)	5.75 a	γ-spectroscopy	Residues from water treatment	1 Bq/kg
^{226}Ra	1600 a	α-spectroscopy γ-spectroscopy	Radium-adsorbing planar discs Residues from water treatment	5 mBq/l 3 Bq/kg
^{222}Rn	3.89 d	Liquid scintillation	Water samples	100 mBq/l
^{210}Po	138.4 d	α-spectroscopy	Polonium-adsorbing planar discs	15 mBq/l
Gross-Alpha **Gross-Beta**	- -	Liquid scintillation Liquid scintillation	Untreated water samples Untreated water samples	0.3 Bq/l 2.0 Bq/l

A fast and reliable method to determine radon in drinking water is the counting of short-lived beta-emitting radon decay products, which are adsorbed onto glass fibre filters (Philipsborn, 1997). This method was utilised for radon measurements using a beta proportional counter LLM 500 by the German manufacturer MAB. The instrument is able to detect radon activities between 1 Bq and 10^4 Bq. It was calibrated regularly using a calibration sample containing long-lived radionuclides. This method was applied regularly for reasons of quality assurance to verify the results of the used liquid scintillation counter (LSC).

8.4 Selectively Adsorbing Discs for the Radiometry of Natural Radionuclides

As mentioned earlier, the main natural radionuclides of interest in European water supply are minimized to be isotopes of uranium and radium. This is in accordance with the current legislation within the European Drinking Water Directive.

Water suppliers will be compelled to determine the concentrations of uranium and radium in their drinking waters. However, the expenses for a classical radiochemical analysis of uranium and radium isotopes are comparably high. The method of co-precipitating radium and uranium with other compounds is especially expensive and troublesome. Consequently, it was a main objective of this study to assess innovative and low-priced methods for the determination of the most important natural radionuclides in potable waters.

Two different selectively extraction methods have been investigated and optimized:

- Adsorption of ^{226}Ra, ^{210}Po onto manganese-impregnated polyamide discs
- Adsorption of ^{238}U, ^{234}U onto polyamide-oxime (PAMOX) discs, covered with a cation exchanger

The following sections provide detailed information about the utilization of selectively adsorbing discs for the radiometry of uranium, radium and polonium in aqueous samples.

8.4.1 Discs for the Extraction of Radium and Polonium from Water Samples

The radiometry of the α-emitting isotope ^{226}Ra is of great interest for various purposes, such as application in geochronology, hydrology and dose assessment in water supply.

Co-precipitation of ^{226}Ra with $BaSO_4$ was the most widely accepted method until extraction and subsequent measurement of the immediate progenitor, ^{222}Rn, was developed. The latter method is still the technique of choice for ^{226}Ra determination in many laboratories. However, it is very time consuming to measure ^{222}Rn in secular equilibrium with its mother isotope ^{226}Ra. This is because it will take approx. 30 days after sampling until the secular equilibrium between ^{226}Ra and ^{222}Rn is achieved. On top of that, the volatile noble gas radon may escape from the sample during the standing time.

In December 1973, Moore & Reid introduced a new method for the extraction of radium from natural waters by the use of manganese-impregnated acrylic fibers. This procedure was chiefly applied for the determination of ^{226}Ra and ^{228}Ra (via ^{228}Ac) in seawater by extracting radium from 20-liter samples. During the past years, this innovative method has been optimized for ground- and drinking water application. Surbeck (1995) published the first appliance of the procedure for simple and rapid measurements of radium in potable waters. Instead of using acrylic fibers, Surbeck preferred polyamide and poly-acrylonitrile for the preparation of MnO_2-coated discs.

Selective radium-adsorption onto thin films and subsequent α-spectrometry has great advantages for the radiometry of ^{226}Ra. The sample disc can be used directly for low-level α-spectrometry without the requirement of further separation and preparation methods (Eikenberg, 2001). Thus, time consuming sample preparation and costly chemical procedures can be renounced. The energy resolution of the obtained α-spectra is still far better than spectra obtained from liquid scintillation counting (Surbeck, 2000).

MnO_2 efficiently adsorbs radium even at high calcium levels. The exposure of a small MnO_2-coated disc with a diameter of 28 mm may extract more than 90% of the radium present in a 100 ml water sample after only 6 hours (Surbeck, 2000). The adsorption efficiency strongly depends on the chemical composition of the water sample. High barium concentrations (> 1 mg per liter) can interfere with the adsorption of radium onto the MnO_2-layer (Surbeck, 2000). The chemical recovery for radium and polonium is influenced by several parameters, such as sorption temperature, pH-value, salt concentration and manganese layer density (Eikenberg et al., 2001).

Detection limits of less than 5 mBq/l for ^{226}Ra and ^{224}Ra can be achieved by measuring times of some days – in dependence of the detector properties. In addition to that, ^{228}Ra may be determined on the same polyamide disc via ingrowth of its progenitor ^{228}Th after a standing time of 6-12 months (Eikenberg et al., 2001). However, the quality of energy resolution becomes worse after a long period of standing time. This is due to the migration of adsorbed isotopes into the inner layers of the MnO_2-coating. Moreover, MnO_2-coated discs can even adsorb ^{210}Po in water samples at high efficiencies. The adsorption yield can be determined by adding tracer solutions (e.g. ^{223}Ra, ^{209}Po) or by the subsequent exposure of several discs in the same water sample.

The basic principle for radionuclide adsorption onto MnO_2-coated thin films is surface complexation. This process is strongly regulated by the pH of the solution. The range of pH may vary from pH 3 – 8, because at lower pH the MnO_2-layer will be destroyed and higher pH may lead to precipitation of carbonates and hydroxides (Eikenberg et al. 2001). The influence of pH can be observed by the adsorption behavior of radium and polonium. Polonium is probably present in water as negatively charged polonate (PoO_3^{2-}) and adsorbs efficiently at low pH values. On the other hand, Ra^{2+} is the predominating radium species present in aqueous solutions below pH 11 and adsorbs efficiently onto negatively charged surface groups (Figure 11).

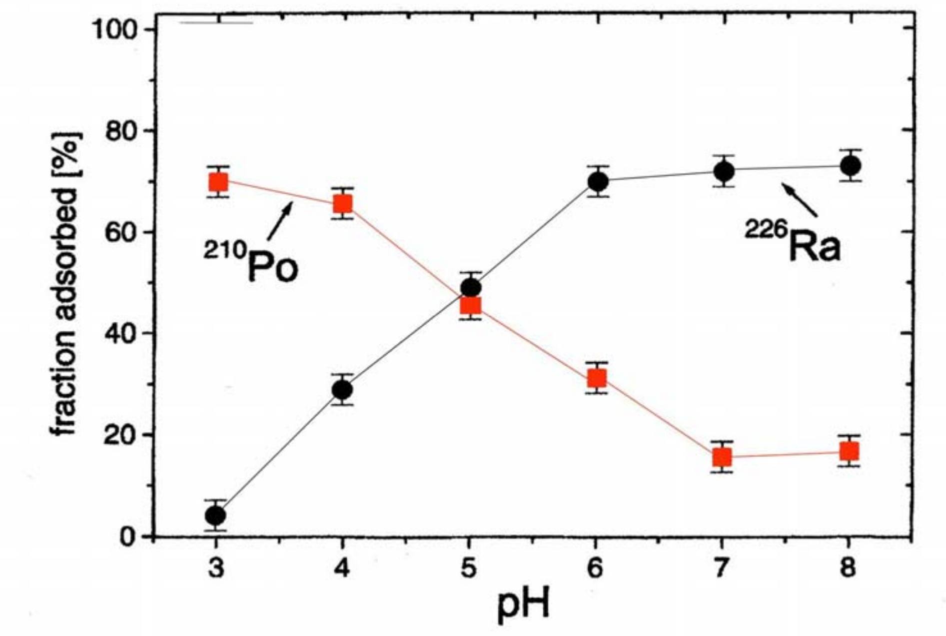


Figure 11: Adsorption efficiencies for ^{226}Ra and ^{210}Po onto MnO_2-coated discs with respect to pH-value. Sorption time: 45 hours at 20°C (modified after Eikenberg, 2001)

The maximum chemical recovery for radium is achieved between pH 7-8. On the contrary, the adsorption yield for polonium decreases rapidly with an increasing pH-value. High salt concentrations (> 1 g/l) negatively affect the adsorption yield for radium. This is due to the presence of competing earth-alkaline elements, such as Ba^{2+}. In such a case, the water sample has to be diluted before the discs can be exposed. The pH value of drinking water (usually pH 6.5 - 7.5) is ideal for an effective usage of manganese-dioxide-coated discs for radium extraction. At low pH, functional H^+-groups predominate on the surface (S) of the MnO_2-layers and make a quantitative adsorption of negatively charged compounds possible. With increasing pH, more functional OH^--groups develop on the surface (S) and positively charged species undergo complexation (Eikenberg et al., 2001).

As a summary, the following simplified surface reactions demonstrate the principle of surface complexation (after Eikenberg et al. 2001):

$$\text{(eq. 20)} \qquad \mathbf{2\ S(H)^+ + PoO_3^{2-} \Leftrightarrow (SO)_2Po + H_2O}$$

$$\text{(eq. 21)} \qquad \mathbf{2\ S(OH)^- + Ra^{2+} \Leftrightarrow (SOH)_2Ra}$$

Meanwhile, MnO_2-coated discs for α-spectrometry are commercially produced by TECOST (Fribourg, Switzerland) and by SARAD (Dresden, Germany). Of course, it is possible to produce the discs for oneself by exposing polyamide in a hot $KMnO_4$ solution. However, the process is cumbersome and the commercially available discs are affordable and of high quality.

8.4.1.1 Application of Radium and Polonium Adsorbing Discs

The discs used for the determination of ^{226}Ra and ^{210}Po for this study were manufactured by SARAD (Dresden, Germany). They consist of MnO_2-coated polyamide and have a diameter of 25 mm. The thickness of a single disc is 0.5 mm and the density of the manganese dioxide layer is 180 µg/cm^{-2}. All radionuclide extractions via SARAD discs have been performed in Teflon beakers to avoid adsorption of radioisotopes onto the container material. A sample volume of 80 ml has been poured into the beakers and the exposure time of the discs was kept constant at 6 hours. To ensure a uniform adsorption of the dissolved radionuclides, the sample was stirred with a magnetic stirring rod covered with Teflon.

To avoid disturbance caused by calcium and barium, all water samples have been treated with addition of Na_2EDTA (max. 100 mg/80ml). This was done to complex calcium and barium compounds, which precludes these elements from adsorption and precipitation onto the discs, respectively. Calcium may particularly precipitate onto the disc after degassing of CO_2 by permanent stirring of the sample. After the exposure, the discs get rinsed with distilled water and dried with an ordinary hair-dryer. Figure 12 illustrates the entire procedure for the application of MnO_2-coated discs for radionuclide determination.

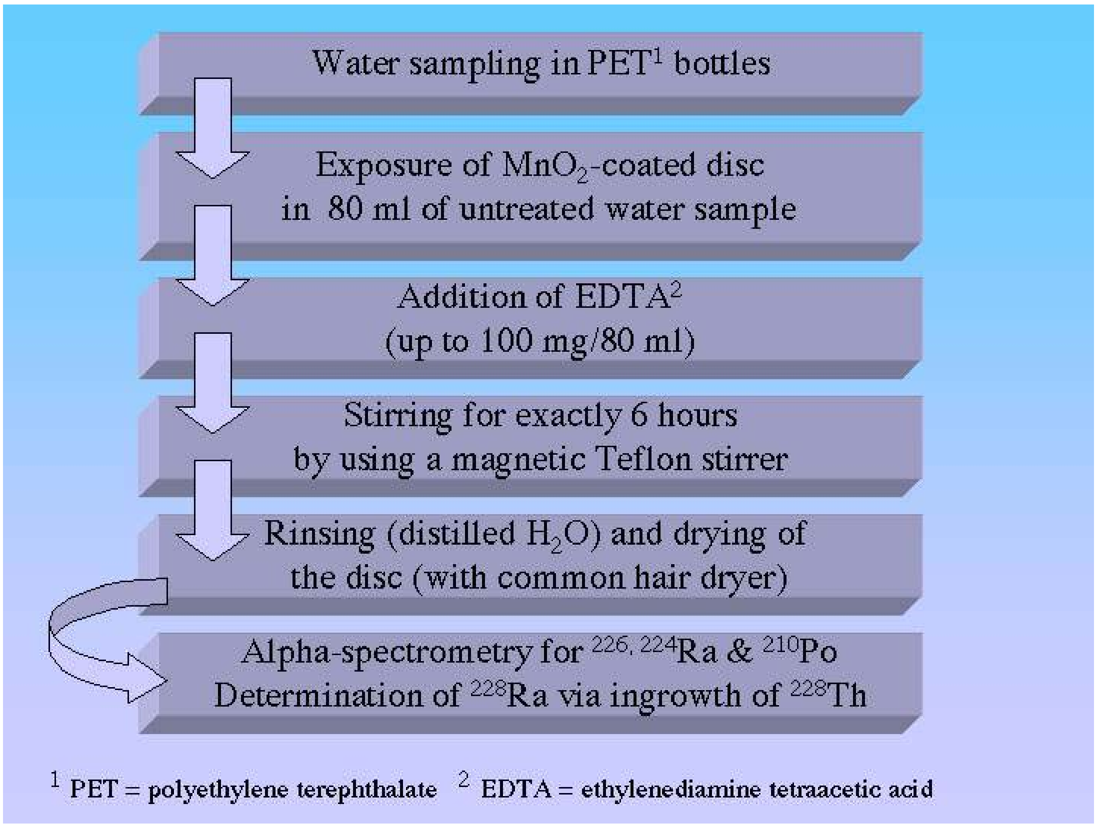


Figure 12: Flow-chart for application of MnO_2-coated discs

It is crucial to expose the SARAD discs at a constant temperature, preferably at room temperature. After the measurement, polyamide discs have been stored in suitable plastic vessels. The stability of the discs seems to be excellent and it is even possible to determine the ^{228}Ra activity concentration after a standing time of 6-12 months.

The exposure of the discs has always been performed as illustrated in Figure 13. It was important to expose the disc in the central part of the water column, so that there was no contact with the magnetic stirrer. The stirring velocity was kept constant at 250 rpm.

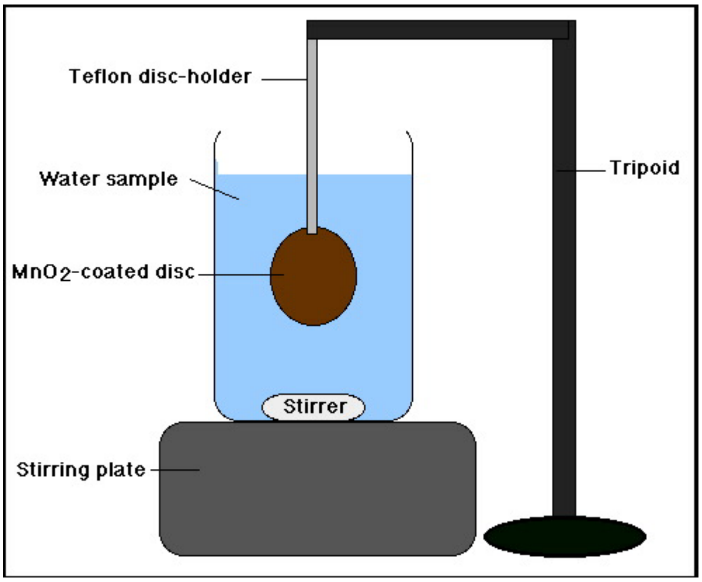


Figure 13: Schematic illustration of the MnO_2-coated disc exposure

The stirring process leads to different adsorption yields on both sides of the coated polyamide discs. Table 16 provides data of eight different discs measured with the same detector to prove the assumption that both sides of a disc adsorb different fractions of the dissolved radium.

In this example, the ratio of front/back side varies from approx. 1.1 to 1.7. It can be concluded that the front-side, which is exposed towards the stirring direction of the water, takes up more radium than the "lee side". As a consequence, it is not possible to measure a single side of a disc and to multiply the number of counts by two as a result for the entire disc. Both sides of the discs have always to be measured separately.

Table 16: Count rates of the two different sides of ^{226}Ra-loaded polyamide discs

Sample	^{226}Ra-counts front side	^{226}Ra-counts back side	Ratio front / back
K1	1102 ± 66	634 ± 50	1.73
K2	693 ± 52	645 ± 51	1.07
K3	317 ± 35	231 ± 30	1.37
K4	78 ± 17	51 ± 14	1.53
K5	130 ± 23	109 ± 21	1.19
K6	832 ± 57	514 ± 45	1.62
K7	95 ± 19	85 ± 18	1.12
K8	2044 ± 90	1520 ± 78	1.34

In the first step, the adsorption yield for radium and polonium was determined by subsequent exposure of two different discs in the same water sample (80 ml). This was performed for 5 samples, which contained exactly the same ground water. It can be assumed that the adsorption capacity of discs from the same production line is uniform. The pH-value of the investigated water was between pH 6-7 and the water temperature was kept at room temperature. The results of the determination of adsorption yields are presented in Table 17. It has to be mentioned that the discs were measured with different α-detectors, which might explain the slight deviations in the net count rates of the respective samples.

Table 17: Determination of adsorption yields for ^{226}Ra and ^{210}Po

	^{226}Ra			**^{210}Po**		
Sample	Net Counts 1st disc	Net Counts 2nd disc	Adsorption yield	Net Counts 1st disc	Net Counts 2nd disc	Adsorption yield
P1	1480 ± 77	116 ± 21	**92%**	90 ± 19	40 ± 12	**56%**
P2	1437 ± 76	167 ± 26	**88%**	111 ± 21	42 ± 13	**62%**
P3	1506 ± 77	138 ± 23	**91%**	99 ± 20	36 ± 12	**63%**
P4	1601 ± 80	183 ± 27	**88%**	78 ± 17	28 ± 10	**64%**
P5	1537 ± 78	159 ± 25	**89%**	93 ± 19	39 ± 12	**58%**

The calculation of the adsorption efficiency was very simple, under the pre-condition that each disc adsorbs the same fraction of the radium that was present in the water sample:

$$\text{(eq. 22)} \qquad Ad_{eff} = 1 - \left(\frac{\text{net counts disc 2}}{\text{net counts disc 1}}\right)$$

The adsorption efficiency of SARAD discs for ^{226}Ra is excellent and amounts to 90 ±2 %. Despite the good reproducibility of this determination, the adsorption yield for ^{226}Ra has regularly been analyzed, especially for ground and drinking waters with unknown chemical composition.

Expensive tracer solutions for the spiking of samples were not used because of the excellent reproducibility of the above mentioned yield determination. However, the chemical recovery was calculated via a second procedure by adding ^{226}Ra-standard solution to a drinking water, which contained only very low levels of ^{226}Ra (<< 1 mBq/l). Five samples of the same “radium-free” drinking water were filled in Teflon beakers and 47 mBq of ^{226}Ra have been added with a high-precision pipette. The pH-value of the final sample had to be neutralized with NaOH and a buffer solution, because the adding of acidified standard decreased the pH from 7.2 to 1.4.

The results of the second yield determination are presented in Table 18. Again, it is obvious that the adsorption yield is outstanding and amounts to 87 ±3 %. It has to be kept in mind that the addition of standard and neutralizing the pH with NaOH and buffer solution are possible sources of systematical errors. For this reason, the almost uniform adsorption efficiencies obtained by this method indicate the reproducibility of the ^{226}Ra determination with SARAD discs.

Table 18: Yield-determination for ^{226}Ra by use of a standard solution (47 mBq)

Sample	^{226}Ra activity on disc (mBq)	Adsorption yield
1	40.8 ± 3	87 %
2	42.2 ± 4	89 %
3	41.7 ± 4	88 %
4	39.4 ± 3	84 %
5	40.9 ± 3	87 %

After the results of the two independent determinations of chemical recovery for ^{226}Ra, it can be assumed that the adsorption yield of SARAD discs for radium is constant at 90 ±5 %. It has to be mentioned again, that this method is only applicable for ground and drinking waters, which possess neutral pH-values and salt concentrations of less than 1g per liter. The application of MnO_2-coated discs for wastewater, saline water or sea water require a special pre-treatment of the sample, such as dilution and addition of EDTA.

Polonium adsorption onto the discs is comparably constant and amounts to 60 ±4 % for low-mineralized ground waters. However, the net count rates presented in Table 17 are low and the 2-sigma-errors range between 19 % and 35 %. This indicates the difficult estimation of the adsorption efficiency. It has also to be mentioned that polonium determination was not always achievable via SARAD discs in this study. This is mainly attributed to variations in the pH value of the different waters, which is a crucial factor for polonium adsorption onto the MnO_2-layers.

8.4.2 Discs for the Extraction of Uranium from Water Samples

Determination of uranium isotopes in water samples is feasible by different methods, such as liquid scintillation and α-spectrometry. Unfortunately, sample preparation for these techniques is difficult and costly. Precipitation or extraction of uranium with classical chemical procedures is especially cumbersome. On the contrary, the measurement of uranium isotopes by the application of adsorbing discs is an affordable and simple alternative.

In principle, the procedure for uranium works in the same way as the above-mentioned method for radium extraction. Uranium can be removed selectively from ground and drinking waters via adsorbing discs, which chiefly consist of a cation exchanger. For instance, diphosphonate and sulfonate groups have shown good results for extracting uranium from water samples (Surbeck, 2000).

Presently, the so-called PAMOX discs are commercially available from TECOST (Fribourg, Switzerland). These discs are mainly composed of a cation exchanger and they are capable to removing actinides from water. The application of the discs for determining uranium isotopes in ground and drinking waters is very simple and a special pre-treatment of the sample is not required. Additionally, the discs are relatively cheap (30-40 ¤ each) and are able to provide a rapid technique for extracting actinides from waters. Since most ground- and drinking waters do not contain high amounts of thorium and artificial actinides, only uranium isotopes adhere quantitatively onto the surface of PAMOX discs.

Positively charged and comparably heavy uranium complexes (UO_2^{2+}) displace the single charged and lighter K^+ and Na^+ of the cation exchanger material. During the exposure of the disc, the pH-value of the water sample increases from neutral to pH 8-8.5. This is a proof for formation of OH^- groups in the water after the release of K^+ and Na^+ from the cation exchanger material.

After the exposure, the disc itself can be measured through α-spectrometry. It is important to measure both sides of the disc, because as previously noted the adsorption onto the disc is not consistent for both sides. Since α-spectrometers possess a very low background radiation, the detection limit for uranium isotopes chiefly depends on the adsorption yield and the measuring time. Detection limits of less than 5 mBq/l for ^{234}U and ^{238}U can be achieved by measuring times of some days – in dependence of the detector properties. In addition to that, even ^{235}U may be determined on the same PAMOX disc. However, the energy resolution may not be sufficient to discriminate the three peaks for natural uranium isotopes present in the α-spectrum. This is due to the closeness of uranium isotope decay energies in the range from 4.2 to 4.8 MeV.

8.4.2.1 Application of Uranium Extracting Discs for this Study

For the first time, uranium-extracting discs have been used for determination of uranium isotopes in water supply. The used actinide-adsorbing discs were produced by TECOST and every disc has a diameter of 25 mm and a thickness of 0.8 mm. The application of PAMOX discs has always been performed as illustrated in Figure 14. Most importantly, Teflon beakers, Teflon disc-holders and Teflon magnetic stirrers have been used to avoid adsorption of uranium from the water onto the material.

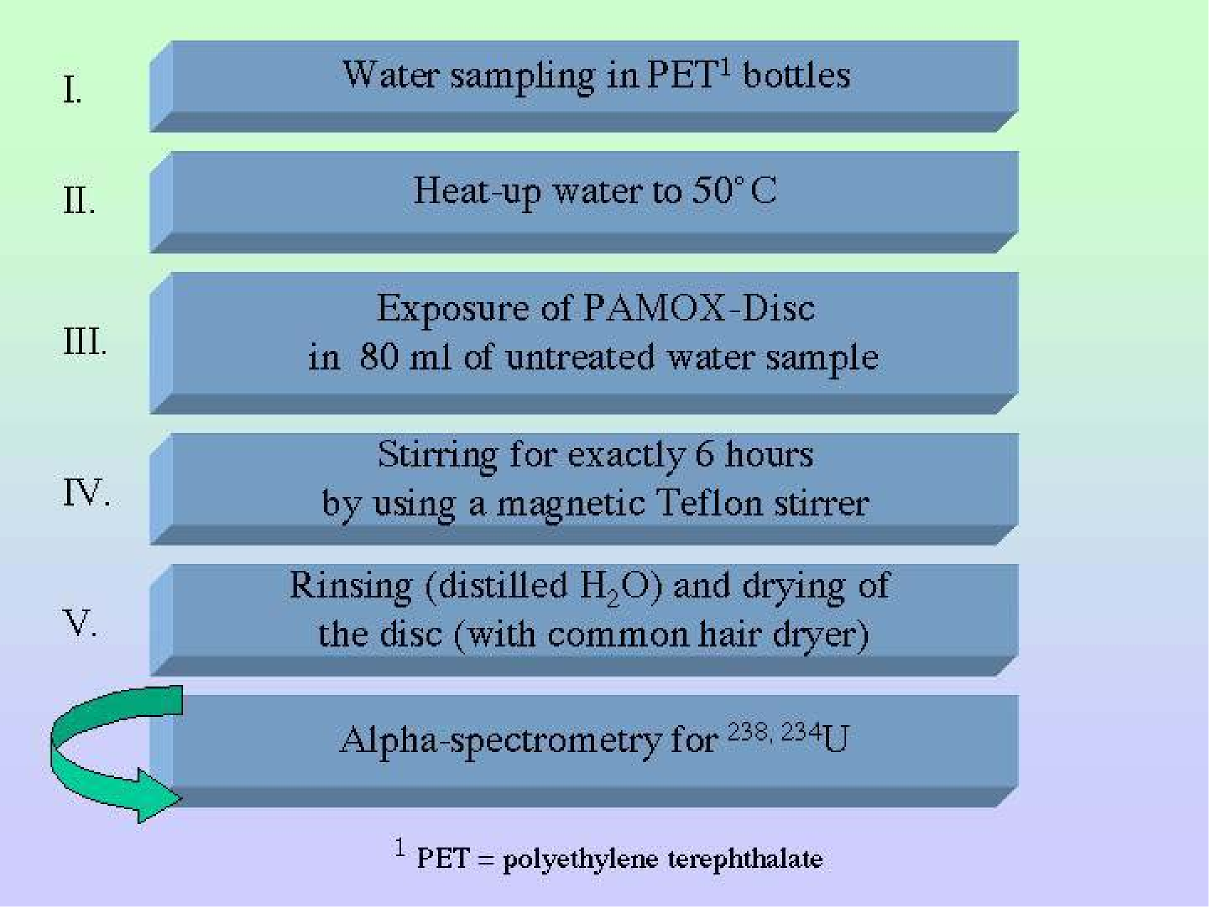


Figure 14: Flow-chart for application of PAMOX discs

A stable water temperature is required for a uniform adsorption of uranium onto the discs. This was achieved by the use of a hot plate and the online-measurement of temperature with a high-quality thermometer. The desired water temperature for this study was 50°C. De-ionized water was regularly poured into the sample container to compensate the loss of water as a result of evaporation.

The chemical recovery of PAMOX was determined by the subsequent exposure of two discs in the same water sample. This was done for 5 equal water samples and ^{234}U & ^{238}U peaks were used for the analysis of the α-spectrum. Before the exposure of the second disc took place, pH was neutralized with formic acid and a buffer solution. Table 19 provides the results of the determination of adsorption yield. It has to be mentioned that the discs have been measured with different α-detectors, which might explain the differences in the net count rate.

Table 19: Determination of uranium uptake of PAMOX-discs in water samples

	^{238}U			^{234}U		
Sample	Net Counts 1st disc	Net Counts 2nd disc	Adsorption yield	Net Counts 1st disc	Net Counts 2nd disc	Adsorption yield
U1	612 ± 49	116 ± 21	**81%**	433 ± 41	70 ± 16	**84%**
U2	732 ± 54	88 ± 19	**88%**	515 ± 45	72 ± 17	**86%**
U3	688 ± 52	83 ± 18	**88%**	513 ± 45	76 ± 17	**85%**
U4	654 ± 51	111 ± 21	**83%**	449 ± 42	69 ± 16	**84%**
U5	760 ± 55	121 ± 22	**84%**	537 ± 46	98 ± 20	**82%**

Again, calculation of the adsorption efficiency was simple, under the pre-condition that each disc adsorbs the same fraction of the uranium that was present in the respective water sample:

$$\text{(eq. 23)} \qquad Ad_{eff} = 1 - \left(\frac{\text{net counts disc 2}}{\text{net counts disc 1}}\right)$$

The chemical recovery of PAMOX discs for uranium is very good and amounts to 84 ±5 %. The differences in the net count rate of ^{238}U and ^{234}U are mainly attributed to the statistical nature of radioactive decay. Despite the good reproducibility of this determination, the adsorption yield for uranium has frequently been determined by using a ^{232}U tracer solution, which was added to the water samples. The chemical behavior of uranium isotopes is similar and it can be assumed that the adsorption yield of ^{232}U is representative for ^{238}U and ^{234}U.

During the performance of this study, it was possible to determine the ^{238}U concentrations of certain water samples from Ontario, Canada, by ICP-MS and by using PAMOX discs. The results indicate the reliability of the uranium extracting discs, because the measured concentrations never deviated more than ± 15 % (Table 20).

Table 20: Comparison of ^{238}U levels from ICP-MS and PAMOX-disc determination

Sample	**^{238}U ICP-MS**	**^{238}U PAMOX-discs**	**Deviation of PAMOX**
C1	4.1 µg/l	3.6 µg/l	- 13 %
C2	2.08 µg/l	2.10 µg/l	+ 1 %
C3	9.2 µg/l	10.2 µg/l	+ 10 %
C4	4.5 µg/l	5.0 µg/l	+ 10 %
C5	3.3 µg/l	2.9 µg/l	-12 %
C6	7.4 µg/l	8.7 µg/l	+15 %

Another confirmation of the reliability and reproducibility of PAMOX-discs was obtained through the participation in an inter-laboratory study organized by the *Bundesamt für Strahlenschutz* (German Radiation Protection Authority). The results for ^{238}U and ^{234}U in the "model water" were exceptionally on target compared with other competing laboratories. However, the determination of ^{235}U was insufficient due to the poor energy resolution. Moreover, uranium determination in a waste water was not possible because of the very high uranium content in this sample of more than 10 Bq/l. The adsorption capacity of PAMOX discs is apparently not sufficient to determine such high concentrations.

The method described above is only applicable for untreated ground- and drinking waters, which contain uranium concentrations of less than 5-10 Bq/l. Experiments with waste waters and saline thermal waters completely failed due to the presence of competing ions or too high uranium concentrations. It is recommended to optimize a special sample preparation for these waters.

9 Balancing Natural Radionuclides in Water Supply

The first-time balancing of natural radionuclides in water supply was a major objective of this study. The reason behind this is that a comprehensive assessment of fate and behavior of natural radionuclides in water supply is only achievable, if the pathways of natural radionuclides are entirely identified. The most practicable way to investigate the major pathways is a detailed balance, which records the input and output of natural radionuclides in waterworks. This includes raw and treated waters and residues from water treatment. By definition, the calculated balance has to include all the important natural radionuclides in water supply at a certain cutoff-date. This approach traces natural radioisotopes from the aquifer to the water tap of the consumer and to the disposal site, respectively (Figure 15).

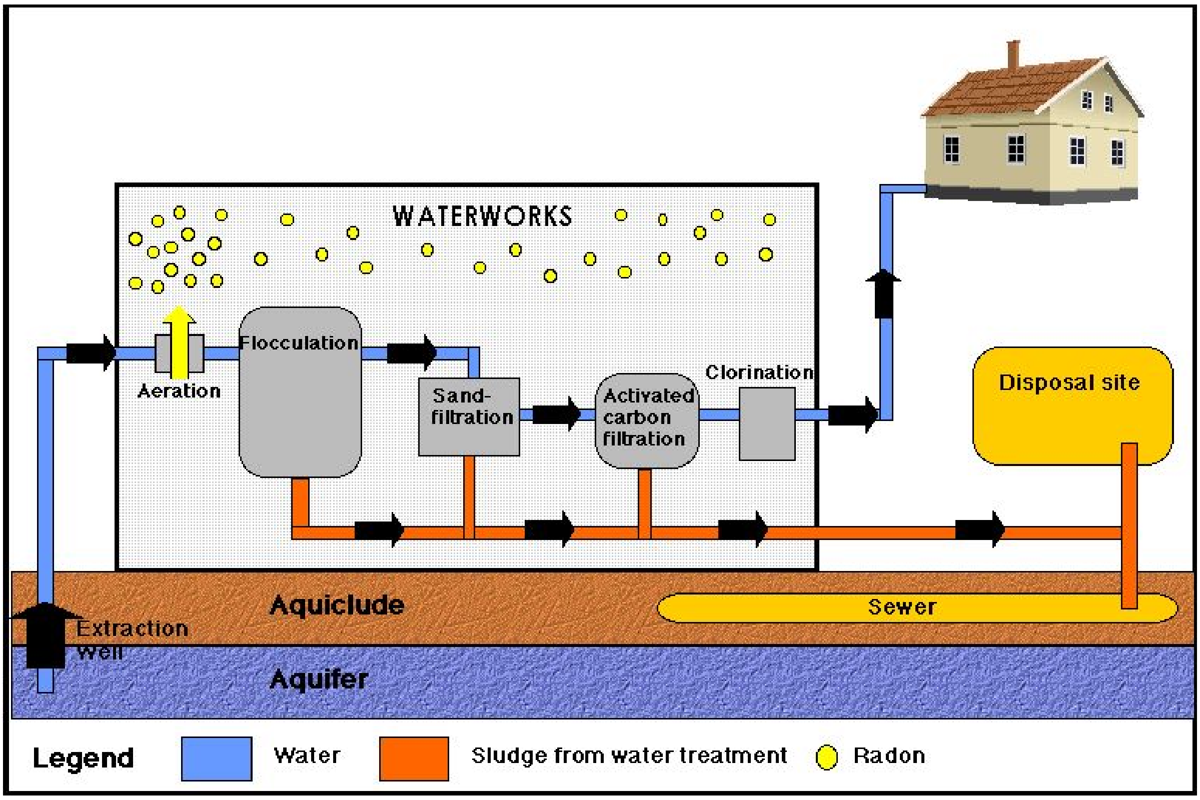


Figure 15: Possible paths of radionuclides in water from the aquifer to the consumer

Determining the quality of a drinking water only after the final treatment in a waterworks is not sufficient, because minor changes in water quality may occur via the delivery to the consumer. Furthermore, it is possible that radionuclides (e.g. ^{228,226}Ra) precipitate onto water pipes during transport from waterworks to the consumers (Wisser, 2002). Enrichment of ^{222}Rn during the transport in water pipes has also been reported (Wisser & Wilken, 2002). In addition to that, the new European Water Directive is a *"Tapwater Directive"*, since the point of water use is the point of compliance with the water quality standards.

As already known from balances in other fields, such as economy, the input and output variables have to be in agreement. This is difficult to achieve for radionuclides, because of the statistical nature of radioactive decay and the possible influence of measurement errors. The application of *stock-flow analysis* supported the initially balancing of natural radionuclides in water supply. This innovative tool will be introduced and discussed in the following section.

9.1 Stock-flow Analysis

Stock-flow analysis is a means in natural sciences for quantifying stock-flow in defined areas with respect to a certain period of time. This progressive instrument was introduced by Baccini & Bader (1996) and is a method for compilation, description and interpretation of processes of stock-flow.

Generally, stock-flow analysis includes four principal steps:

I. *Selection and definition of the system*
II. *Data acquisition and measurement of substances or goods*
III. *Calculation of the stock-flow within the system*
IV. *Interpretation and graphical presentation of the results*

Several goods, processes and at least one substance define the system. The physical laws for mass and energy conservation are applied to the system. The interpretation of results leads to the identification of sources and sinks for the respective substances. This is exactly why stock-flow analysis was adapted and modified for the purpose of balancing natural radionuclides. In fact, this innovative tool was applied for the very first time in this project to assess natural radionuclides in water supply. The defined system for this study is the **entire pathway of water supply**, i.e. from the aquifer to the consumer. Table 21 provides a brief overview of the key input and output goods with regards to water treatment.

Table 21: System analysis for the process of water treatment

Input goods	***Process***	***Output goods***
Raw water *Chemicals* *Energy sources* *Air*	**Water treatment**	*Drinking water* *Solid wastes* *Liquid sludge* *Exhaust air*

After the system analysis is carried out, the determination of natural radionuclides within the defined system (water supply) can then take place. It has to be acknowledged that the calculation of stock-flow is only feasible for a single cutoff-date. Otherwise, the changes in water quality and properties of the abstraction wells (e.g. pumping time, amount of extracted water) may lead to miscalculations.

In this study, sampling from different locations within the defined system was crucial and had to be performed carefully. In addition to that, multiple samples have been taken from each location to ensure a qualitative and representative sampling and measuring. If the determination of a single radioisotope for a single sampling location failed, the entire process of sampling and measuring has to be repeated. This is why only a few natural radioisotopes have been balanced in the system of water supply. Nevertheless, it is sufficient to detect a few substances to recognize the main pathways within the system. A detailed stock-flow analysis is only possible, if the substances of interest (e.g. radionuclides) can be identified throughout the entire system. If the levels of radionuclides in raw waters were below the detection limit, balancing calculation of the isotopes cannot be performed.

The following natural radionuclides have been included in the calculation of stock-flow:

- **^{238}U and ^{234}U**
- **^{226}Ra and ^{222}Rn**

^{210}Po was not integrated explicitly in stock-flow because the determination of this particular radionuclide with radionuclide-adsorbing discs has not been fully optimized to achieve the low 2-sigma-errors as necessary for the calculation of stock-flow. The interpretation and graphical illustration of stock-flow in water supply will be provided in the following sections were the investigated waterworks are described in detail.

9.2 Selection of Waterworks for this Study

Two waterworks from Germany and one water treatment facility from Ontario, Canada have been investigated. It was necessary to compare waters from several locations due to the diverse geology and different background radiation. First of all, three new categories for natural radioactivity in ground waters are suggested in this thesis, based on the geological and hydrological settings of the respective areas. This was done to possess a simple tool to classify natural aquifer waters **with regards to the new limitation values** for drinking water. The screening parameters for the categories are gross-alpha and gross-beta activity, **excluding radon and short-lived radon daughter isotopes.**

The categories being suggested are:

- ***L**ow **R**adioactive **A**quifer **W**aters (LRAW)*
  gross-alpha activity < 0.1 Bq/l and gross-beta < 1.0 Bq/l
  → Exceeding of limitation values very unlikely

- ***M**edium **R**adioactive **A**quifer **W**aters (MRAW)*
  gross-alpha activity 0.1 - 1.0 Bq/l or gross-beta 1.0 - 10.0 Bq/l
  → Exceeding of limitation values possible, if suitable water treatment is not performed

- ***H**igh **R**adioactive **A**quifer **W**aters (HRAW)*
  gross-alpha activity > 1.0 Bq/l or gross-beta > 10.0 Bq/l
  → Exceeding of limitation values is very likely, if suitable water treatment is not conducted

The classification for a certain location can be achieved by comparing available concentrations of radionuclides in ground waters from the respective area. Furthermore, expectation values can be derived from geological information, such as cross-sections and geological maps. This classification is obviously a fairly simple one and can only be applied for a rough categorizing.

This study focuses on waterworks, which abstract medium and high radioactive aquifer waters. Nevertheless, one water treatment facility from a low background radiation area was investigated to complete the picture. The desirable waterworks for this study could be found within the different geological settings, which occur in Germany and Ontario, Canada:

- **1 waterworks** abstracting high radioactive aquifer water (Rhine-Nahe-Area, Germany)
- **1 waterworks** taking water from a medium radioactive aquifer (Central Ontario, Canada)
- **1 waterworks** abstracting low radioactive aquifer water (Northern Black Forest, Germany)

The main focus of the study lies on the water treatment facility from the Rhine-Nahe-Area because of the amount of radionuclides present in the raw waters there and the opportunity of obtaining several sampling replicates during the past years. In addition to that, sampling of residues from this waterworks was accessible as well.

The procedure of investigation was identical for each examined water treatment facility and can be summarized as follow:

- *Water sampling and measuring of radon in indoor air*
- *Measurement of radon, gross-alpha and gross-beta activity in waters*
- *Exposure of radionuclide adsorbing discs*
- *Measurement of planar discs for uranium, radium and polonium*
- *Investigation of residues from water treatment*
- *Calculation of results, including balancing*
- *Dose assessment for the population*

The investigation of waterworks took place during several sampling campaigns from January 2001 to December 2002. In agreement with the water supply companies, all obtained results will be treated as confidential. The actual positions of the examined water treatment facilities will not be presented in this thesis. As a consequence, only the geological setting and the geographical region of the waterworks will be mentioned briefly.

All the obtained results will be provided with confidence limits. The measurement errors were calculated from the total net count rate and are provided as 2–sigma values. The systematical errors were not taken into account because it can be assumed that the systematical error is constant, as long as sampling and sample preparation are always executed in the same way.

The levels of measurement errors are crucial for the calculation of stock-flow. As a consequence, the results for radionuclide determination have always been verified with statistical tests.

9.3 Waterworks A, Rhine-Nahe-Area, Germany

This public water treatment facility (WW A) is situated in the Saar-Nahe-Basin in the western part of Germany and had been selected due to its position within a large complex of uranium-bearing rhyolite. These rocks originated during the Permian and cover an area of about 25 km^2. The average uranium-content of the rhyolite amounts to approx. 220 ppm and uranium mining took place in the area from 1961 – 1970.

Tectonic deformation of the rocks during the past 270 million years lead to an intensive formation of cracks and joints within the bedrock. The magmatic rocks are embedded in sediments from the Rotliegendes period. These sedimentary rocks are mainly composed of consolidated sandstone of red and gray colors. Due to the consolidation of the sandstone, ground waters circulate in joint aquifers within the sediments. A study about radon in aquifer waters from the Rhine-Nahe-Area revealed ^{222}Rn levels from 100 – 460 Bq/l (Haberer & Raff, 1998). Since radon can be regarded as an indicator for the natural decay series, the Rhine-Nahe-Area is highly suitable for investigating natural radionuclides in aquifer waters.

In addition to the previously discovered radon levels and the local geology, WW A was also an appropriate case for balancing natural radionuclides due to the different water treatment steps applied there. Furthermore, residues from water treatment were accessible and could be included in the investigations.

9.3.1 Description of the Waterworks

WW A was put into service in 1989 and abstracts ground waters from three different aquifers. Extraction Wells I and II have a depth of 40 and 50 meters, respectively. They are drilled into rhyolite, tapping joint aquifers within the bedrock. On the contrary, Well III is drilled into sedimentary rock (Rotliegendes) and has a depth of approx. 27 m.

This facility supplies drinking water for three villages in the Rhine-Nahe-Area occupied by approx. 4,000 inhabitants. In 2002, the total amount of produced drinking water was about 196,000 m^3.

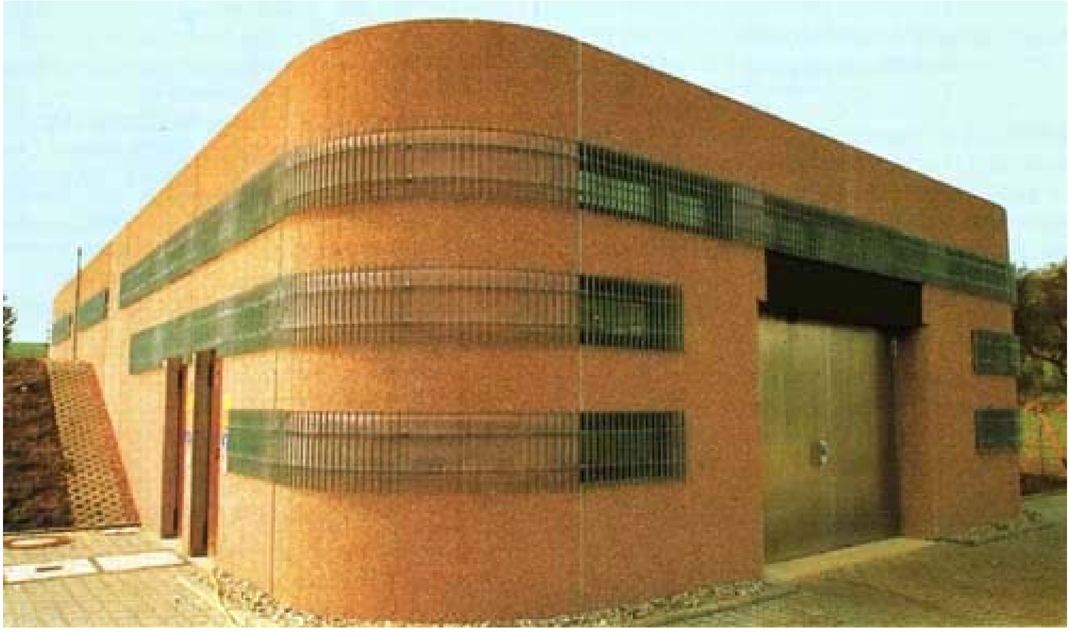


Figure 16: Picture of WW A at the Rhine-Nahe-Area

Water treatment:

After the abstraction of raw waters from the deep wells I & II, dissolved CO_2 is stripped out of the water via aeration by the use of Venturi aeration devices. Simultaneously, the raw water is enriched with oxygen.

In the next purification step, two filters are used to remove iron and manganese from the water. Filter 1 was installed for removing iron and is composed of different layers of quartz-sand (5 m^3) and activated carbon (3 m^3), while the manganese filter (Filter 2) only contains quartz-sand (9 m^3). The maximum water-throughput for both filter-systems amounts to 50 m^3/h. The pressure within the filters is only attributed to the hydrostatic pressure, which is caused by the altitude difference (4 m) from the entrance and exit of the filters.

The following phase consists of a simple mixing of the treated waters from Well I + II with the raw water from Well III. This is done because the water from Well III is of high quality and does not require any treatment. Finally, the mixed water is pumped into pure-water tanks. Before the pure-water leaves the facility, it is treated with ClO_2 for disinfecting purposes (Figure 17). The sludge from filter backwashing is collected in a large slurry tank located next to the waterworks.

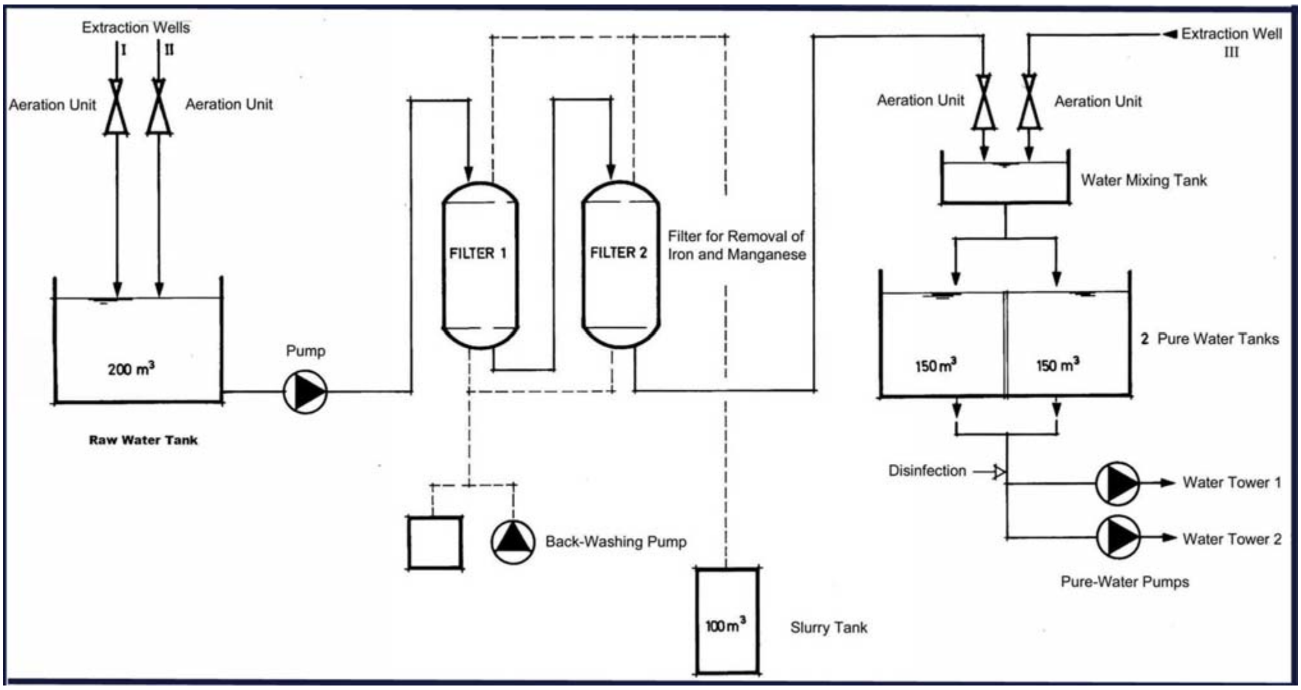


Figure 17: Scheme of WW A in the Rhine-Nahe Area, Germany

The waterworks building primary consists of a large filter hall and a small chamber, where the water tanks are situated. Previous investigations revealed extremely high radon concentration in the indoor air of the aeration chamber. The average concentration of ^{222}Rn in the room was higher than 60 kBq/m^3. This is mainly attributed to the degassing of ^{222}Rn from the raw water during aeration. Assuming 100 annual working hours in this chamber, the radiation exposure of the staff would amount to almost 1.0 mSv per year (F=0.4). However, the indoor ^{222}Rn concentration in the room can be decreased efficiently by using a ventilation system. During the operation of the installed fan, radon levels decline to about 1 kBq/m^3 (Raff, 1999).

9.3.2 Determination of Natural Radionuclides

In accordance to the different treatment steps in WW A, the following waters have been subsequently sampled and analyzed for natural radioisotopes:

I. Raw waters from Well I, Well II & Well III
II. Mixed water from Well I and II (after aeration)
III. Exit Filter 1
IV. Exit Filter 2
V. Pure water (treated water, including water from Well III)
VI. Tap water from a private household

Several sample replicates have been taken from each sample location. The results provided in the following section will generally represent the mean value of the multiple measurements.

9.3.2.1 Gross-Alpha and Gross-Beta Activity

Gross-alpha and gross-beta activity are the parameters of choice when it comes to screening for natural radioactivity in water. The determination of these parameters was achieved with a *Triathler Multilabel Tester* via α-/β-separation. Table 22 provides the results of the measurements in WW A, which were performed only a few hours after sampling. It has to be mentioned, that the results include the activity concentrations of ^{222}Rn and its short-lived decay products. The samples were measured for 1,800 sec, leading to a LLD of < 2.0 Bq/l for gross-alpha and < 10.0 Bq/l for gross-beta activity.

Table 22: Gross-Alpha and Gross-Beta activity concentrations in waters from WW A

Sample	*07 May 2001 Gross-Alpha (Bq/l)*	*07 May 2001 Gross-Beta (Bq/l)*		*06. March 2002 Gross-Alpha (Bq/l)*	*06. March 2002 Gross-Beta (Bq/l)*
Well I	686 ± 7.5	446 ± 9.0		621 ± 28	416 ± 12
Well II	660 ± 7.5	426 ± 8.5		551 ± 14	360 ± 12
Well III	260 ± 4.5	170 ± 6.0		220 ± 9.0	147 ± 7.5
Mixed water (I + II)	153 ± 3.5	110 ± 5.0		97 ± 6.0	62 ± 4.5
Exit Filter 1	175 ± 3.8	113 ± 5.0		118 ± 6.5	79 ± 5.5
Exit Filter 2	148 ± 3.5	94 ± 4.5		110 ± 6.0	72 ± 5.0
Pure water	89 ± 2.7	63 ± 4.0		71 ± 5.0	50 ± 4.0
Consumer	45 ± 2.0	28 ± 3.0		28 + 3.0	18 ± 2.5

Radon and radon decay products are the main cause to the extremely high activities for gross-alpha and gross-beta. The same samples were analyzed once more after a standing time of 3 months, assuming that radon and its short-lived daughter isotopes decayed entirely during the storage. This time, each sample was measured for 72,000 sec, to improve the lower limit of detection (Table 23).

Table 23: Gross-Alpha and Gross-Beta activity concentrations after a sample standing time of 3 months

Sample	*07 May 2001 Gross-Alpha (Bq/l)*	*07 May 2001 Gross-Beta (Bq/l)*		*06. March 2002 Gross-Alpha (Bq/l)*	*06. March 2002 Gross-Beta (Bq/l)*
Well I	2.0 ± 0.30	< 2.0		1.8 ± 0.30	< 2.0
Well II	0.9 ± 0.20	< 2.0		0.8 ± 0.20	< 2.0
Well III	0.3 ± 0.10	< 3.0		0.3 ± 0.10	< 2.0
Mixed water (I + II)	0.9 ± 0.20	< 2.0		0.8 ± 0.20	< 2.0
Exit Filter 1	1.0 ± 0.20	< 2.0		0.8 ± 0.20	< 2.0
Exit Filter 2	0.7 ± 0.20	< 2.0		0.7 ± 0.20	< 2.0
Pure water	0.6 ± 0.15	< 2.0		0.6 ± 0.15	< 2.0
Consumer	0.3 ± 0.10	< 2.0		0.6 ± 0.15	< 2.0

The results of the 2nd measurement clearly testify the dominance of ^{222}Rn and its decay products in the first samples. After ^{222}Rn completely depletes from the waters by radioactive decay, the gross-alpha and gross-beta activities decline to only a few Bq/l in the raw waters and to very low levels in the treated waters. The gross-beta activities of all investigated waters were below the LLD. During the storage of 3 months, ^{222}Rn decay has undergone at least 20 half-lives, leading to a remaining activity of only 0.0001 % of the initial activity concentration. Another method to remove radon from a water sample is to aerate the sample with radon-free air, such as nitrogen.

It has to be acknowledged that the LLD's for gross-alpha and gross-beta in this study were higher than required by the legislator. The reason for this is the inadequate shielding of the used *Triathler Multilabel Tester*. However, the LLD for a *Triathler* can be reduced by optimizing the electronic equipment and by using an additional lead shielding. Furthermore, a particular sample preparation can also be applied to achieve lower LLD's for gross-alpha and gross-beta determination. This special sample treatment can be performed by evaporating the water sample with a freeze dryer and by subsequent dissolving of the residue in 0.5N HCl to which scintillation cocktail is added (Salonen & Hukkanen, 1997).

The comparison of radon-containing and radon-free samples elucidates the importance of applying screening methods after radon is decayed or removed from the water. Otherwise, many drinking water samples will exceed the limitation values for gross-alpha and gross-beta. In accordance to the categories suggested for aquifer waters, the water from Well I is classified to be of *high radioactive* (2.0 Bq/l gross-alpha) and Well II abstracts *medium radioactive aquifer water* (0.9 Bq/l). On the contrary, the ground water from Well III can be considered as *low radioactive aquifer water*, since the gross-alpha activity is only 0.3 Bq/l.

9.3.2.2 Radon in Water

The samples were measured for 1,800 sec, leading to a detection limit of < 1.0 Bq/l. Table 24 indicates the radon activity concentration of the samples taken from WW A with respect to different sampling dates.

Table 24: ^{222}Rn levels in WW A with regards to different sampling dates

Sample	*07 May 2001* *^{222}Rn (Bq/l)*	*14 May 2001* *^{222}Rn (Bq/l)*		*06. March 2002* *^{222}Rn (Bq/l)*	*25 March 2002* *^{222}Rn (Bq/l)*
Well I	228 ± 8.0	238 ± 8.0		205 ± 7.2	209 ± 7.2
Well II	218 ± 7.0	225 ± 7.5		186 ± 6.8	183 ± 6.7
Well III	85 ± 4.5	86 ± 4.5		73 ± 4.2	63 ± 4.0
Mixed water (I + II)	49 ± 3.5	56 ± 4.0		33 ± 2.8	36 ± 3.0
Exit Filter 1	60 ± 4.0	61 ± 4.0		39 ± 3.0	43 ± 3.2
Exit Filter 2	50 ± 3.5	55 ± 3.5		37 ± 3.0	35 ± 3.0
Pure water	29 ± 3.0	36 ± 3.0		24 ± 2.5	24 ± 2.5
Consumer	15 ± 2.0	18 ± 2.0		9.0 + 1.5	17 ± 2.0

Within a period of a few weeks, the determined ^{222}Rn levels were relatively constant, as indicated in Figure 18. However, the ^{222}Rn concentrations of the respective sampling locations vary notably from May 2001 to March 2002. This provides the reason why the balance for natural radionuclides has to be calculated for a single cutoff-date.

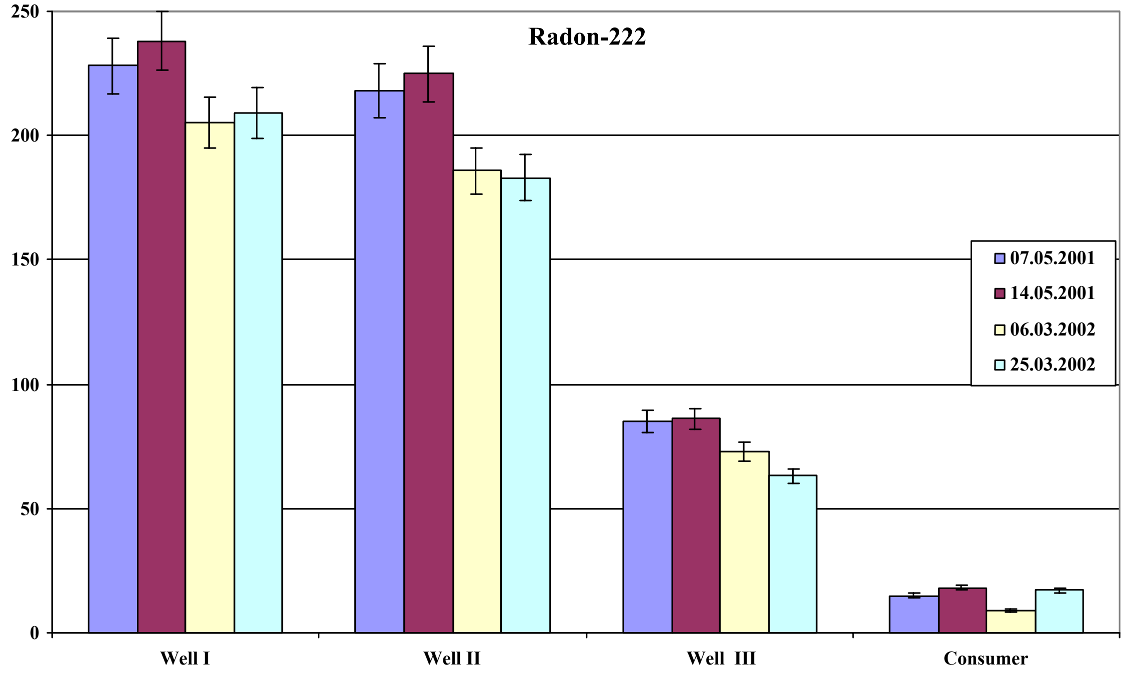


Figure 18: Radon-222 in the different waters from WW A

There is a tendency that the radon concentration increases after the water is treated in Filter 1. The effect becomes more obvious when the radon-levels are illustrated as provided in Figure 19.

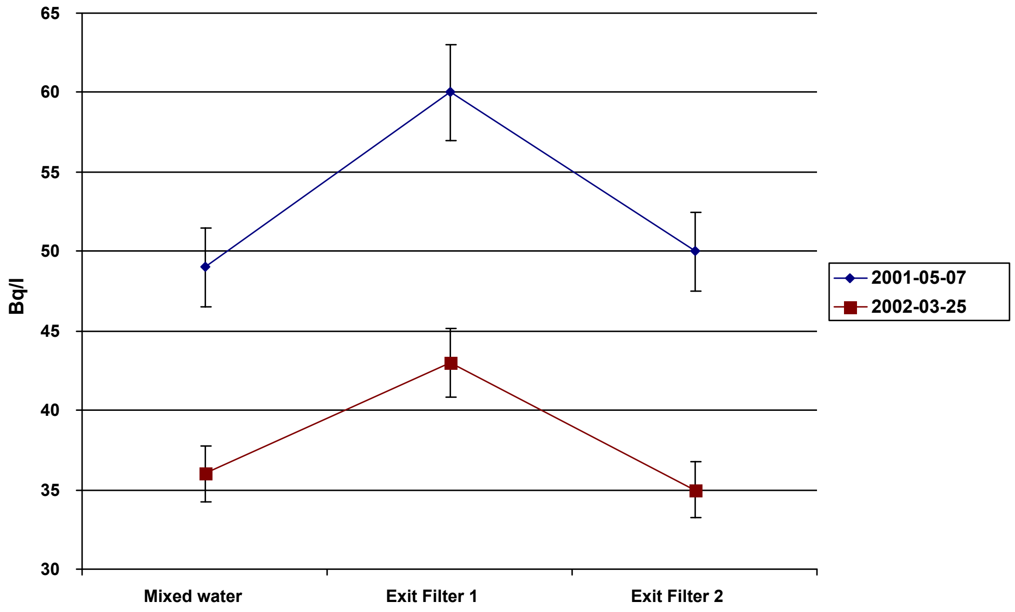


Figure 19: Increase of ^{222}Rn after treatment in Filter 1

Waterworks A was frequently monitored with respect to ^{222}Rn and the mentioned radon-increase at the exit of Filter 1 was detected regularly. A possible explanation for this phenomenon is the buildup of ^{222}Rn by radioactive decay of its progenitor ^{226}Ra, which is deposited in the filter material by removal of radium from raw water.

9.3.2.3 Uranium Isotopes in Water

The determination of the uranium isotopes ^{238}U and ^{234}U was crucial for this study, because uranium is a major element of health concern in water supply. The given results were obtained by measuring uranium using adsorbing PAMOX discs. For reasons of quality assurance, a ^{232}U tracer solution was added to determine the adsorption yield. The measuring time for the planar discs was at least 160.000 sec, leading to a LLD of 10 mBq/l. The results for uranium in WW A are presented in Table 25.

Table 25: ^{238}U & ^{234}U levels in WW A at different sampling dates

Sample	*06. March 02* *^{238}U (mBq/l)*	*06. March 02* *^{234}U (mBq/l)*	**Ratio** **^{234}U/^{238}U**		*25. March 02* *^{238}U (mBq/l)*	*25 March 02* *^{234}U (mBq/l))*	**Ratio** **^{234}U/^{238}U**
Well I	861 ± 73	1033 ± 80	1.20		738 ± 57	927 ± 64	1.25
Well II	329 ± 48	467 ± 57	1.42		300 ± 39	415 ± 46	1.38
Well III	124 ± 28	114 ± 27	0.91		84 ± 15	84 ± 15	1.00
Mixed water (Well I + II)	404 ± 53	547 ± 62	1.35		304 ± 38	417 ± 46	1.33
Exit Filter 1	367 ± 30	473 ± 32	1.38		309 ± 40	426 ± 47	1.37
Exit Filter 2	344 ± 28	460 ± 33	1.25		278 ± 29	382 ± 34	1.37
Pure water	290 ± 38	372 ± 44	1.28		236 ± 27	286 ± 30	1.21
Consumer	314 ± 33	390 ± 48	1.24		94 ± 12	132 ± 15	1.40

The uranium content of the raw waters only slightly changes over the period of 3 weeks. The isotope-ratios for ^{234}U/^{238}U are constant under the consideration of the confidence limits and vary from 0.91 to 1.42. Since the ground waters contain free oxygen and a sufficient amount of carbonate-ions, uranyl carbonate is probably the dominating uranium species in these waters.

Variations of the uranium content of the mixed water are due to different mixing ratios in the waterworks. The portion of raw water from Well I was evidently higher on 06th March than on 25th March 2002. Surprisingly, the two filters do not remove uranium quantitatively, despite the fact that the first filter has a layer of activated granulated carbon. This result is in contradiction to the published removal yields of GAC for uranium, which reached up to 95 %. A possible explanation for this effect will be discussed in section 9.3.3.2, page 91. The uranium levels of tap water are low in comparison to the raw waters from Well I and II.

9.3.2.4 ^{226}Ra in Waters from WW A

Only the radium isotope ^{226}Ra was analyzed in waters from WW A, because the determination of ^{228}Ra is relatively complicated and time-consuming. Since both isotopes have similar chemical properties, it was sufficient to only determine ^{226}Ra for finding out the main pathways of the radium element. The measurements were performed via the use of radium adsorbing MnO_2-discs. The measuring time was at least 200.000 sec per sample, which leads to a LLD of 5 mBq/l. The results for ^{226}Ra determination are compiled in Table 26.

Table 26: ^{226}Ra levels in WW A at different sampling dates

Sample	*16. October 01* *^{226}Ra(mBq/l)*	*06. March 02* *^{226}Ra (mBq/l)*	*25. March 02* *^{226}Ra(mBq/l)*
Well I	66 ± 8	58 ± 6	47 ± 5
Well II	217 ± 25	85 ± 9	94 ± 10
Well III	53 ± 6	18 ± 2	16 ± 2
Mixed water (Well I + II)	126 ± 15	79 ± 9	55 ± 6
Exit Filter 1	-	45 ± 5	50 ± 5
Exit Filter 2	-	60 ± 7	74 ± 8
Pure water	-	48 ± 5	60 ± 7
Consumer	-	38 ± 4	46 ± 5

The ^{226}Ra levels detected in WW A range from 16±2 to 217±25 mBq/l and are comparably low. During the period of sampling in March 2002, the ^{226}Ra activity concentrations remained quite constant in the three raw waters wells. However, there is a clear difference in the ^{226}Ra content of the ground waters between October 2001 and March 2002. In October 2001, the levels of ^{226}Ra in the respective waters are remarkably higher than in March 2002. This indicates the fluctuation of natural radioactivity in aquifer dependent on the season of the year. Unfortunately, the determination of radium at the other sampling locations was not performed in October 2001.

The results also indicated an increase of ^{226}Ra after the water has been treated at Filter 2. This effect is probably attributed to re-mobilization of adsorbed radium from the surface of the filter material. It has to be kept in mind that the filters are operated under pressure conditions. In fact, the ^{226}Ra concentration in the tap water is lower than expected. On the other hand, the hydrochemistry of the raw waters rather favors the mobilization of uranium than radium. As discussed in section 3.1.2.1, page 17, uranium is especially mobile under aerobic conditions and radium is preferably transported in an anoxic environment.

9.3.2.5 Natural Radioactivity in Indoor Air

A sophisticated balance for radionuclides has to consider the deficiency of ^{222}Rn due to degassing during water aeration. Hence, it was necessary to measure the indoor radon concentration in the aeration room at the cutoff-date. This was achieved by use of a pulse ionization chamber, which was placed in the room where the water aeration takes place. For the duration of the measurements, the room was locked and the installed fan was out of operation. The course of the indoor radon concentration over the period of seven days is presented in Figure 20.

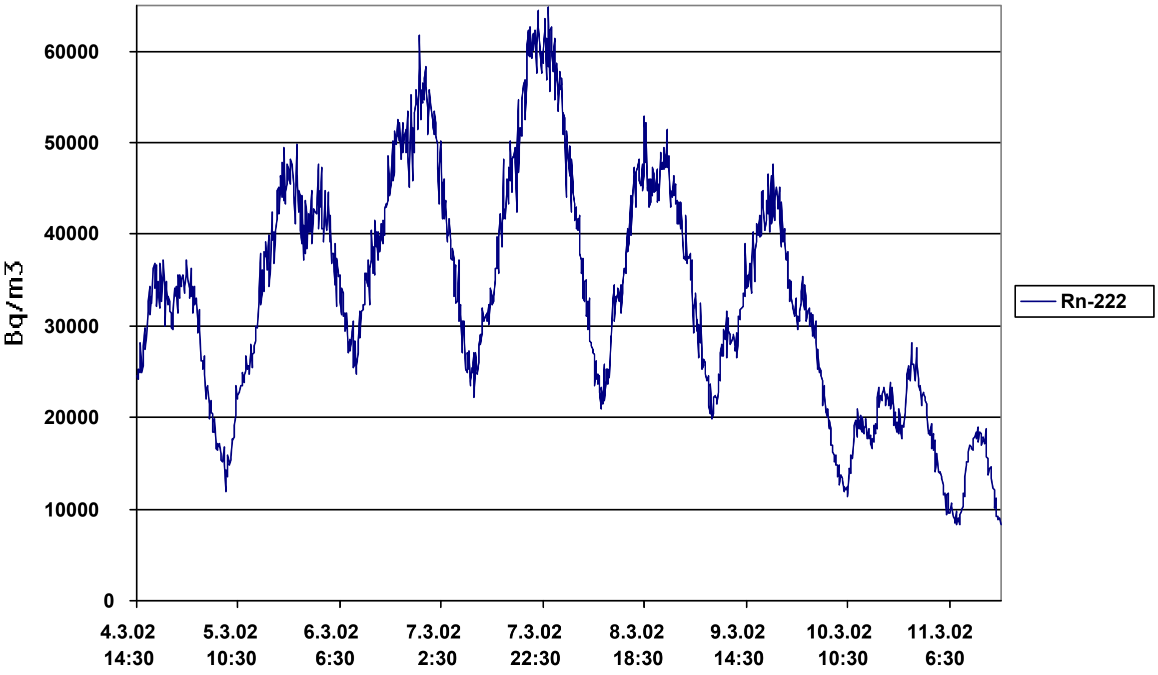


Figure 20: ^{222}Rn in indoor air of the water aeration chamber in WW A

The results of ^{222}Rn determination in the aeration chamber are remarkably high and amount to 33 kBq/m^3 in average. The maximum value for radon in indoor air is close to 65 kBq/m^3. As mentioned earlier, a ventilation system is usually in operation to reduce the ^{222}Rn content due to radiation protection grounds. It is obvious that the radon concentration (refer to Figure 20) fluctuates extremely within the 7 days of measuring. This is mainly attributed to the operation times of the abstraction wells. If raw water is pumped into the chamber, aeration takes places and waterborne radon degasses very quickly. This would always lead to an increase of radon in indoor air. On the contrary, the radon concentration decreases rapidly when the wells are out of order. The reason behind is that "radon-free" air enters the chamber from adjacent rooms because the sealing of the chamber is inadequate. Furthermore, there is breeze of fresh air from outside into the building, in dependence of the air pressure conditions. Radioactive decay of ^{222}Rn is not a major contributor to the decrease since the half-life of ^{222}Rn is much larger than the observed decrease of activity concentration. It is apparent that the radon concentration especially decreases during the night, when the water demand of the population is comparably low and no water abstraction takes place. This pattern is also evident in Figure 21, where the course of the indoor radon concentration is presented for the cutoff-date.

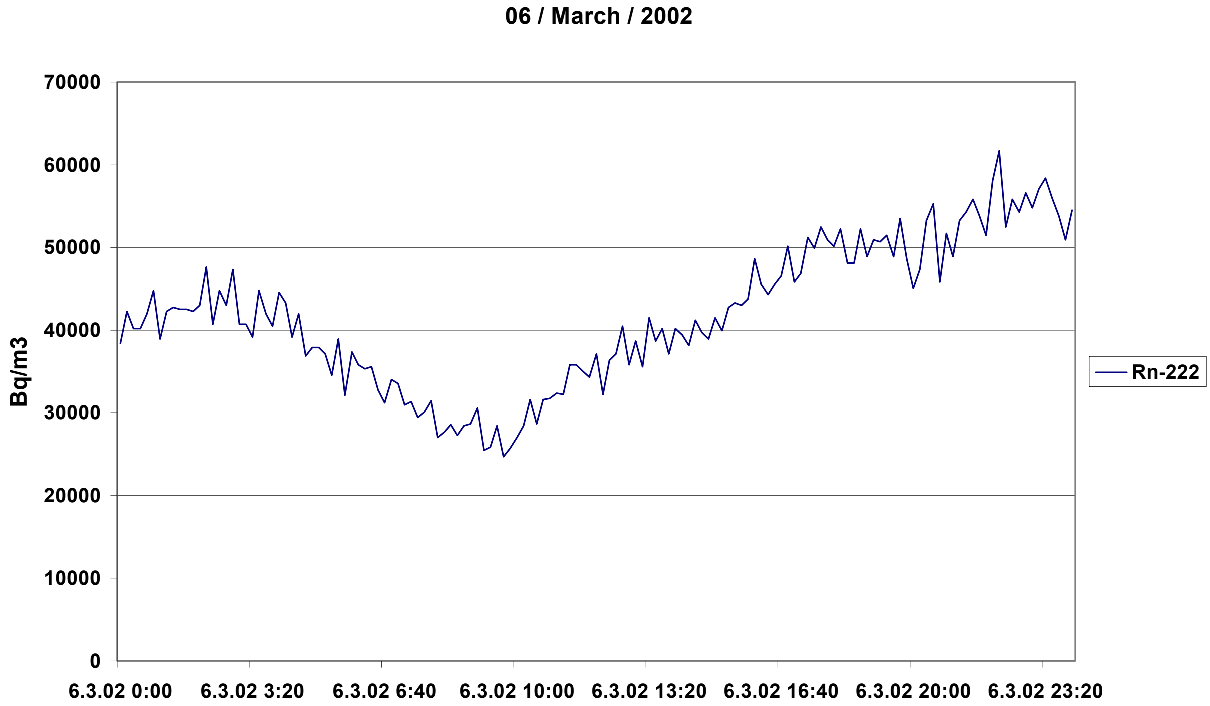


Figure 21: ^{222}Rn in indoor air on 6th March 2002

The average ^{222}Rn concentration for the cutoff-date is 41.5 kBq/m^3, whereas the minimum concentration amounts to 24 kBq/m^3. The maximum radon level was detected in the final hours of the day and is close to 62 kBq/m^3. Sampling in WW A took place in the early afternoon of 06th March 2002. The ^{222}Rn reference concentration considered for the calculation of the balance is 40 kBq/m^3. This value was detected at 2 p.m. while the water sampling was performed.

High levels of radon in indoor air may possibly lead to an accumulation of solid radon decay products within air dehumidifiers. These devices are commonly used to remove humidity from the indoor air in waterworks for protecting electronic equipment. However, solid radon decay products (e.g. ^{214}Pb, ^{214}Bi, ^{212}Pb) may accumulate within the filter fleece of these devices. The gamma dose rate in the vicinity of an air dehumidifier positioned in the water aeration chamber of WW A amounts to 2.1 µSv per hour (Wisser & Stüber, 2001). The fleece itself revealed an effective dose of almost 80 µSv per hour. Consequently, the staff has to treat the fleece with care and the period of stay in the aeration chamber should be restricted, even when the fan is in operation.

9.3.2.6 Radionuclides in Residues from Water Treatment

The residues from WW A are mainly composed of liquid sludge from filter-backwashing. According to the facility management, the Filters 1 + 2 are backwashed once a week to remove iron- and manganese-containing particles from the filter grains. The sludge from backwashing are collected in a large basin, situated next to the waterworks building. This basin has not been emptied for at least 10 years. This is due to the comparably low amount of waste arising from water treatment.

Another source of waste is the filter material itself. However, this material is rarely exchanged. The last exchange took place approximately seven years ago. Fortunately, it was possible to obtain a sample of the activated carbon layer from Filter 1 and two samples of the sludge from the basin. Gamma-Spectrometry was applied for the measurement of the radioisotopes present in the wastes. ^{226}Ra activity could be determined directly, whereas ^{238}U and ^{228}Ra concentrations were determined by measuring their immediate daughter isotopes in secular equilibrium (^{234}Th and ^{228}Ac, respectively). The levels of ^{234}U were calculated from the average isotope ratio of ^{234}U/^{238}U present in the raw waters. As a consequence, the error bars for ^{234}U represent an estimated error of about 20 %. The results of radionuclide determination in residues are illustrated in Table 27 and represent the activity concentrations for the dry-matter of the respective radionuclides. The primary water content of the samples was about 15-20 %.

Table 27: Long-lived radioisotopes in residues from WW A (dry-matter)

	GAC from Fe-Filter (Bq/g)	**Sludge from Basin (Inlet) (Bq/g)**	**Sludge from Basin (Margin) (Bq/g)**
^{238}U	8.8 ± 2.0	6.1 ± 1.3	5.8 ± 1.2
^{234}U	11.5 ± 2.3	7.7 ± 1.6	7.5 ± 1.5
^{226}Ra	9.5 ± 2.0	4.5 ± 1.0	5.6 ± 1.2
^{228}Ra	6.9 ± 1.5	2.5 ± 0.5	2.7 ± 0.6
SUM	36.7 ± 7.5	20.8 ± 4.5	21.6 ± 4.5

The total activity concentrations for long-lived natural radionuclides are extremely high and amount to 36 ± 7.5 Bq/g in GAC and 21 ± 4.5 in the liquid sludge. This is especially shown with the granulated activated carbon from Filter 1, which is highly contaminated by natural radionuclides. The total activity of long-lived radionuclides in the GAC-layer is approx. 86 MBq, assuming a density for GAC of 0.8 g/cm^3 and a total volume of 3 m^3. However, the levels of long-lived natural radioisotopes in the residues stem from water treatment processes that were performed over a period of several years.

Figure 22 provides a graphical illustration of radioactivity present in residues from water treatment in WW A.

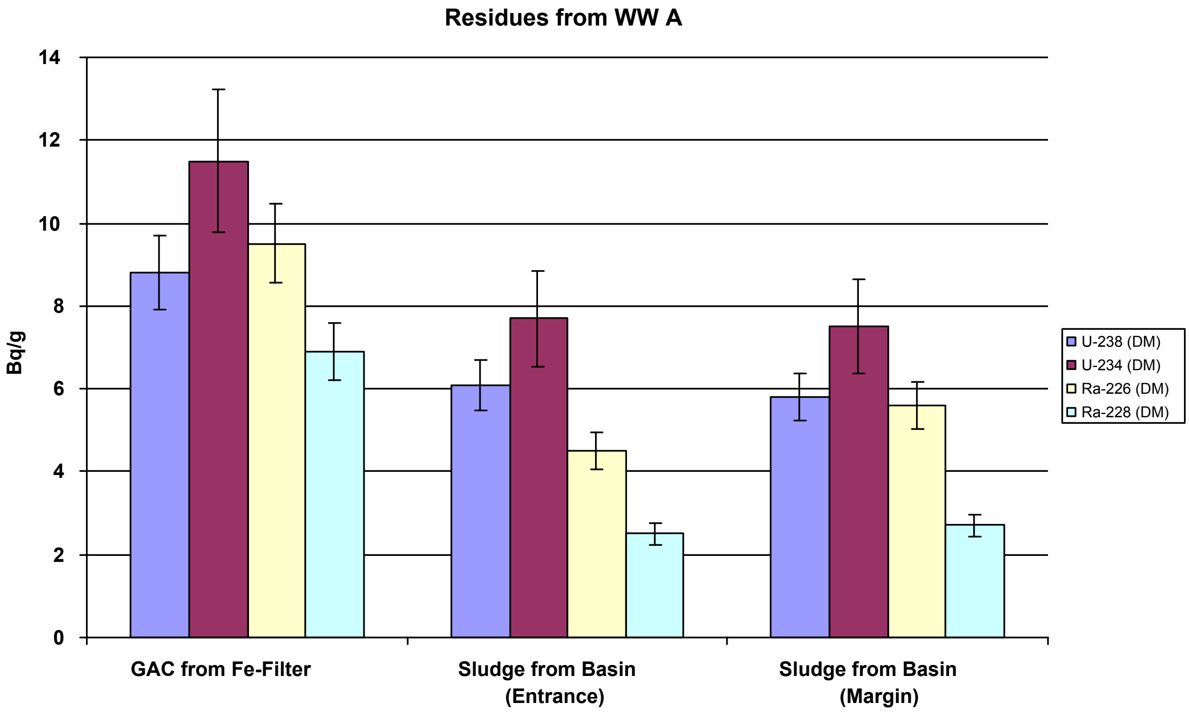


Figure 22: Long-lived Natural Radioisotopes in Residues from WW A

These elevated levels of radioactivity demonstrate the importance of a proper waste disposal arising from water treatment. In accordance to the German Radiation Protection Ordinance, the polluted residues from WW A should be deposited in agreement with the responsible authorities (§ 102, StrlSchV).

The deposited long-lives radionuclides in the filter material lead to an enhanced gamma dose rate in the vicinity of the filters as indicated in Table 28. The results were obtained during the sampling campaign on the cutoff-date (06th March, 2002).

Table 28: Effective doses in the vicinity of Filters 1 + 2 at WW A

Location / (distance)	Effective Dose per hour	Effective Dose 2000 hours / year
Fe-Filter (~20 cm)	1.47 µSv	2.94 mSv
Mn-Filter (~ 20 cm)	0.20 µSv	0.40 mSv
Control desk next to Fe-Filter (~ 50 cm)	0.62 µSv	1.24 mSv
Filter hall	0.15 µSv	0.3 mSv

The effective dose next to the Fe-Filter is comparably high and amounts to almost 1.5 µSv per hour. Assuming an annual working time of 2000 hours, the staff would receive a radiation dose of about 3.0 mSv, if they stayed in the direct proximity of the filter tank (20 cm distance). Obviously, this scenario is a rather unrealistic one because of the shorter working periods of the employees in WW A. Nonetheless, the radiation dose at the control desk is still high and the working time here is about 100 hours per year, leading to an annual effective dose of 62 µSv.

9.3.3 Stock-flow and Balances for Waterworks A

The cutoff-date for balancing radionuclides in WW A was March 06, 2002. Water production and treatment were performed without any disturbances on that special day. The total amount of abstracted water from the wells was 450 m^3, which roughly corresponds to the average value of water production at this waterworks per day. It can be assumed that March 06, 2002, stands for a typical day of water treatment at this site. In addition to that, water sampling and determination of radioisotopes could be accomplished without any problems and the results seem to be coherent.

Water production on March 06, 2002 (rounded):

- Well I: 45,000 liters (10 %)
- Well II: 270,000 liters (60 %)
- Well III: 135,000 liters (30 %)

In the first step, stock flow will be illustrated for the important radionuclides, followed by a detailed balance for the respective isotopes. The data presented in the following figures was calculated in accordance to Baccini's method of stock-flow analysis. The levels of stock-flow of radionuclides are provided in Bq/d **above the arrows** and the radon concentrations in the waters are indicated as Bq/l **below the arrows**. The size of the arrows indicates the contribution of the respective water, but they are not to scale. Furthermore, it has to be kept in mind that the statistical nature of radioactivity is a major uncertainty for the calculation of stock-flow.

9.3.3.1 Stock-flow Analysis and Balance for ^{222}Rn

The calculation of stock-flow for ^{222}Rn is a sophisticated one because this particular isotope is stripped out off the water in the first purification step. On the other hand, the count rate for radon was very high, which results in small 2-sigma errors. Stock-flow for radon is illustrated in Figure 23.

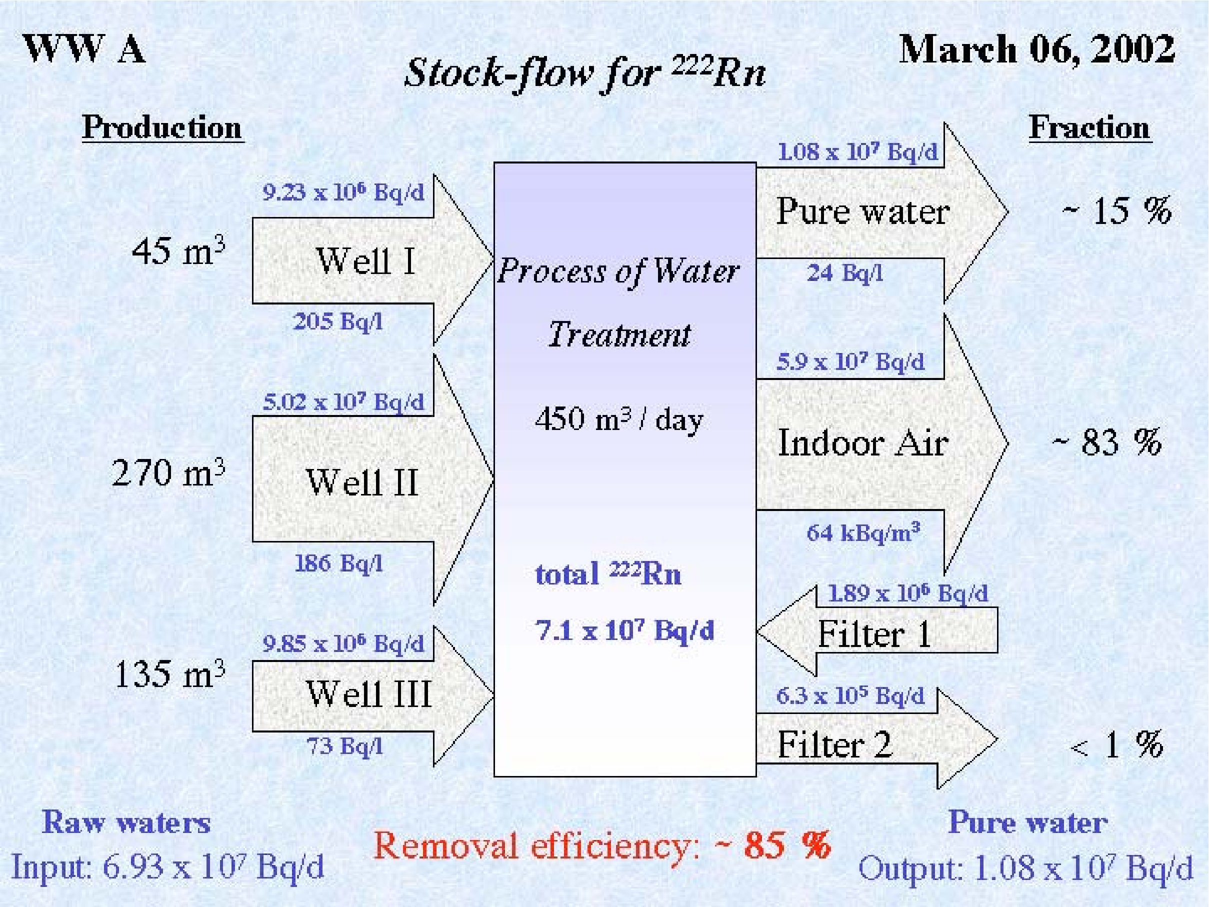


Figure 23: Stock-flow analysis for ^{222}Rn in Waterworks A on March 06, 2002

The analysis clearly reveals that Well II is the dominant radon source in WW A on the cutoff-date. Well II provides more than 70 % of the radon input. On the other hand, the well with the highest radon levels, Well I, only contributes to about 13 % of the total radon input. Another important source for ^{222}Rn is Filter I, which releases almost 2 MBq of radon per day. This clearly results from the decay of deposited ^{226}Ra in the GAC-layer of Filter 1. As mentioned in the previous section, the activity concentration of ^{226}Ra in the GAC amounts to 9.5 Bq/g.

The total amount of radon input is more than 70 MBq per day. The major sink for radon in water is aeration of the raw waters from Well I and Well II. More than 80 % of the total radon concentration is released to the indoor air of the aeration chamber. The theoretical radon concentration in the indoor air is 64 kBq/m^3, calculated from the difference in radon levels before and after water aeration and also by considering the degassing of radon from Well III in the water tank. The measured radon concentration in the aeration chamber was 40 kBq/m^3, which amounts to about 62 % of the theoretically present radon concentration. This deviation is lower than expected, because there is always an air exchange between the aeration chamber and adjacent rooms. Earlier investigations in WW A only detected 20 % - 40 % of the theoretically degassed radon in the indoor air of the aeration room (Molner, 2001).

Filter 2 only removes a tiny fraction of radon from the water, since the filter-bed is mainly composed of quartz-sand. The treated water, which is delivered to the consumer, has a radon concentration of only 24 Bq/l, which amounts to approx. 15 % of the initially present radon concentration. Hence, the removal efficiency for radon in WW A is on a high level and amounts to about 85 %.

The stock-flow analysis for ^{222}Rn in WW A revealed that Well II is the major radon source and the main sink is aeration of the waters from Well I and Well II. The total amount of radon input in WW A amounts to 70 MBq/d and the daily output amounts to only approx. 10 MBq, distributed in 450.000 liters of water. Furthermore, it became obvious that filters in waterworks may rather represent sources for ^{222}Rn than sinks for this isotope. The importance of work protection at radon-related workplaces is stressed by the illustration of this stock-flow. Almost 60 MBq of ^{222}Rn are released into the indoor air of the aeration room per day, distributed in a volume of 916 m^3.

Figure 24, provides the balance for ^{222}Rn on the cutoff-date in WW A. The input of radon at this waterworks is composed of three raw waters and the decay of ^{226}Ra in Filter 1.

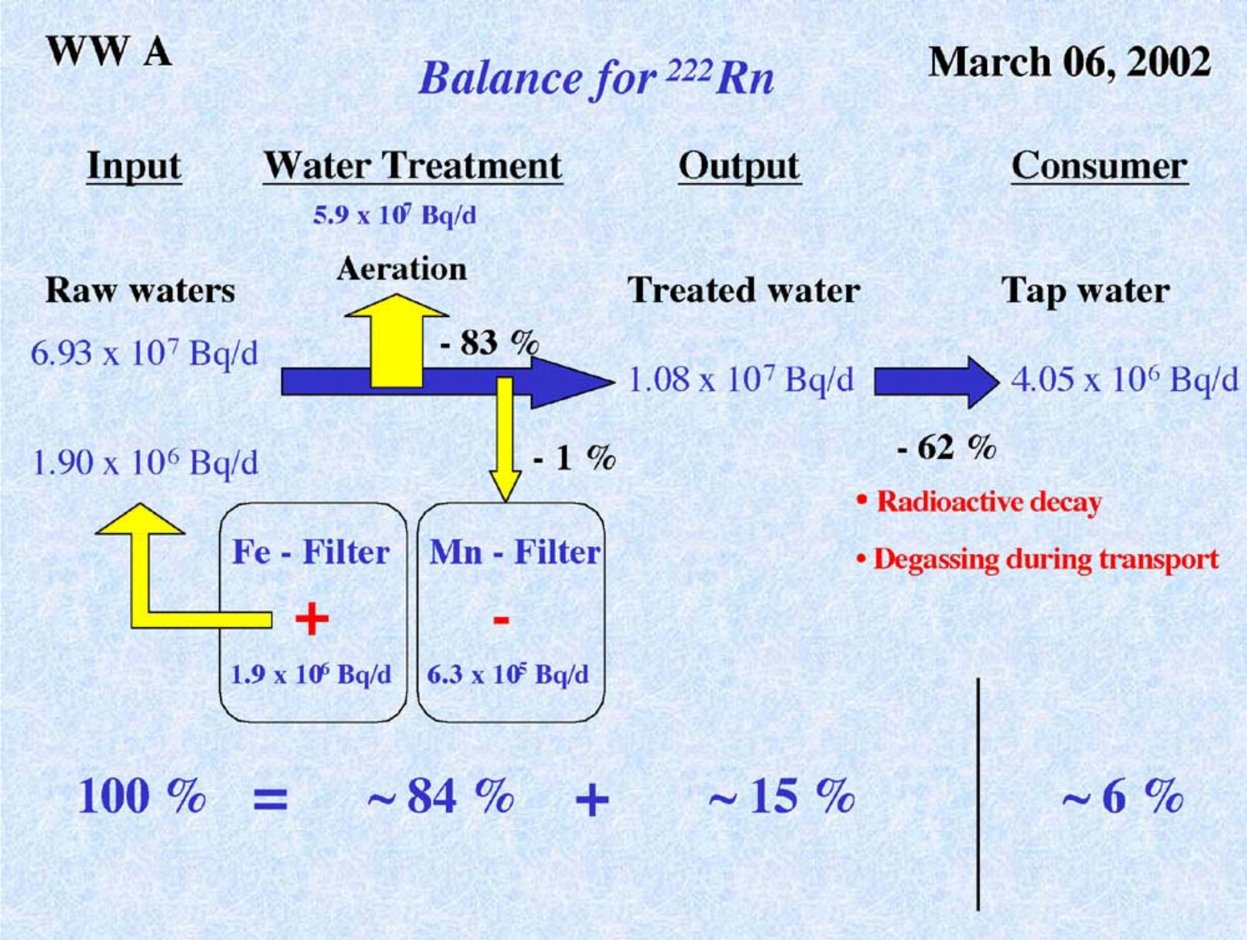


Figure 24: Balance for ^{222}Rn in WW A on March 06, 2002

Despite the uncertainties arising from the statistical nature of radioactive decay, the balance for radon in WW A is almost exactly in agreement. The difference in radon levels between output and input are equalized by the amount of radon that remains in the indoor air of the waterworks. The contribution of Filter 2 to the removal of radon is negligible and amounts to < 1%. However, more than 60 % of the radon present in the pure water vanishes during the transport from the waterworks to the consumer. This is mainly attributed to radioactive decay and the degassing of radon in the high reservoir. Only about 6 % of the initially present radon in raw water reaches the consumer via the delivered drinking water. Consequently, The level of radon present in tap water are not of any health concern, even under the assumption that radon in tap water may increases the indoor radon concentration significantly.

9.3.3.2 Stock-flow Analysis and Balance for Uranium Isotopes

Stock-flow analysis for the uranium isotopes ^{238}U and ^{234}U is illustrated in Figure 25. The data concerning ^{238}U is indicated in blue and the stock-flow for ^{234}U can be recognized in red.

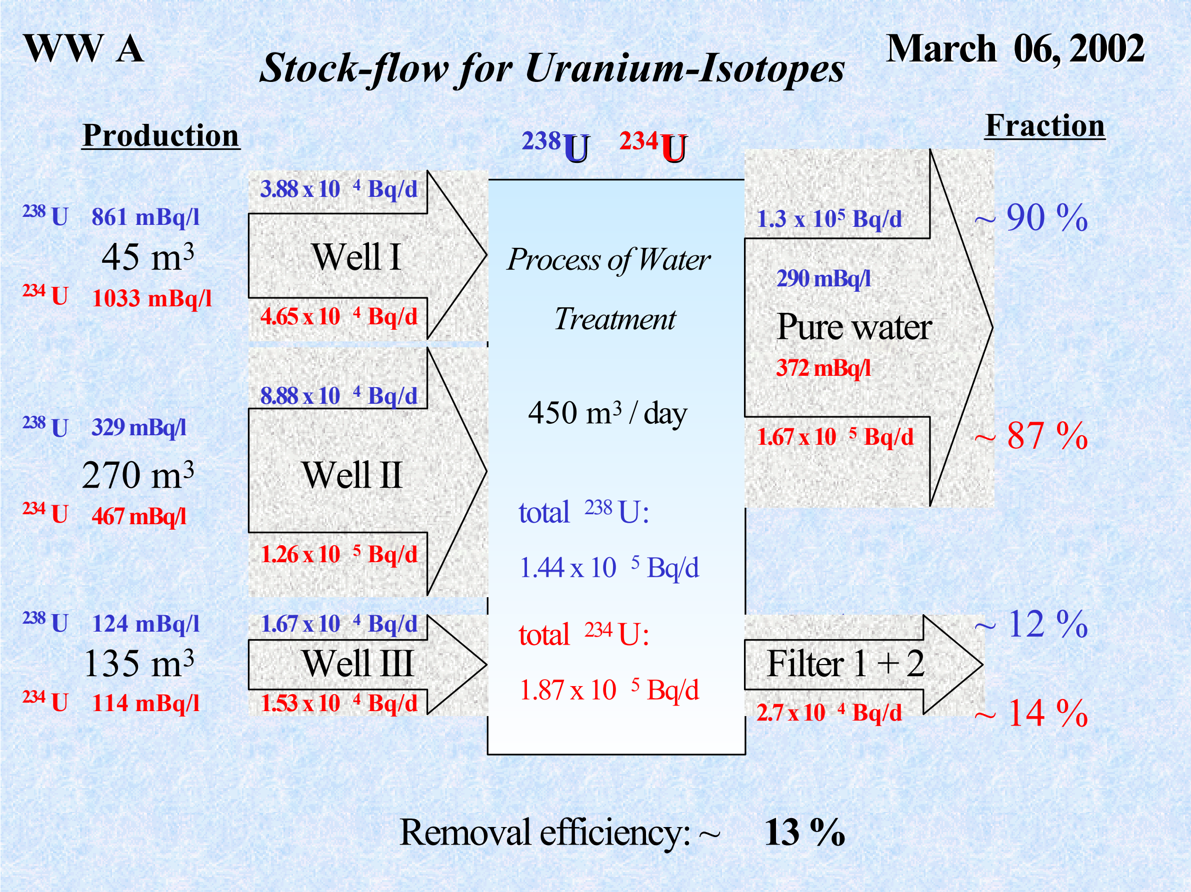


Figure 25: Stock-flow for Uranium Isotopes in WW A on March 06, 2002

As can be seen from the illustration above, the most important source for uranium in WW A is Well II, contributing to about 70 % of the total ^{238}U & ^{234}U concentration of 3.3 x 10^5 Bq/d. Surprisingly, stock-flow analysis for uranium isotopes does not reveal any major sinks for these substances. The removal efficiency only amounts to about 13 % and the largest fraction of uranium can be found in the “treated” water. The appropriateness of the entire method is confirmed by the stock-flow analysis for ^{238}U and ^{234}U, because the deviation of the results for these two isotopes is relatively small (± 2 %). This is an excellent outcome under consideration of possible sample preparation and measurement errors.

The amount of uranium accumulated in Filters 1 + 2 is about 45,000 Bq per day. Under the assumption that the cutoff-date is representative for any day of the year, about 16 MBq of uranium would be enriched in the filters per year. Most of this activity concentration will probably be poured into the sludge basins during filter backwashing. The total removal efficiency for uranium only amounts to ~13 %. This result is quite astonishing since granulated activated carbon usually removes uranium at high efficiencies. The most probable explanation for the poor removal yield is the fact that this GAC is in use for approx. 7 years. It is obvious that the adsorption capacity of this GAC-layer is almost exhausted. This explanation is proven by the extremely high amount of uranium in the previously investigated GAC sample. The concentration of total uranium in the GAC sample was about 20 ±4 Bq/g. In fact, it seems more surprising that this old and used GAC layer is still adsorbing uranium at levels of about 45,000 Bq/d. A renewal of the GAC-layer in Filter 1 would surely increase the removal yield for uranium and other natural radioisotopes, such as ^{222}Rn and ^{226}Ra.

Figure 26 provides a detailed balance for uranium in WW A on the cutoff-date. The activity concentrations for ^{238}U and ^{234}U have been summed up due to the similar chemical properties of these isotopes.

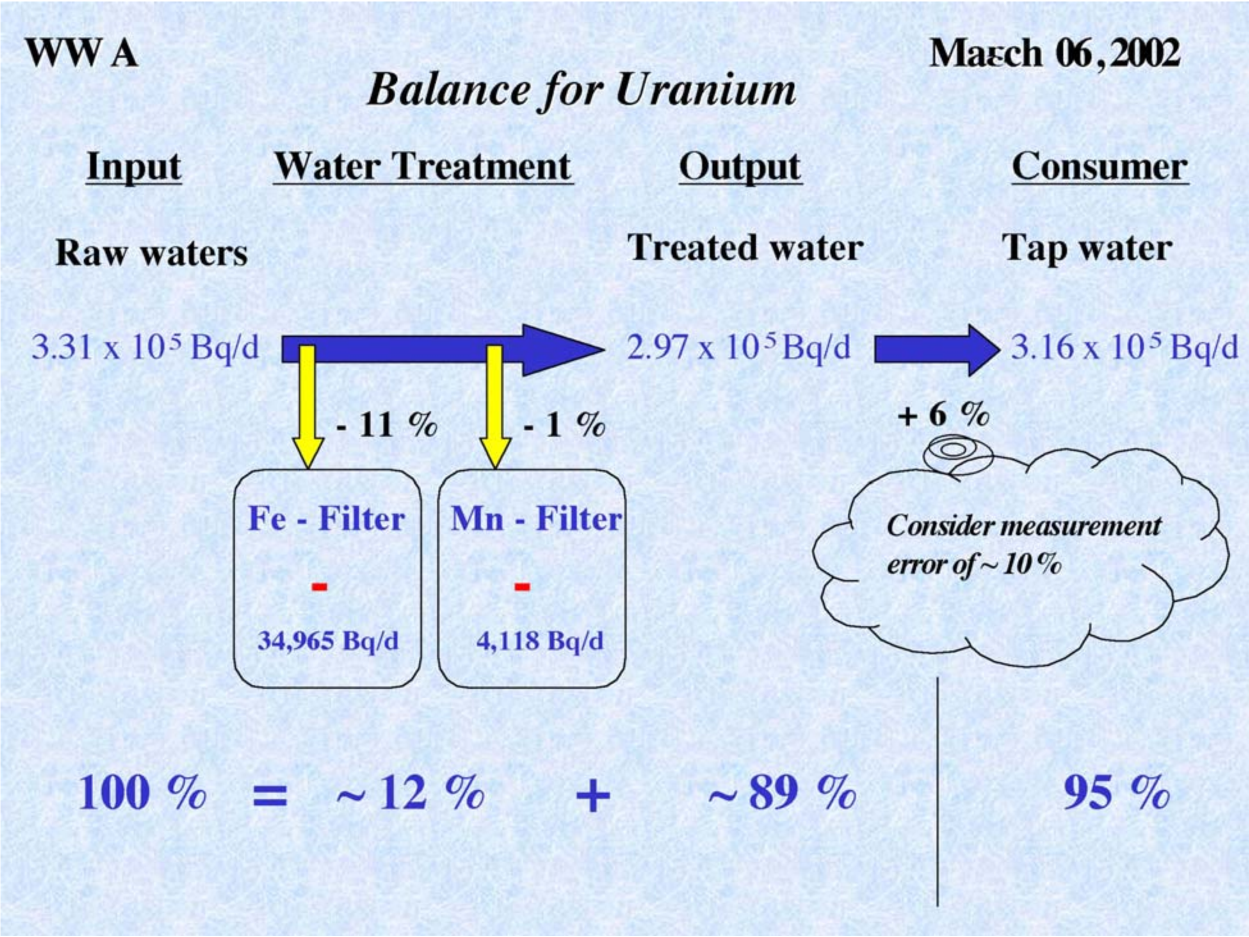


Figure 26: Balance for Uranium Isotopes in WW A on March 06, 2002

The difference between input and output of uranium in WW A is only slightly higher than 10 % due to the poor removal efficiency for uranium in the two water filters. However, the uranium level at the water tap of the consumers is greater than the uranium concentration in the pure water. This phenomenon indicates the influence of measurement error for the entire method of balancing radionuclides. On the other hand, the water samples taken from the consumers were already in the high reservoir and covered a distance of few kilometers. The levels of natural radionuclides in the aquifers are not stable over a period of several days and the mixing ratio for the raw waters is not constant. Thus, it can be assumed that the water from the tap was not of the same composition as the water samples taken in the waterworks. The exact transportation time for the water from the waterworks to the consumer can hardly be estimated since the water demand of the population is not constant.

The uranium concentrations in the drinking waters from private households are significant but not at a very high level. The levels for ^{238}U and ^{234}U are in the order of 0.3 Bq/l and 0.4 Bq/l, respectively. A dose assessment for the population will be presented later in section 9.3.4, page 95.

9.3.3.3 Stock-flow Analysis and Balance for ^{226}Ra

Radium isotopes are of great interest in water supply due to their radiotoxicity, especially the isotopes ^{228}Ra and ^{226}Ra. Since the determination of ^{228}Ra in water samples is difficult and time consuming, only ^{226}Ra was included in the investigation. The graphical illustration of stock-flow for ^{226}Ra is presented in Figure 27.

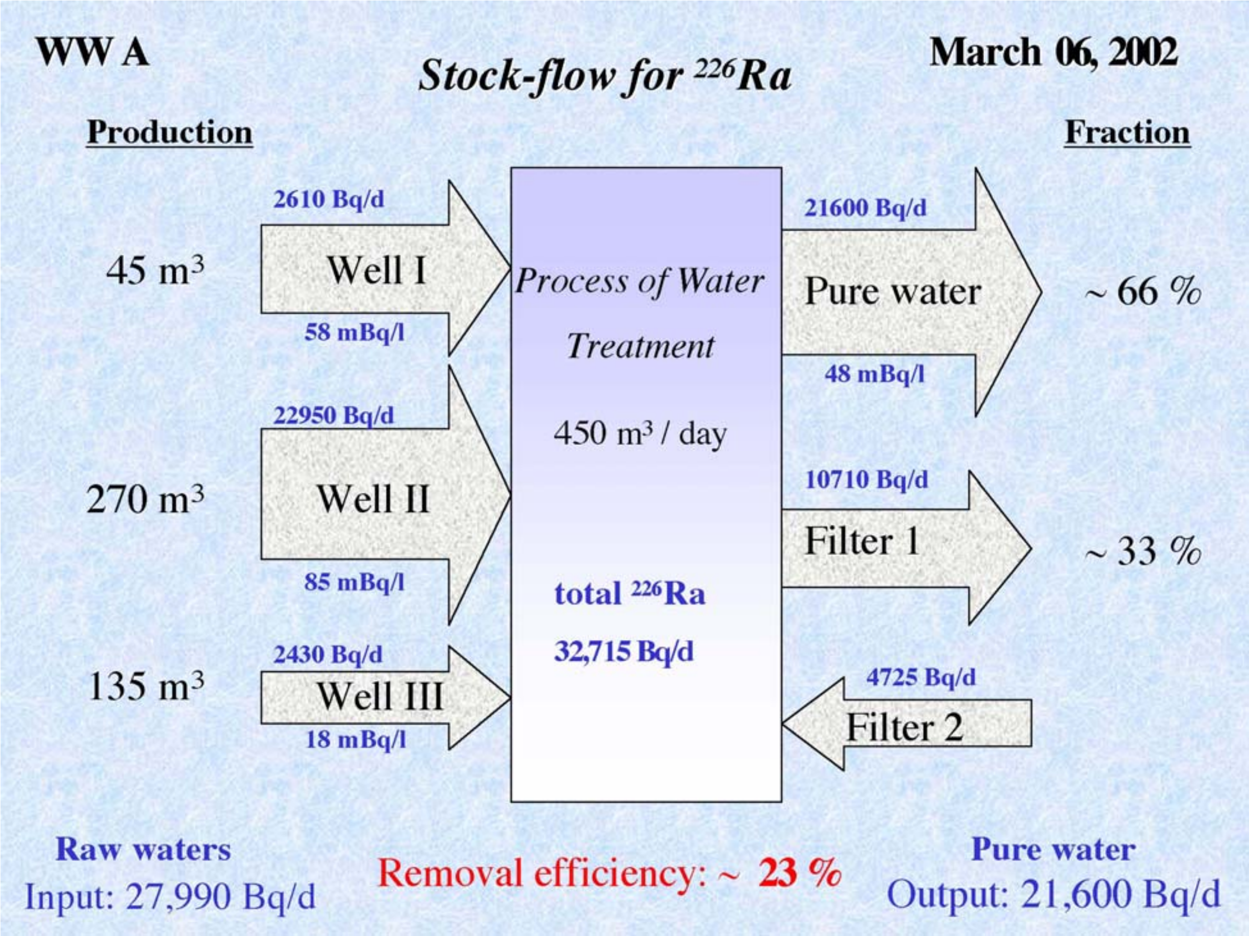


Figure 27: Stock-flow for ^{226}Ra in WW A

From the stock-flow analysis presented above, the major radium source for WW A is Well II, contributing to more than 70 % of the total radium activity concentration. Well III is of minor interest due to the very low radium levels and Well I is not of concern because of the low production rate. The largest amount of the abstracted ^{226}Ra can be found in the treated pure water. Filter 1 eliminates only 1/3 of the present radium. However, this filter is still accumulating radium unless the ^{226}Ra concentration in the GAC-layer is already at 9.5 ±2.5 Bq/g.

Stock-flow analysis reveals that Filter 2 releases ^{226}Ra during water treatment. This effect is obvious even under consideration of the calculated 2-sigma errors. The contribution of Filter 2 to the total ^{226}Ra concentration is almost as high as the input of Wells I + II. The reason behind this is the release of previously adsorbed radium from the filter bed. It has to be kept in mind that the filters are operated under pressure conditions. Filter 1 does not discharge radium since the adsorption onto GAC is probably more stable than adsorption onto the sand layers of Filter 2.

The calculated removal efficiency for radium is higher than for uranium and amounts to 23 % with respect to the initially activity concentrations present in the raw waters. The particular balance for ^{226}Ra is provided by Figure 28.

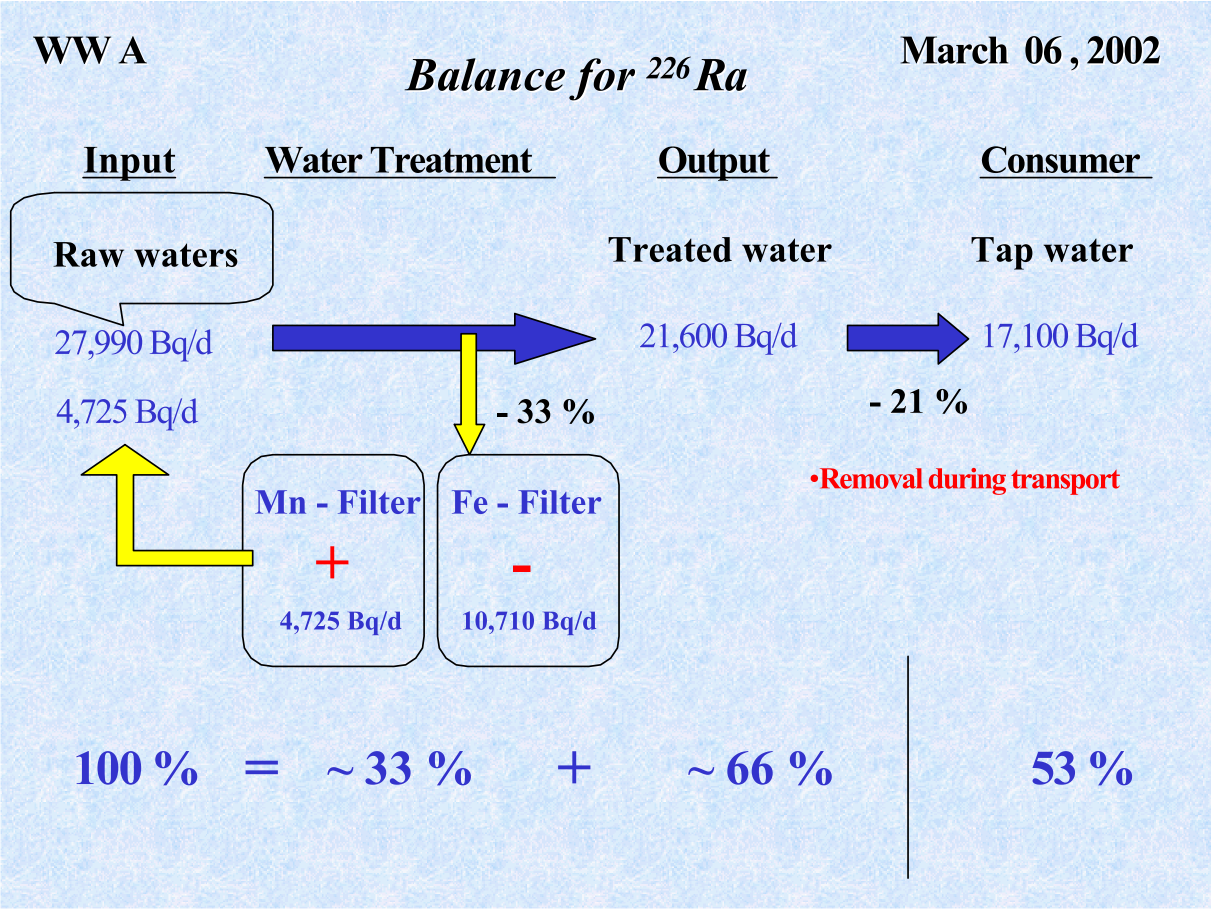


Figure 28: Balance for ^{226}Ra in WW A on the cutoff-date

The balance for radium is complete and it becomes obvious that 2/3 of the initially present ^{226}Ra are not affected by any water treatment step. This is not problematic since the radium concentration decreases during transport to the consumer. It is likely that radium co-precipitates onto the water pipes along with iron and manganese compounds. In fact, approx. 53 % of the total radium concentration reaches the consumer via the delivered drinking water.

9.3.4 Dose Assessment for the Population

The calculation of the annual total indicative dose (TID) for the consumers has to be calculated in agreement with the current legislation within the European Union. The respective dose conversion factors were taken from Annex III, Table A of European Council Directive 96/29/EURATOM.

Radon and radon decay products are not included in the present legislation. Therefore, only isotopes of uranium and radium will be included in the following calculation of the TID. The committed dose arising from ingested ^{228}Ra was calculated assuming that the ratio for ^{226}Ra/^{228}Ra in the liquid sludge is representative for the ratio of these isotopes present in the waters as well. Since the ratio of ^{226}Ra/^{228}Ra in the sludge is about 1.8, the assumed ^{228}Ra concentration in the tap water is approx. 26 ± 4.5 mBq/l. This estimation was confirmed recently by a determination of ^{228}Ra in tap waters from the village, because the measured levels of ^{228}Ra range from 22-28 mBq/l.

Table 29 provides the calculated TID for adults, children & babies on the basis of different water consumptions per year. The average annual water consumption is 350 liters for adults, 100 liters for children and 55 liters for babies. These numbers were taken from Annex VII, Part B (Table 1) of the German Radiation Protection Ordinance (*Strahlenschutzverordnung*).

Table 29: Total Indicative Dose for adults, children and babies from one year's consumption of drinking water from WW A, Rhine-Nahe-Area, Germany

	Adults (> 17 years) **350 l/a**	**Children (2-7 years)** **100 l/a**	**Babies (< 1 years)** **55 l/a**
^{238}U *(314 mBq/l)*	5.0 µSv/a	2.5 µSv/a	6 µSv/a
^{234}U *(390 mBq/l)*	7.0 µSv/a	3.5 µSv/a	8 µSv/a
^{226}Ra *(48 mBq/l)*	5.0 µSv/a	3.0 µSv/a	13 µSv/a
^{228}Ra *(26 mBq/l)*	7.0 µSv/a	9.0 µSv/a	43 µSv/a
TOTAL	24 µSv/a **0.024 ± 0.005 mSv/a**	18 µSv/a **0.018 ± 0.003 mSv/a**	70 µSv/a **0.070 ± 0.014 mSv/a**

Remark: The dose conversion factors used for calculating the TID consider the **committed dose** for adults (50 years), babies and children (70 years). In agreement with the current legislation, radon and long-lived radon decay products were not taken into account.

The most important point recognizable from Table 29 is that the TID for all different age groups is below the limitation value of 100 µSv per year. Even the considered error of the calculation of 20 % does not lead to an infringement of the limit. The most significant radionuclide for the TID seems to be ^{228}Ra, especially for young children and babies. More than 60 % of the dose for babies is attributed to ^{228}Ra. Therefore, uranium isotopes and ^{226}Ra are not of major concern for the TID of the population in this area.

It can be concluded that there is no threat to the local population in the area of WW A with regards to natural radionuclides in drinking waters. However, parents should take care that their babies and young children do not consume considerably more than 55 l or 100 l of tap water per year, respectively.

9.3.5 Interpretation of Results from WW A, Rhine-Nahe-Area

The most important result from the investigations in the waterworks at the Rhine-Nahe-Area is that the amounts of natural radioisotopes in tap waters do not exceed the new limitation values for the TID, as laid down in the amended *Trinkwasserverordnung*. On the contrary, the residues from water purification are highly contaminated with long-lived natural radionuclides. This is chiefly attributed to the successive accumulation of the removed radioisotopes during water treatment processes within the past 7-10 years. According to the guidelines laid down in the *Strahlenschutzverordnung*, the residues from WW A should be deposited in agreement with the responsible authorities. This particular deposition could be very costly, however, the volume of residues from WW A is only about 1-2 tons in 10 years and the water content of the sludge is about 15 - 20 %. Hence, a desiccation of the residues would decrease the volume of the sludge to at least 15 %.

Balancing of radionuclides in the presented waterworks was highly applicable to investigate the major **pathways of natural radioactive substances**:

- ^{222}Rn is accumulated in indoor air and is not removed efficiently by filtration processes in WW A. The main sink for radon in water is the aeration of raw waters.
- Filter 1 is an additional source for ^{222}Rn and Filter 2 can also be recognized as a source for the isotope ^{226}Ra
- Radium is present in waters at low levels and the removal efficiency for this element is comparably poor
- Uranium-isotopes are not removed efficiently due to the exhaustion of the two filters

In addition to that, stock-flow analysis revealed that the well with the highest concentration of radionuclides (Well I) only contributes to about 10-20 % of the input concentration for the respective isotopes. This is mainly attributed to the mixing of three well waters at WW A. Thus, it is not sufficient to determine radionuclide concentrations in the raw waters without knowing the amount of water abstracted from each well.

It has to be concluded that the iron- and manganese filters are (almost) entirely exhausted and that they are consequently not capable of removing long-lived radioisotopes (such as Ra and U) from the raw waters. The residues from WW A contain significant amounts of radium and uranium and it can be assumed that the majority of the total activity concentration stems from the removal processes in the past 5-10 years as the filter material was not exhausted yet.

Surprisingly, the stock-flow of radionuclides in WW A lead to an excellent agreement of the input and output of radionuclides, despite the possible influence of measurement and sampling errors. In conclusion, balances seem to be an adequate tool to assess the occurrence of radionuclides in WW A. The radioactive decay of the radionuclides ^{238,234}U and ^{226}Ra was not taken into account for calculating balances, since the half-lifes of those isotopes are very high in comparison to the duration of a single cutoff-date. A decay correction for ^{222}Rn in water was not necessary as well, because the retention period of radon in the closed system “waterworks” is only in the order of a few hours.

Furthermore, balances are capable of identifying the major sources and sinks for substances in waterworks, such as radionuclides and heavy metals. Even work-protection can benefit from stock flow analysis and balances, because the main areas of radionuclide enrichment have been discovered at this facility. These locations were the aeration chamber and the vicinity of the filter tank for iron- and manganese removal.

The different levels of natural radionuclides in the aquifer waters are due to the geological settings of the respective aquifers. Wells I + II extract waters from rhyolitic joint aquifers which contain high amounts of uranium and radon, respectively. On the contrary, the concentrations of radionuclides in Well III are negligible because of the low content of uranium and thorium series isotopes in the Rotliegendes sandstone.

9.4 Waterworks B, Central Ontario, Canada

The municipal water supply situation in Ontario, Canada, is quite different from the conditions in Germany. The vast majority of the abstracted raw waters for public water supply are extracted from rivers and lakes, especially for the drinking water demand of larger communities. Ground waters are extracted as well, but only a minor fraction of Ontario’s public waterworks takes raw water from aquifers. On the contrary, thousands of families satisfy their drinking water demand by the abstraction of ground waters from private well supplies. However, the geological conditions in Ontario – dominated by the Canadian Shield – may lead to an increased enrichment of natural radionuclides in ground waters due to the widespread occurrence of acidic igneous rocks such as granite. Furthermore, the regulations for radionuclides in Ontario’s current drinking water do not apply for individual well supplies at this point. For this reason, some private well waters from Central Ontario have been investigated in this study as well.

In fact, ground water treatment facilities in Ontario are only obliged to disinfect the raw waters (“minimum treatment”) before they are supplied to the consumer. Unfortunately, residues from an Ontario waterworks could not be included in this study, since wastes arising from water treatment are mainly produced in surface water treatment facilities. It is well understood that surface waters do not generally contain significant amounts of natural radioactivity and are consequently not of concern for this study.

Several waterworks in Ontario have been investigated in summer 2002, but only WW B was suitable for a calculation of stock-flow because the other facilities did not contain significant amounts of all the important natural radioisotopes in their waters. This is quite surprising because the expected values of natural radioactivity due to the geology were not discovered in any of the studied raw waters from Ontario. An explanation for this outcome will be provided later in section 9.4.6, page 112.

9.4.1 Geological Overview of Ontario

The Province of Ontario is characterized by a complex bedrock geology, of which rocks cover an age period of about 3 billion years (Thurston et al., 1992). Ontario can be subdivided into two main geological regions:

- The **Canadian Shield**, which underlies most of Ontario and represents some of the oldest crustal material known to exist on Earth.
- The younger, relatively flat-lying rocks of the **Borderlands**

Within these general regions, there are a number of sub-regions distinguished by their general geological character as presented in Figure 29.

The Canadian Shield is subdivided into provinces, including:

- The **Superior Province**, which is the oldest and largest Province and which consists of rocks of Archean age. Alternating belts of predominantly volcanic, predominantly sedimentary and predominantly gneissic rocks represent the accreted remains of ancient continents and ocean basins.
- The **Southern Province**, which consists of rocks of Proterozoic age (600 Ma to 2.5 Ga). This geological province represents a zone of orogenesis, which occurred about 1.8 Ga ago.
- The **Grenville Province**, which is the youngest part of the Canadian Shield and can be distinguished from the Southern Province by the details of its structural evolution and orogenesis.

The Borderlands represent sequences of Phanerozoic-aged (< 600 Ma) sedimentary rocks deposited in basins during the periodic inundation of the early North American continent by inland seas. These rocks contain deposits of a wide range of industrial minerals, salt, oil and gas (MNDM, 2002).

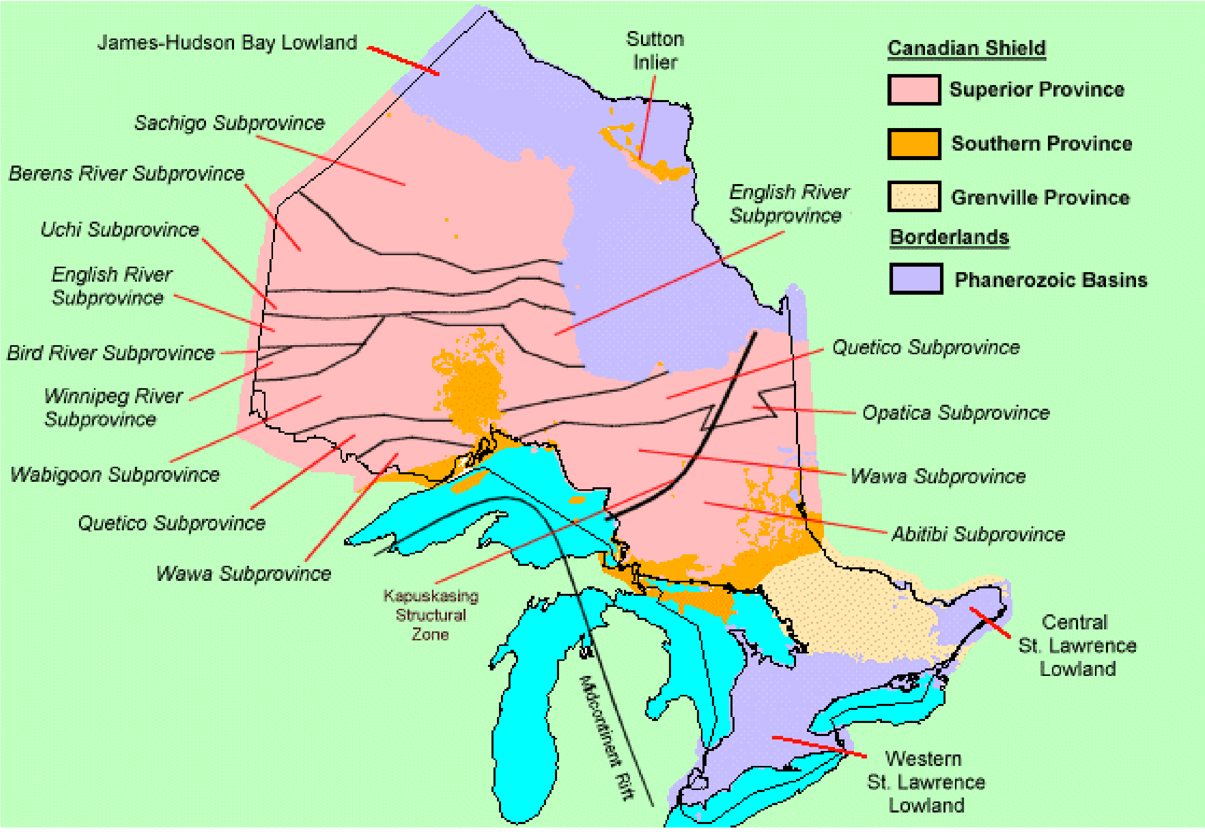


Figure 29: Simplified Geological Map of Ontario
(© Queen's Printer for Ontario. Reproduced with permission).

9.4.2 Description of WW B

This municipal waterworks is located in the central part of Ontario and has been selected due to its position within the famous Sudbury Structure. The Sudbury area is one of the world's most famous mining areas. The nickel, copper, cobalt, platinum, palladium and gold deposits produce some of the earth's most valuable ore. Total reserve (both mined and existing mineral resource inventory) in the Sudbury area is estimated at over 1.6 billion tons of ore (wallbrigdemining.com, 2002).

The formation of the Sudbury Structure has been the subject of great controversy over the last decades, but it is now widely accepted to be the eroded remains of a very large meteorite impact site. Various models for the formation of the ore deposits within the impact structure have been developed over the past 30 years. The Sudbury Impact Event had been dated at 1850 Ma. Estimates of the original diameter of the impact structure range from 150 to 225 km. The current Sudbury Basin is a 60 km by 27 km oval shaped basin, within the larger Sudbury Structure (Dressler et al., 1996).

In addition to the fascinating geology in the Sudbury area, WW B was included in balancing natural radionuclides because of the different water treatment compared with the two studied waterworks in Germany. Furthermore, the number of residents served by the facility is similar to WW A from the Rhine-Nahe-Area in Germany.

In this particular waterworks, two drilled wells were constructed for the extraction of aquifer waters. Well I was drilled in 1946 to 68 feet in an unconfined aquifer in a coarse sand and gravel formation. The permit to take water allows a maximum production rate of 1,000 l/min or 1,440 m^3/d. In the year 2002, almost 72,000 m^3 of raw water was pumped by Well I. Well II was constructed in 1965 to a depth of 74 feet in a water table aquifer consisting of a sand, gravel and boulder formation. The maximum rate of water production at Well II allows an abstraction rate of 2,274 l/m or 3,274 m^3/d. In 2002, the total production of the Well was approx. 344,000 m^3. This facility supplies drinking water for a small town in the Sudbury area occupied by approx. 4,900 inhabitants. In 2002, the total amount of produced drinking waters from well I & II was about 416,000 m^3.

Water treatment:

After the extraction of raw waters from wells I & III, the raw water is disinfected by use of sodium hypochlorite. Before the water enters the distribution system, it is fluoridated with hydrofluosilicic acid at the well site. The general quality of the two raw waters is already a satisfactory that a filtration of the waters is not necessary. As a consequence, residues do not arise from water treatment at this facility.

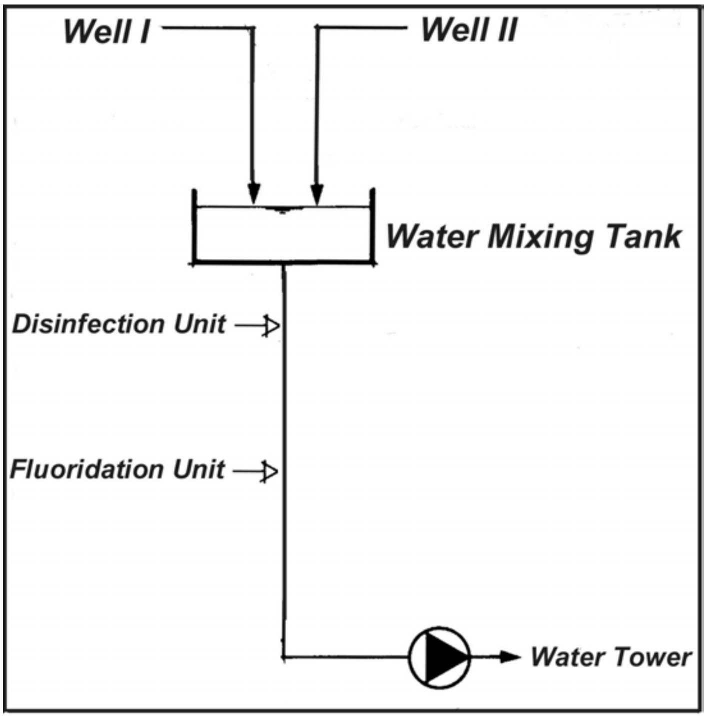


Figure 30: Scheme of WW B in Central Ontario

The waterworks consists of a single building, where the raw water tank and the disinfection utilities are situated. The ^{222}Rn levels in the indoor air of this building are < 50 Bq/m^3. The reason behind is that the raw and treated waters are not aerated and the water is always stored and transported in closed systems. Hence, there is no possibility for dissolved radon to escape **quantitatively** from the water. This fact simplifies the calculation of the balance for WW B because degassing of radon from water into indoor air has not to be considered.

9.4.3 Determination of Natural Radionuclides

In accordance to the main water treatment steps in WW B, the following waters have been subsequently sampled and analyzed for natural radioisotopes:

I. Raw water from Well I
II. Raw water from Well II
III. Exit disinfection site
IV. Exit fluoridation site (pure water)
V. Tap water from a private household

The sampling in WW B took place on July 19th, 2002 during an extended sampling campaign in Ontario. Unfortunately, sampling was only possible to be done on one single day, since the period of stay in Ontario was not sufficient for an additional sampling series. However, sampling and measuring of waters from the Sudbury area was performed carefully and several sample replicates have been taken from each sample location.

The results provided in the following section will generally represent the mean value of the multiple measurements.

9.4.3.1 Gross-Alpha and Gross-Beta

Gross-alpha and gross-beta activity determination was done for screening for long-lived natural radioactivity present in the water samples. The measurements were performed after a sample standing time of 6 weeks. The sample storage was done to discharge radon and its short-lived decay products present in the samples due to radioactive decay. The samples were measured for 72,000 sec, leading to a LLD of < 0.3 Bq/l for gross-alpha and < 2.0 Bq/l for gross-beta activity.

Surprisingly, none of the measured samples contained significant levels of gross-alpha and gross-beta activity, respectively. All the investigated samples contained gross-alpha and gross-beta activities below the LLD. However, the samples have been carefully checked for long-lived natural radionuclides, because the LLD of the used instrumentation for the screening parameters was not satisfactory.

9.4.3.2 Radon in Water

The determination of ^{222}Rn was performed with a *Triathler Multilabel Tester* via α-/β-separation after radon extraction in an organic szintillation cocktail. The samples were measured for 1,800 sec, leading to a detection limit of < 1.0 Bq/l. Table 24 indicates the radon activity concentration of the samples taken from WW B.

Table 30: ^{222}Rn levels in WW B on the cutoff-date

Sample	*July 19, 2002* *^{222}Rn (Bq/l)*
Well I	18 ± 2.0
Well III	18 ± 2.0
Exit disinfection	16 ± 1.5
Exit fluoridation (pure water)	15 ± 1.5
Consumer	11 ± 1.0

The levels of ^{222}Rn in the raw waters are comparably low and only amount to 18±2 Bq/l. During disinfection and fluoridation, the waters lose about 2-3 Bq/l due to a slight degassing of Rn at the site. Under consideration of the measurement errors, the ^{222}Rn levels of the raw and pure waters at this facility can be assumed to be equal.

9.4.3.3 Uranium Isotopes in Water

The determination of the uranium isotopes ^{238}U and ^{234}U was important for this study, because uranium is a major element of health concern in Canadian water supply. The given results for ^{234}U were obtained using uranium extracting PAMOX discs. For reasons of quality assurance, a ^{232}U tracer solution was added to determine the adsorption yield. The measuring time for the planar discs was 220.000 sec, leading to a LLD of approx. 7 mBq/l. On the contrary, ^{238}U was determined by high resolution ICP-MS at the Water Quality Center of Trent University Peterborough, Ontario. All samples have been acidified and filtered before the measurement of ^{238}U by ICP-MS took place. The results for uranium in WW B are presented in Table 31.

Table 31: ^{238}U & ^{234}U levels in WW B on the cutoff-date

Sample	*July 19, 2002* *^{238}U (mBq/l)*	*July 19, 2002* *^{234}U (mBq/l)*	**Ratio** **^{234}U/^{238}U**
Well I	40.5 ± 2.0	85 ± 9.0	2.1
Well III	42.0 ± 2.5	83 ± 9.0	2.0
Exit disinfection	39.0 ± 2.0	78 ± 8.5	2.0
Exit fluoridation (pure water)	37.5 ± 1.9	71 ± 7.5	1.9
Consumer	35.4 ± 1.8	66 ± 7.5	1.9

The uranium content of the different waters only slightly changes after water treatment. The isotope-ratios for $^{234}U/^{238}U$ are relatively constant under the consideration of the confidence limits and vary from 1.9 to 2.1. Since the ground waters contain free oxygen and a sufficient amount of carbonate-ions, uranyl carbonate is probably the dominating uranium species in these waters. As expected, the water treatment steps do not remove uranium significantly. The uranium levels of drinking water are quite low in comparison to the results from WW A.

9.4.3.4 ^{226}Ra in Waters from WW B

Only the radium isotope ^{226}Ra was analyzed in waters from WW B, because the determination of ^{228}Ra could not be performed during the stay in Canada. The measurements for ^{226}Ra were executed via the use of radium adsorbing MnO_2-coated discs. The measuring time was at least 200.000 sec per sample, which leads to a LLD of 5 mBq/l. The results for ^{226}Ra determination are compiled in Table 32, where the ^{226}Ra-levels of two different water sampling series are illustrated.

Table 32: ^{226}Ra levels in WW B on the cutoff-date

	July 19, 2002 ***^{226}Ra(mBq/l)*** ***Series A***	***July 19, 2002*** ***^{226}Ra (mBq/l)*** ***Series B***
Well I	60 ± 7	69 ± 8
Well III	57 ± 7	67 ± 8
Exit disinfection	55 ± 6	63 ± 7
Exit fluoridation (pure water)	56 ± 7	62 ± 7
Consumer	47 ± 6	50 ± 6

The presented results with respect to the two sampling series are in good agreement and indicate the reliability of the measurements, especially under the consideration of the 2-sigma errors. For the calculation of stock-flow and the balance, only Series B will be considered. The reason behind is that the ^{226}Ra activity concentrations of Series B are slightly higher and should be used for the calculation of the total ingested dose to be on the safe side.

The ^{226}Ra levels detected in WW B range from 61±7 to 68±8 mBq/l (Series B). The radium concentrations in the drinking water of the consumers are negligible with regards to the MAC levels provided in Ontario's *Drinking-Water Quality Standards Regulation* (MAC = 600 mBq/l).

The results imply a minor removal of ^{226}Ra during water purification. It is possible that the raw waters are enriched with oxygen during water mixing and water disinfection. The solubility of Ra^{2+} decreases with additional oxygen due to the co-precipitation of radium together with iron- and manganese compounds. However, the presented 2-sigma-errors do not allow a clear statement concerning the removal efficiency, since the errors bars of the respective water overlap.

9.4.4 Stock-flow and Balances for Waterworks B

The cutoff-date for balancing radionuclides in WW B was July 19, 2002. Water abstraction and treatment were performed without any disturbances on that day. The total amount of abstracted water from the wells was 1600 m^3, which roughly corresponds to the average value of water production at this waterworks during the summer months.

It can be assumed that July 19, 2002 stands for a typical day of water production at this site. In addition to that, water sampling and determination of radioisotopes could be performed without any problems and the results seem to be coherent.

Water production on July 19, 2002 (rounded):

- Well I: 280,000 liters (17.5 %)
- Well II: 1,320,000 liters (82.5 %)

In the first step, stock flow will be illustrated for the important natural radionuclides, followed by a detailed balance for the respective isotopes. The levels of stock-flow of radionuclides are provided in Bq/d **above the arrows** and the radon concentrations in the waters are indicated as Bq/l **below the arrows**. The size of the arrows indicates the contribution of the respective water, but they are not to scale. Furthermore, it has to be kept in mind that the statistical nature of radioactivity is a major uncertainty for the investigation of stock-flow.

9.4.4.1 Stock-flow Analysis and Balance for ^{222}Rn

The calculation of stock-flow for ^{222}Rn is comparably simple for WW B because this particular isotope is not quantitatively removed by any purification step. On the other hand, the count rate for radon was high, which results in small 2-sigma errors. Stock-flow for radon is illustrated in Figure 31.

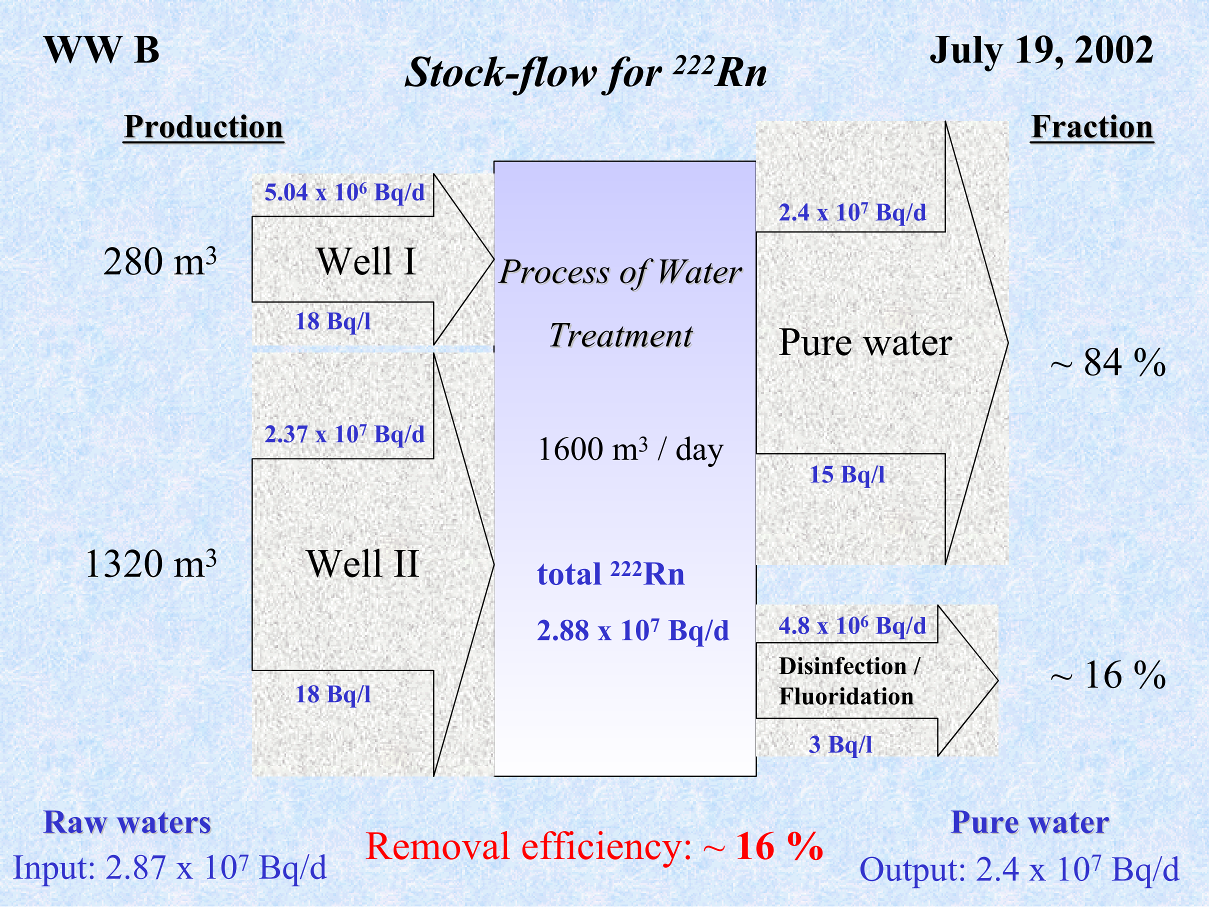
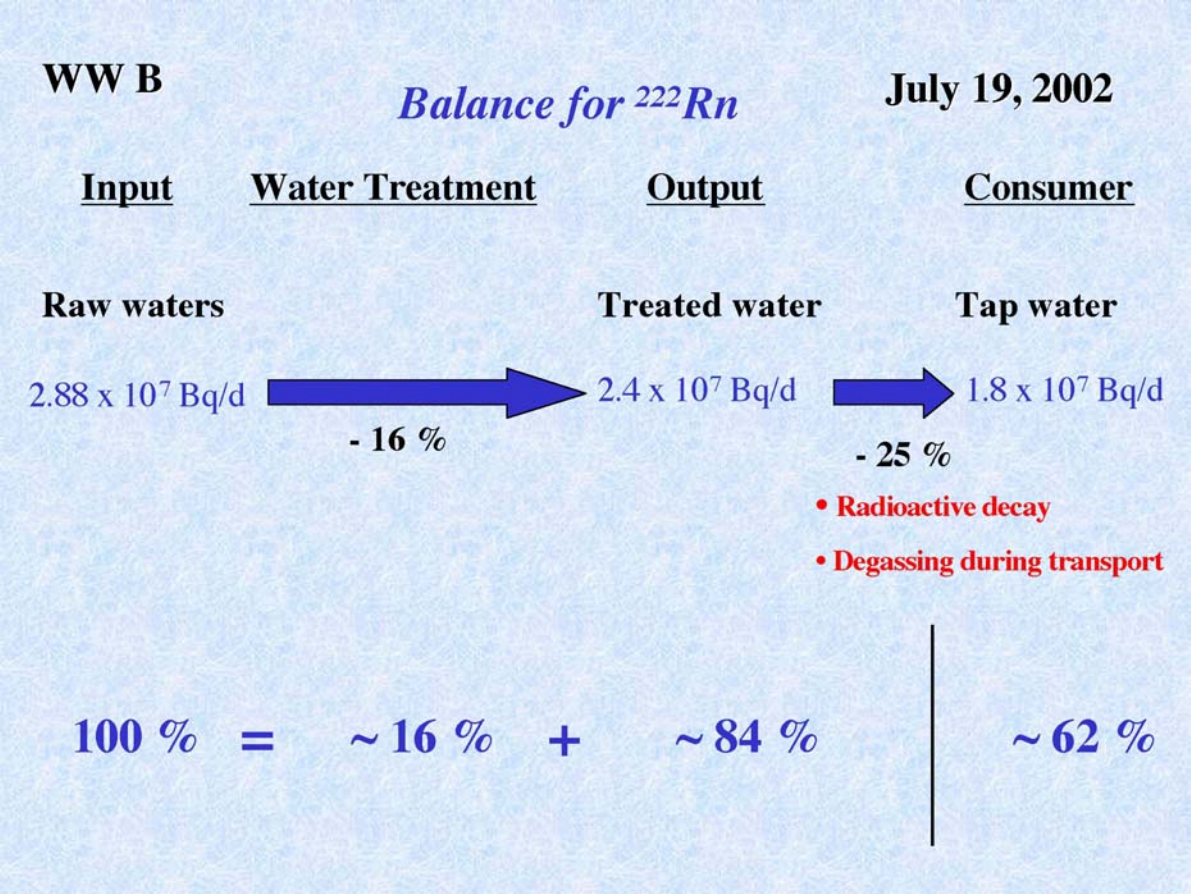


Figure 31: Stock-flow analysis for ^{222}Rn in Waterworks B on July 19, 2002

The stock-flow clearly exposes that Well II is the dominant radon source in WW B on the cutoff-date. Well II provides more than 87 % of the radon input. On the other hand, Well II only contributes to about 13 % of the total radon input. Another important source for ^{222}Rn is not present in this waterworks, since a filter system is not applied here of which might contain ^{226}Ra deposits as an additional source for ^{222}Rn.

The total amount of radon input is more than 28 MBq per day. A major sink for radon in water does not exist at this water distribution system. The treated water, which is delivered to the consumer, has a radon concentration of only 15 Bq/l, which amounts to approx. 85 % of the initially present radon concentration. Hence, the removal efficiency for radon in WW B is on a very low level and amounts to about 15 %.

Figure 32, provides the balance for ^{222}Rn on the cutoff-date at WW B. The input of radon at this water treatment facility is composed of two raw waters only.



WW B

Balance for ^{222}Rn

July 19, 2002

Input **Water Treatment** **Output** **Consumer**

Raw waters **Treated water** **Tap water**

2.88×10^7 Bq/d → 2.4×10^7 Bq/d → 1.8×10^7 Bq/d

- 16 %

- 25 %

- Radioactive decay
- Degassing during transport

100 % = ~ 16 % + ~ 84 % | ~ 62 %

Figure 32: Balance for ^{222}Rn in WW B on July 19, 2002

Despite the uncertainties arising from the statistical nature of radioactive decay, the balance for radon in WW B is exactly in agreement. The difference in radon levels between output and input are equalized by the amount of radon that is stripped out of the water by chlorination and fluoridation.

About 62 % of the initially present radon in water reaches the consumer via the delivered drinking water. The decrease of ^{222}Rn activity during transport is mainly attributed to radioactive decay and a possible degassing in the water tower. The low levels of radon present in tap water are not of any health concern, even under the assumption that radon in tap water may increases the indoor radon concentration significantly.

9.4.4.2 Stock-flow Analysis and Balance for Uranium Isotopes

Uranium is a major element of health concern in Ontario, Canada, especially after the new regulations under the *Safe Drinking Water Act* took place. Stock-flow analysis for the uranium isotopes ^{238}U and ^{234}U is illustrated in Figure 33. The data concerning ^{238}U is indicated in blue and the stock-flow for ^{234}U can be recognized in red.

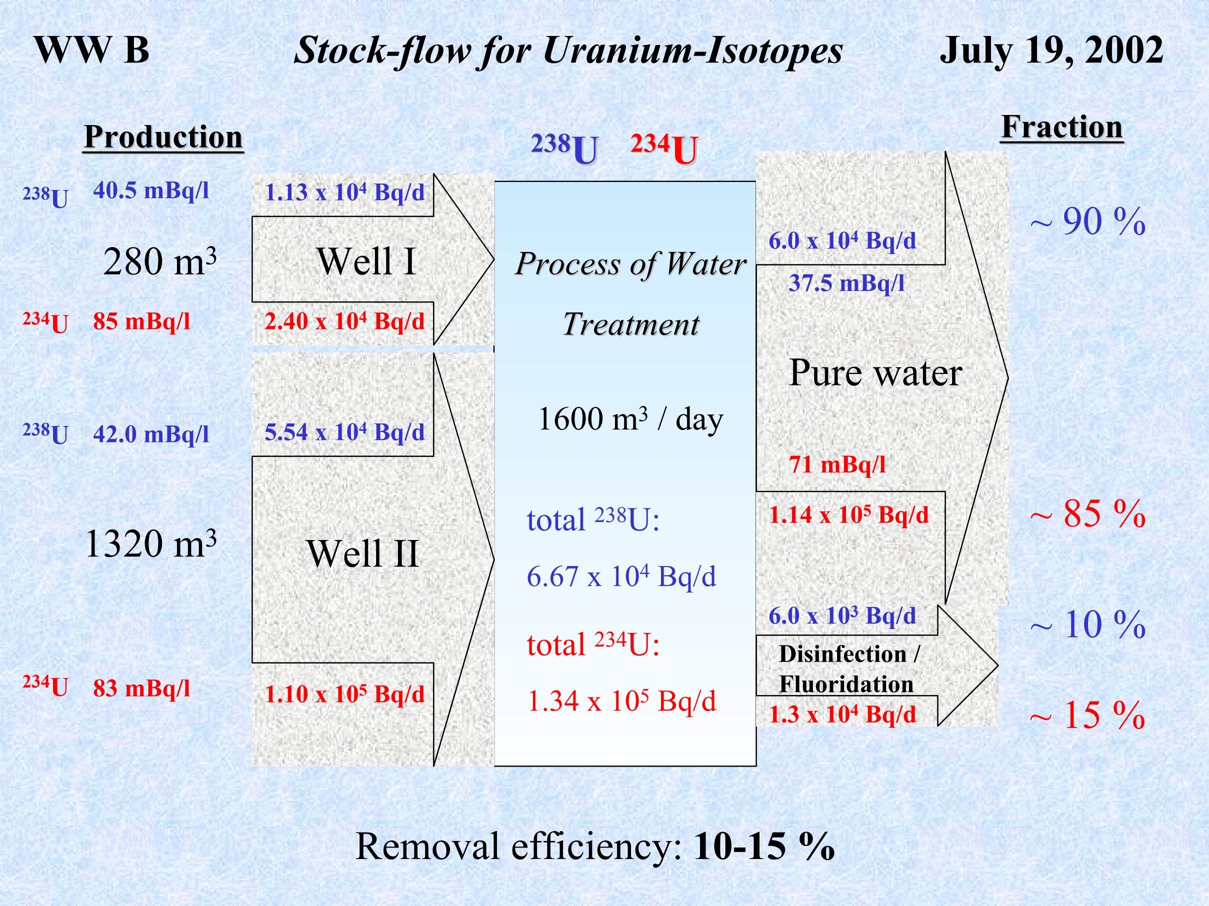
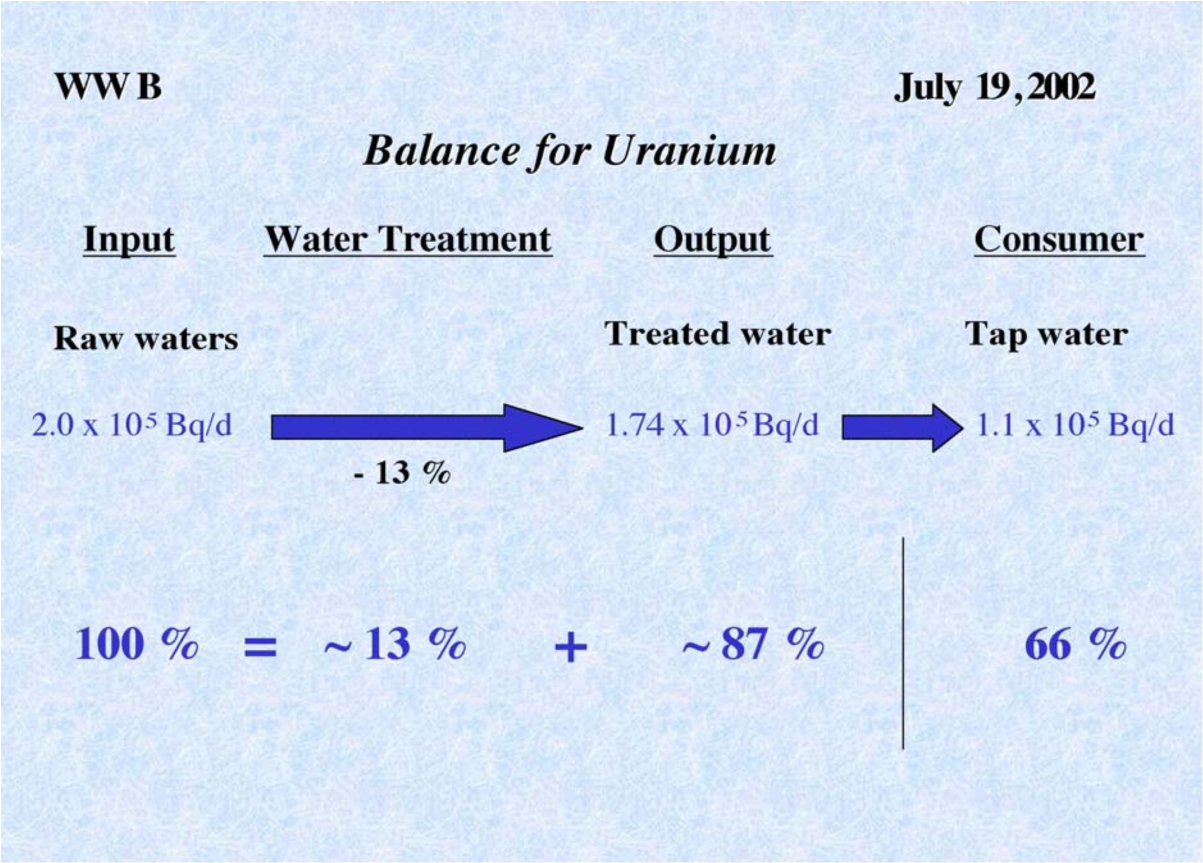


Figure 33: Stock-flow for Uranium Isotopes in WW B on July 19, 2002

As can be seen from the illustration above, the most important source for uranium in WW B is Well II, contributing to more than 80 % of the total ^{238}U & ^{234}U concentration of 1.3 x 10^5 Bq/d. Stock-flow analysis for uranium isotopes does not reveal any major sinks for this element. The removal efficiency only amounts to 10-15 % and the largest fraction of uranium can be found in the pure water. The appropriateness of the entire method is confirmed by the stock-flow analysis for ^{238}U and ^{234}U, because the deviation of the results for these two isotopes is relatively small (± 3 %). This is an excellent outcome under the consideration of possible sample preparation and measurement errors.

Figure 34 provides a detailed balance for uranium in WW B on the cutoff-date. The activity concentrations for ^{238}U and ^{234}U have been summed up due to the similar chemical properties of these isotopes.



WW B July 19,2002

Balance for Uranium

Input Water Treatment Output Consumer

Raw waters Treated water Tap water

2.0 x 10^5 Bq/d → 1.74 x 10^5 Bq/d → 1.1 x 10^5 Bq/d

- 13 %

100 % = ~ 13 % + ~ 87 % | 66 %

Figure 34: Balance for Uranium Isotopes in WW B on July 19, 2002

Again, the difference between input and output of uranium in WW B is only 13 %, due to the poor removal efficiency for uranium in water treatment.

The uranium concentrations in the drinking waters from private households are significant but not at a very high level. The levels for ^{238}U and ^{234}U are in the order of 40 mBq/l and 70 mBq/l, respectively. A dose assessment for the population will be presented later in section 9.4.5, page 111.

9.4.4.3 Stock-flow Analysis and Balance for ^{226}Ra

Radium isotopes are of great interest for dose assessment in water supply due to the high dose conversion factors for the isotopes ^{228}Ra and ^{226}Ra. Since the determination of ^{228}Ra in water samples is difficult and time consuming, only ^{226}Ra was included in the investigation. The graphical illustration of stock-flow for ^{226}Ra is presented in Figure 35.

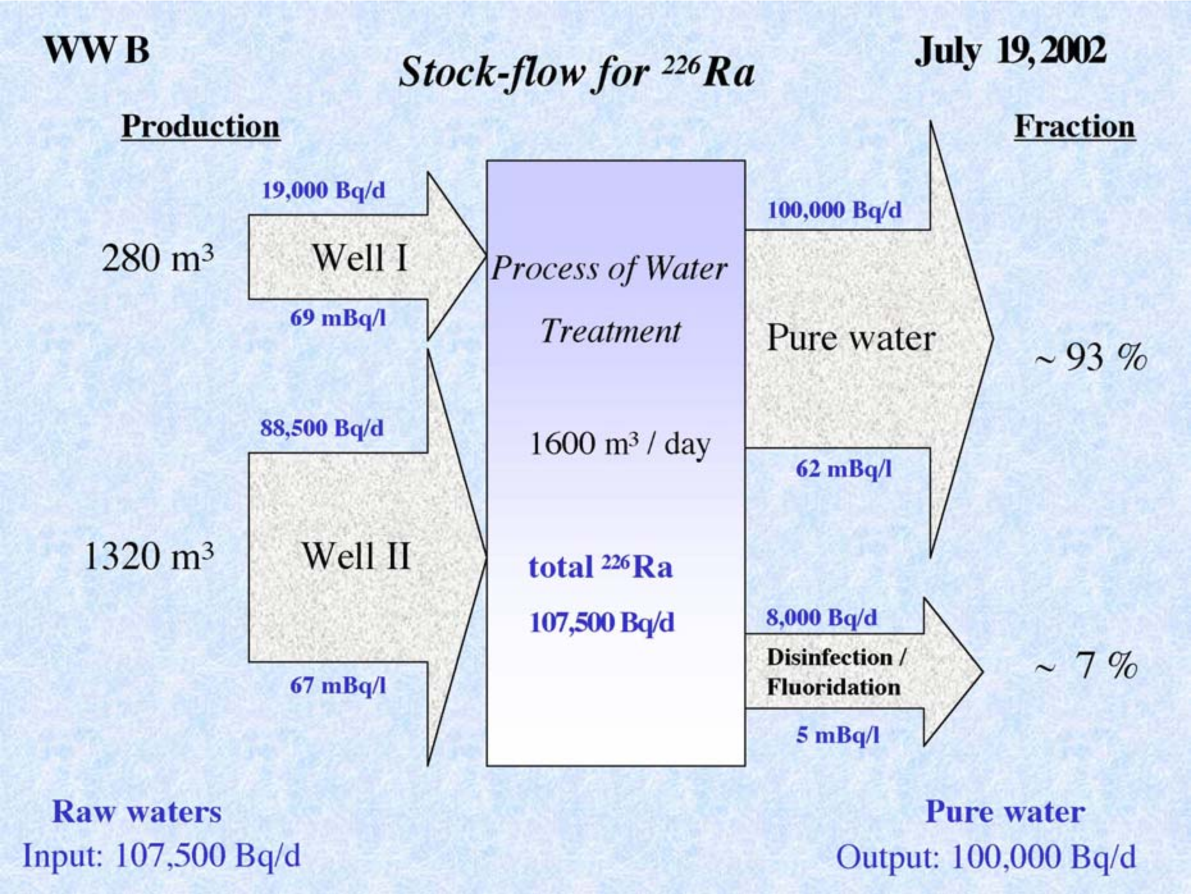
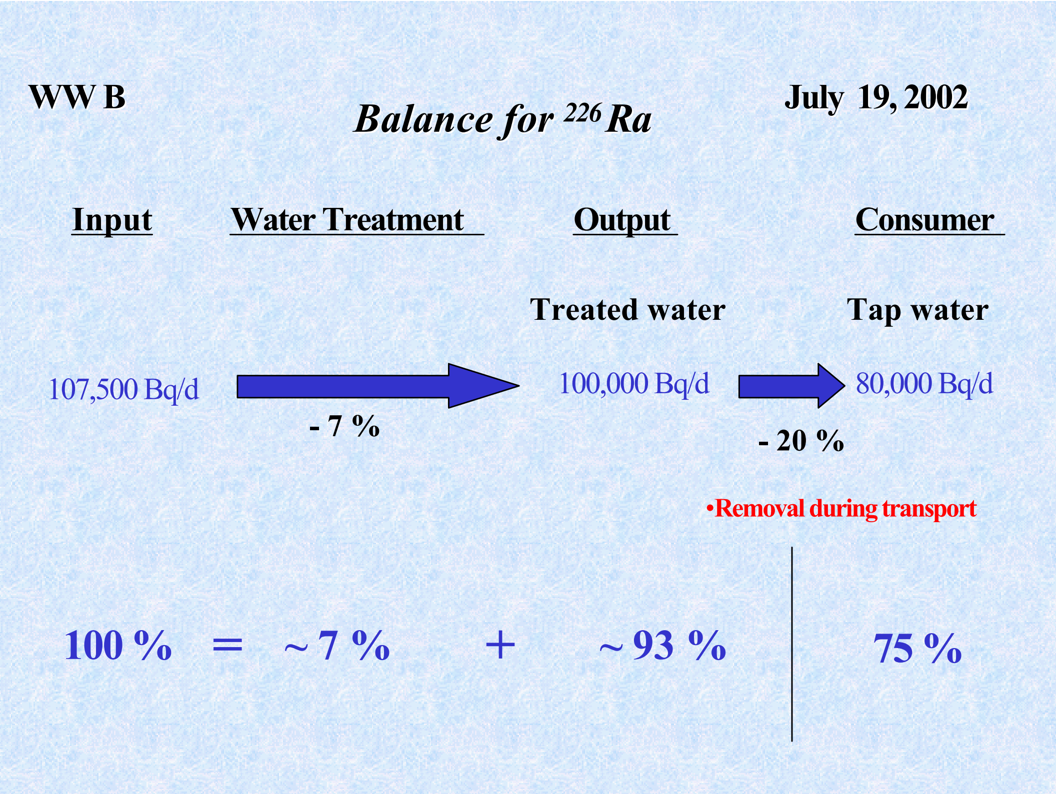


Figure 35: Stock-flow for ^{226}Ra in WW B

From the stock-flow analysis presented above, the major radium source for WW B is Well II, contributing to more than 80 % of the total radium activity concentration. Well I is of minor importance due to the lower production rate. The largest amount of the abstracted ^{226}Ra can be found in the "treated" pure water.

The removal efficiency for radium cannot be calculated because the difference in input and output is only about 7 %. Under the consideration of the minimum measurement error of approx. 10 %, it can be concluded that radium is not removed from the raw waters at WW B. The particular balance for ^{226}Ra is provided by Figure 36.



WW B

Balance for ^{226}Ra

July 19, 2002

Input	Water Treatment	Output		Consumer
		Treated water		Tap water
107,500 Bq/d	→ - 7 %	100,000 Bq/d	→ - 20 %	80,000 Bq/d

•Removal during transport

100 % = ~ 7 % + ~ 93 % | 75 %

Figure 36: Balance for ^{226}Ra in WW B on the cutoff-date

The balance for radium is complete and it becomes obvious that at least 93 % of the initially present ^{226}Ra are not affected by any water treatment step. This is not problematic since the radium concentration decreases during transport to the consumer. It is likely that radium co-precipitates onto the water pipes along with iron and manganese compounds. In fact, approx. 75 % of the total radium concentration initially present at WW B reaches the consumer via the delivered drinking water. The total amount of radium distributed to the population is still 100 kBq/d, dissolved in 1,600 m^3 of treated water.

9.4.5 Dose Assessment for the Population

The calculation of the annual total indicative dose (TID) for the consumers has been calculated in agreement with the future legislation in Ontario, Canada. The respective dose conversion factors were taken from the ICRP Publication 60, as demanded by Ontario's *Drinking-Water Quality Standards Regulation.*

Radon and short-lived radon decay products are not included in the current legislation. Therefore, only isotopes of uranium and radium will be included in the following calculation of the TID. The committed dose arising from ingested ^{228}Ra was calculated assuming that the ratio for ^{226}Ra/^{228}Ra in the drinking water is constant at 2.0. The calculated ^{228}Ra concentration in the tap water is 25 ±5.0 mBq/l. Table 33 provides the calculated TID for adults, children & babies on the basis of a different water consumption per year. The average annual water consumption is 730 liters for adults, 170 liters for children and about 55 liters for babies.

Table 33: Total Indicative Dose for adults, children and babies from one year's consumption of drinking water from WW B, Central Ontario, Canada

	Adults (> 17 a) **730 l/a**	**Children (2-7 a)** **170 l/a**	**Babies (< 1 a)** **55 l/a**
^{238}U *(35.4 mBq/l)*	1.2 µSv/a	0.5 µSv/a	0.7 µSv/a
^{234}U *(66 mBq/l)*	2.4 µSv/a	1.0 µSv/a	1.3 µSv/a
^{226}Ra *(50 mBq/l)*	10 µSv/a	5.3 µSv/a	13 µSv/a
^{228}Ra *(25 mBq/l)*	13 µSv/a	15 µSv/a	42 µSv/a
TOTAL	27 µSv/a **0.027 ± 0.008 mSv/a**	22 µSv/a **0.022 ± 0.005 mSv/a**	57 µSv/a **0.057 ± 0.015 mSv/a**
Remark: The dose conversion factors used for calculating the TID consider the **committed dose** for adults (50 years), babies and children (70 years).			

The most important point recognizable from Table 33 is that the TID for all different age groups is below the limitation value of 100 µSv per year. Even the considered error of the calculation of 25 % does not lead to a violation of the limit. The most significant radionuclide for the TID seems to be ^{228}Ra, especially for young children and babies. Almost 75 % of the dose for babies is attributed to ^{228}Ra. Uranium isotopes and ^{226}Ra are not of major concern for the TID of the local population. The determination of ^{210}Po was not successful for the water samples from Sudbury. As a consequence, the TID may be slightly higher than indicated in the table above.

It can be concluded that there is no threat to the local population in the area of WW B with regards to natural radionuclides in drinking waters. However, parents should take care that their babies and young children do not consume more than 55 l or 170 l of drinking water per year, respectively.

9.4.6 Interpretation of Results from WW B, Ontario, Canada

Balancing of radionuclides in the investigated waterworks from Ontario was useful to investigate the major pathways of natural radioactive substances. However, the analysis did not lead to extraordinary results. The levels of uranium and radium isotopes were comparably low and the absence of modern water-treatment steps makes the balancing appear unnecessary. In fact, the low level of natural radioactivity lead to low net count rates. As a result, the error bars of the different water samples overlap and statements concerning removal efficiency are quite uncertain.

As in the waterworks from Germany, stock-flow analysis of radionuclides at WW B lead to an excellent agreement of input and output of radionuclides, despite the possible influence of measurement and sampling errors. In conclusion, balances seem to even be possible at waterworks without any major water purification steps to assess the stock-flow of radionuclides and other substances. However, the obtained results are not leading to additional information about major sinks and sources for natural radionuclides. As a consequence, work protection and dose-assessment do not profit from stock-flow in waterworks with the absence of water filtration processes.

The levels of natural radionuclides in the aquifer waters are in agreement with the geological settings of the respective aquifer. Wells I + II extract waters from a pore aquifer containing sediments that consist of sand and gravel, which originated from the weathering of meta-volcanic and igneous rocks from the Sudbury Structure. These rocks do not contain very high amounts of thorium and uranium, but the levels of radionuclides present in the water are still significant. The abstraction wells take water from a *medium radioactive* aquifer, since the summed up gross-alpha activity for long-lived radioisotopes in the raw waters is about 200 mBq/l. The radon concentrations are comparably low and originate from radium deposits within the aquifer. Since the velocity of the ground water in the aquifer is relatively low, the radon content of the raw water obviously stems from the immediate vicinity of the waterworks.

In fact, the levels of natural radioisotopes discovered in the Sudbury area were below the initial expectations. Geological maps and cross-sections were used to find hot spots of natural radioactivity the area, but the aquifer waters in the region contained less radioactivity than expected. This clearly implies that geological maps are not appropriate to identify areas with enhanced radioactivity on a small scale. It is recommended to always consider the individual case of a water treatment facility.

9.5 Investigation of Private Well Supplies in Ontario

During the sampling campaign in Ontario of summer 2002, several water samples from private well supplies have been investigated as well. The sampling locations were selected randomly in the Sudbury, Timmins, North Bay and Bancroft areas of Central and Northern Ontario. Only a few private well waters from North Bay and Bancroft areas revealed significant amounts of uranium, radium and radon.

Following the collection of waters, each sample has been acidified with nitric acid to assure a stable environment in the containers and to avoid an adsorption of radionuclides onto the container's material. The determination of uranium was performed by ICP-MS, which is the current state-of-the-art method for the measurement of uranium in water samples (refer to chapter 8.2.3, page 57). The investigated private well waters from Bancroft will be discussed in the following section.

9.5.1 Investigations in the Bancroft Area, Ontario, Canada

Bancroft is situated in the Grenville Province of the Canadian Shield (refer to Figure 29, page 100) and is considered as the "Mineral Capital of Canada" because of the famous variety and quality of mineral species, which can be discovered there. The region has been subject to many geological processes and the geology of the region is a complex mixture of different rock types, which accommodate many different minerals. The rocks in the Bancroft area are between 1.1 and 1.8 billion years old and have been subject to volcanic activity, glacial scouring, extreme heat and pressure, and intense faulting and folding. Further to the north toward Bancroft, the mineralization changes from base metals to the radioactive uranium ores.

Thirteen private households in the central and northern part of the City have been selected for random sampling. Some drinking waters from Bancroft revealed considerable amounts of ^{238}U. The maximum ^{238}U concentration encountered during the entire campaign in Ontario was found at a dwelling in Bancroft (126 mBq/l). The mean ^{238}U concentration of the investigated waters from Bancroft is about 30 mBq/l. Furthermore, the ^{222}Rn contents of tap waters were significant as well, ranging from 30 to 440 Bq/l. On the contrary, the discovered radium levels of the investigated drinking waters were comparably low and amount to a maximum concentration of only 17 mBq/l (Wisser & Hintelmann, 2003).

In the following section, one representative household from Bancroft will be discussed in detail and a dose assessment for the inhabitants will be provided.

9.5.1.1 Private Well water from a Household in Bancroft, Ontario

The five-person family living in the examined household gets drinking water from a private well, located in the immediate vicinity of the house. Ground water is abstracted via a deep well, which has been drilled into granitic rocks to a depth of 330 feet. The water is not treated by any water purification system and about 600-800 liters of water are produced per day (Wisser & Hintelmann, 2003).

The results of radionuclide determination are provided by Table 34. Samples have been taken from the kitchen's tap and the bathroom of the house.

Table 34: Natural radionuclides present in waters at a private household from Bancroft, Ontario

	^{238}U mBq/l	^{234}U mBq/l	^{226}Ra mBq/l	^{222}Rn Bq/l
Kitchen	114 ± 4	150 ± 18	17.2 ± 3.5	440 ± 45
Bathroom	126 ± 5	165 ± 20	15.0 ± 4.0	400 ± 40
Method	*ICP-MS*	*α-spectrometry*	*α-spectrometry*	*LSC*

As can be seen from the table above, the levels of long-lived natural radionuclides are significant. The radon concentrations can be regarded as minimum levels, because the sampling was difficult due to a spray nozzle at the water tap. It is very likely that a large portion of radon escaped from the tap during sampling. Unfortunately, it was not possible to take a sample from the raw water itself, because the well was not accessible. The levels of radioisotopes in the kitchen and bathroom can be considered to be equivalent. However, the levels of long-lived radionuclides present in tap water from the kitchen were used for the dose assessment (Table 35), since the kitchen is the major place for tapping drinking water. The maximum concentration of ^{228}Ra has been estimated to be about 10 mBq/l under the assumption that the ratio of ^{226}Ra/^{228}Ra is at least about 1.7 – 2.0.

Table 35: Total Indicative Dose for adults, children and babies from one year's consumption of drinking water from a private well in Bancroft, Ontario

	Adults (> 17 a) **730 l/a**	**Children (2-7 a)** **170 l/a**	**Babies (< 1 a)** **55 l/a**
^{238}U *(114 mBq/l)*	3.8 µSv/a	1.5 µSv/a	2.2 µSv/a
^{234}U *(150 mBq/l)*	5.4 µSv/a	2.3 µSv/a	3.0 µSv/a
^{226}Ra *(17.2 mBq/l)*	3.5 µSv/a	1.8 µSv/a	4.5 µSv/a
^{228}Ra *(10 mBq/l)*	5.0 µSv/a	5.8 µSv/a	16.5 µSv/a
TOTAL	18 µSv/a **0.018 ± 0.004 mSv/a**	11 µSv/a **0.011 ± 0.003 mSv/a**	26 µSv/a **0.026 ± 0.007 mSv/a**
Remark: The dose conversion factors used for calculating the TID consider the **committed dose** for adults (50 years), babies and children (70 years).			

The total indicative dose for babies, children and adults is far below the current limitation value of 100 µSv per year. The determination of ^{210}Po via MnO_2-coated discs was not successful for the water samples from Bancroft. As a consequence, the TID may be slightly higher than indicated in the table above. On the other hand, the total uranium concentration is 10 µg/l, which slightly exceeds the chemical limit of 9 µg/l for natural uranium that was recently proposed by the WHO.

It can be summarized that the levels of natural radioactivity in the private well supplies from Bancroft were higher than the levels of radionuclides in the investigated municipal waterworks from Ontario. The reason behind is that the Bancroft geological corridor hosts granitic magmatic rocks with a higher amount of natural radioactivity than the basic rocks from the Sudbury and Timmins area. Furthermore, the individual well waters were not treated at all and therefore a removal of radionuclides was not achieved.

The results are not representative at this point. Further investigations will be necessary to evaluate the situation in Ontario. Up to now, it is not possible to give any recommendations with respect to natural radioactivity in drinking waters from Ontario, due to inadequate number of wells that were investigated at this. Measurements of additional natural radionuclides (^{228}Ra, ^{210}Po) in the selected areas have to be performed to calculate a comprehensive dose assessment. The study was designed only as a first screening measurement in the colossal Province of Ontario and the results provide a first trend of which there will only be few private well waters with enhanced levels of natural radioactivity in the investigated areas of Timmins, Sudbury, North Bay and Bancroft.

9.6 Waterworks C, Black Forest, Germany

This public water treatment facility (WW C) is situated in the northern margin of the Black Forest and had mainly been selected for balancing due to the comparably low contents of natural radioactivity in the raw water. As mentioned earlier, a waterworks abstracting low radioactive aquifer waters should be included in this study as well. Another reason for investigating this facility is the water treatment, which involves different steps and residues from water treatment could be investigated as well.

The famous Black Forest is located in the southwestern part of Germany and mainly consists of a crystalline basement composed of granites and gneisses of variszic and pre-variszic origin. Sediments of the Permian and Triassic cover these magmatic and metamorphic rocks, especially in the eastern and southeastern part of the region. The crystalline basement of the northern part is covered by sediments of the Rotliegendes period, mainly composed of conglomerates, arkoses, sandstones and siltstones. The investigated waterworks is situated in the Baden-Baden-Basin, where different clastic sediments of more than 800 m thickness have been deposited in alternating layers during the Permian period (Walter, 1995).

The granitoid rocks of the Black Forest host a variety of mineral deposits; including lead, zinc, silver and uranium ore. Uranium exploration took place in Menzenschwand, a small mining location in the St. Blasien area in the southern part of the Black Forest. The uranium content of this deposit is present in a fluorite and barite association (Walter, 1995). It is well known that the Black Forest belongs to the regions in Germany with the highest levels of natural radioactivity in ground- and drinking waters.

9.6.1 Description of the Waterworks

WW C was put into service in 1992 and collects raw waters from 18 natural springs. This facility supplies drinking water for several villages in the Baden-Baden area occupied by 4,000 inhabitants altogether. In 2002, the total amount of produced drinking water was about 226.500 m^3.

Water treatment:

The raw waters from the natural springs are collected and subsequently given into the two de-acidification filters. These filters have a volume of about 10 m^3 each and contain a special dolomite for water de-acidification.

The following phase consists of a simple mixing of the treated waters. Finally, the filtered water is treated with a UV-unit for disinfecting purposes. After the disinfection, the water is collected in a pure water chamber before it is pumped to a high reservoir, which is located next to the villages. The sludge from filter backwashing is collected in a large slurry tank located next to the waterworks. The waterworks building primary consists of a large filter hall and a small chamber, where the pure water tanks are situated. Adjacent to the building, a huge slurry tank was installed for collecting residues from filter-backwashing.

9.6.2 Determination of Natural Radionuclides

In accordance to the different treatment steps in WW C, the following waters have been subsequently sampled and analyzed for natural radioisotopes:

I. Raw water
II. Exit Filter 1
III. Exit Filter 2
IV. Pure water
V. Tap water from a private household

Several sample replicates have been taken from each sample location. The results provided in the following section will generally represent the mean value of the multiple measurements.

9.6.2.1 Gross-Alpha and Gross-Beta Activity

The determination of these screening parameters was achieved with a LSC counter via α-/β-separation. The samples were measured for 72,000 sec, leading to a LLD of 0.3 Bq/l for gross-alpha and 2.0 Bq/l for gross-beta activity. The samples were analyzed after a standing time of 3 months, assuming that radon and its short-lived daughter isotopes decayed entirely during the storage.

As expected, the water samples from WW C did not expose enhanced levels of gross-alpha and gross-beta activities. However, it has to be mentioned that the LLD's for the screening parameters were higher than required by the legislator. As a consequence, the different samples have been carefully checked for long-lived natural radionuclides.

9.6.2.2 Radon in Water

The determination of ^{222}Rn was performed after radon extraction in an organic szintillation cocktail. The samples were measured for 1,800 sec, leading to a detection limit of < 1.0 Bq/l.

Table 36 indicates the radon activity concentration of the samples taken from WW C with respect to different sampling dates.

Table 36: ^{222}Rn levels at WW C with regards to different sampling dates

Sample	*May 14, 2002 ^{222}Rn (Bq/l)*	*May 29, 2002 ^{222}Rn (Bq/l)*
Raw water	42 ± 4.0	19 ± 2.5
Exit Filter 1	34 ± 3.5	16 ± 2.5
Exit Filter 2	32 ± 3.5	14 ± 2.5
Exit disinfection (UV)	30 ± 3.0	14 ± 2.0
Pure water	15 ± 2.0	8 ± 1.0

Within a period of only two weeks, the determined ^{222}Rn levels revealed an immense fluctuation of the radon concentration. On May 29th, the radon levels were only about 50 % of the radon concentrations measured 14 days ago. The reason behind is that the spring waters are influenced by rainwater that enters the aquifers rapidly. After a raining event, almost radon-free rainwater dilutes the radon concentrations.

9.6.2.3 Uranium Isotopes in Water

The water samples were investigated for uranium by using uranium extracting PAMOX discs and subsequent alpha-spectrometry. Unfortunately, uranium isotopes were not detectable in the different waters from WW C. All the samples contained uranium levels only below the LLD of 10 mBq/l. As a consequence, stock-flow analysis and balancing could not be calculated for uranium at this particular water treatment facility.

9.6.2.4 ^{226}Ra in Waters from WW C

The measurements for ^{226}Ra were performed via the use of radium adsorbing MnO_2-discs and results for ^{226}Ra determination are compiled in Table 37.

Table 37: ^{226}Ra levels in WW C at different sampling dates

Sample	*May 14, 2002 ^{226}Ra (mBq/l)*	*May 29, 2002 ^{226}Ra (mBq/l)*
Raw water	9.3 ± 2.0	15.7 ± 3.0
Exit Filter 1	< 5.0	13.9 ± 2.5
Exit Filter 2	< 5.0	11.6 ± 2.5
Pure water	< 5.0	10.2 ± 2.0
Consumer	< 5.0	< 5.0

The first sampling did not lead to satisfactory results for radium determination, since ^{226}Ra was only detected in the raw water. However, the second sampling campaign discovered radium in all samples from WW C, except the drinking water at the water tap of a private household.

The ^{226}Ra levels detected on that special day range from 10.2±2 to 15.7±3.0 mBq/l and are comparably low. The results indicate a removal of radium during water purification in the order of 30 %. However, the measurement errors are comparably high due to the low count rate for ^{226}Ra. Hence, an assessment of the removal efficiency for radium is not possible.

9.6.2.5 Natural Radioactivity in Indoor Air

A complete balance for radon has to consider the deficiency of ^{222}Rn due to degassing during water collection in the pure water tank. Hence, it was necessary to measure the indoor radon concentration in the aeration room on the cutoff-date. This was achieved by use of a pulse ionization chamber, which was placed in the pure water chamber. For the duration of the measurements, the room was locked. The course of the indoor radon concentration over the period of nine days is presented in Figure 37.

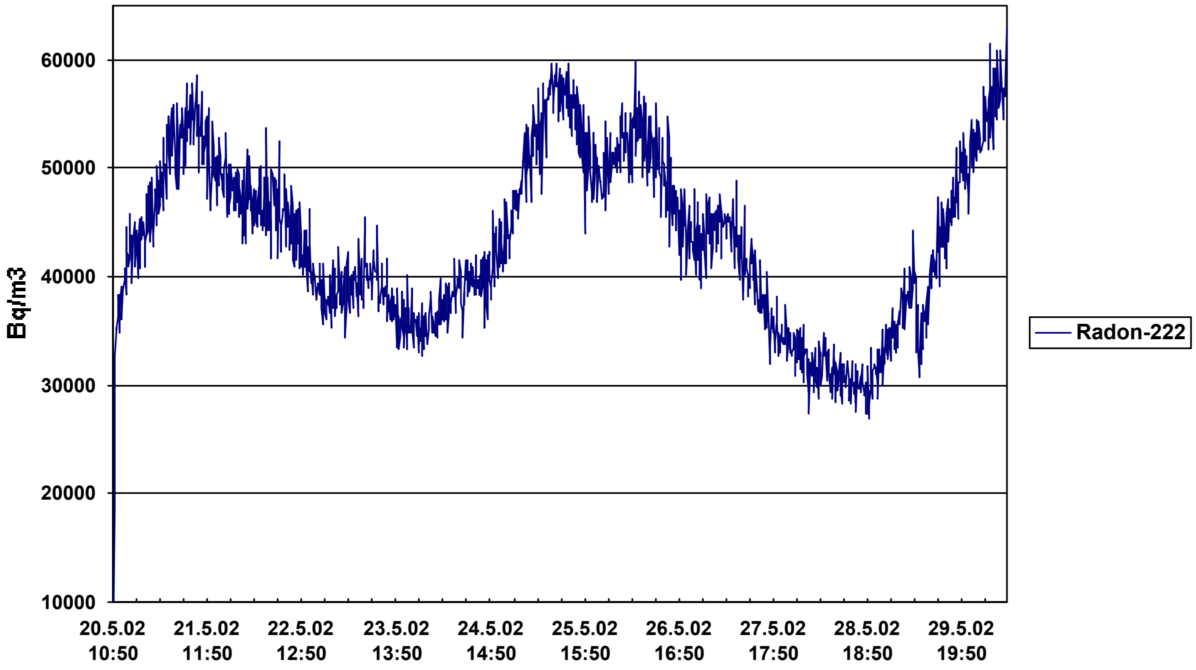


Figure 37: ^{222}Rn in indoor air of the water collection chamber in WW C

The results of ^{222}Rn determination in the aeration chamber are surprisingly high and amount to 43 kBq/m^3 in average. The maximum value for radon in indoor air is close to 62 kBq/m^3. It is obvious that the radon concentration fluctuates extremely within the 9 days of measuring. This is mainly attributed to the natural fluctuations of the radon content in the spring waters. If pure water is pumped into the chamber, degassing takes places and waterborne radon degasses very quickly. This would always lead to an increase of radon in indoor air. On the contrary, the radon concentration decreases rapidly when no treated water is pumped into the chamber. The reason for this is that “radon-free” air enters the chamber from adjacent rooms because the sealing of the chamber is insufficient. Furthermore, there is breeze of fresh air from outside into the building, in dependence of the air pressure conditions. Radioactive decay of ^{222}Rn is not a major contributor to the decrease since the half-life of ^{222}Rn is much larger than the observed decrease of activity concentration.

The average ^{222}Rn concentration for the cutoff-date is 43 kBq/m^3, whereas the minimum concentration amounts to 18.5 kBq/m^3. The maximum radon level was detected in the final hours of the 9th day and is close to 62 kBq/m^3. Sampling in WW C took place in the early afternoon of May 29, 2002. The ^{222}Rn reference concentration considered for the calculation of stock-flow is 40 kBq/m^3. This value was detected at 2.00 p.m., while the water sampling was performed.

9.6.2.6 Radionuclides in Residues from Water Treatment

The residues from WW C are mainly composed of liquid sludge from filter-backwashing. According to the facility management, the Filters 1 + 2 are backwashed once in a fortnight to remove iron- and manganese-containing particles from the filter grains. The sludge from backwashing is collected in a large slurry tank, situated adjacent to the waterworks building. This basin is frequently emptied and the sludge is then taken to agricultural fields as fertilizer. The total amount of sludge is only about 1-2 tons per year.

The determined amount of natural radioactivity in the sludge is really low. Only ^{226}Ra could be detected at negligible concentrations about 20 Bq/kg (dry-matter). Since the raw water of this facility does not contain significant amounts of natural radioisotopes, the sludge is consequently not contaminated with long-lived radionuclides.

9.6.3 Stock-flow and Balances for Waterworks C

The cutoff-date for balancing radionuclides in WW C was May 29, 2002. Water abstraction and treatment were performed without any disturbances on that special day. The total amount of extracted water from the springs was 683 m^3. It can be assumed that May 29, 2002, stands for a typical day of water treatment at this facility. In addition to that, water sampling and determination of radioisotopes could be accomplished without any problems.

Due to the low levels of radionuclides at this waterworks, stock-flow will only be provided for ^{222}Rn and ^{226}Ra. Since these two isotopes are not removed quantitatively from the raw water, the calculation of detailed balances seems to be unnecessary.

The levels of stock-flow of radionuclides are provided in Bq/d **above the arrows** and the radon concentrations in the waters are indicated as Bq/l **below the arrows**. The size of the arrows indicates the contribution of the respective water, but they are not to scale. Furthermore, it has to be kept in mind that the statistical nature of radioactivity is a major uncertainty for the calculation of stock-flow.

9.6.3.1 Stock-flow Analysis and Balance for ^{222}Rn

The calculation of stock-flow for ^{222}Rn is sophisticated because this particular isotope is stripped out off the water in the pure water tank. On the other hand, the count rate for radon was high, which results in low 2-sigma errors. Stock-flow for radon is illustrated in Figure 38.

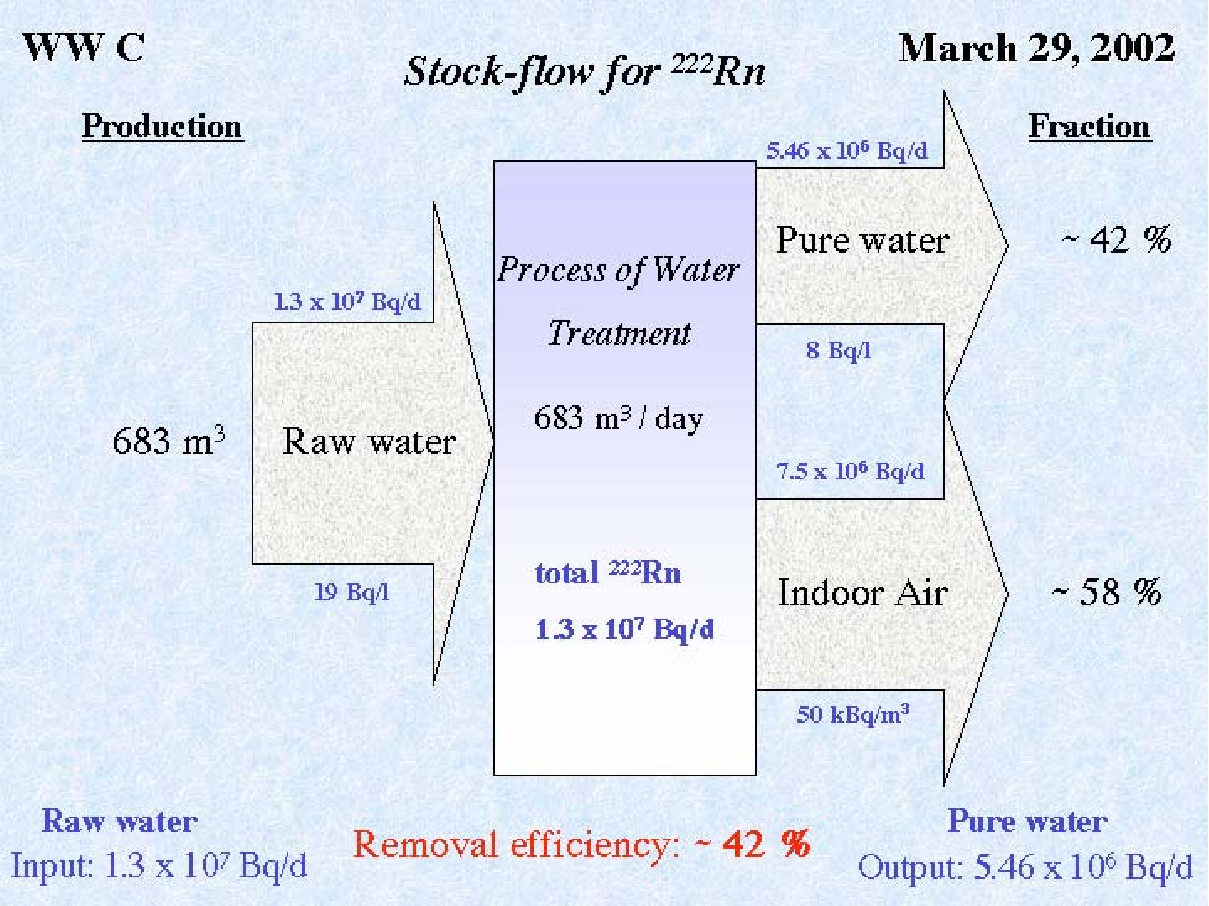


Figure 38: Stock-flow analysis for ^{222}Rn in Waterworks C on March 06, 2002

The stock-flow analysis for ^{222}Rn at WW C revealed that only the degassing of radon in the pure water chamber removed radon from the water. The total concentration of radon input in WW C amounts to 13 MBq/d and the daily output amounts to only approx. 5.5 MBq, distributed in 683.000 liters of water. Furthermore, it became obvious that the filters in this waterworks do not remove dissolved radon from the raw waters quantitatively. The importance of work protection at radon-related workplaces is strained by the illustration of stock-flow. Almost 8 MBq of ^{222}Rn are released into the indoor air of the aeration room per day, distributed in a volume of 150 m^3. The theoretical radon concentration in the indoor air of the investigated chamber is 50 kBq/m^3. The measured radon concentration on the cutoff-date was approx. 40 kBq/m^3. Since the chamber is not perfectly sealed, the deviation between calculated and measured radon concentration can be neglected.

9.6.3.2 Stock-flow Analysis and Balance for ^{226}Ra

Since the determination of ^{228}Ra in water samples is difficult and time consuming, only ^{226}Ra was included in the investigation. The graphical illustration of stock-flow for ^{226}Ra is presented in Figure 39 under the assumption that the measurement errors for ^{226}Ra are negligible.

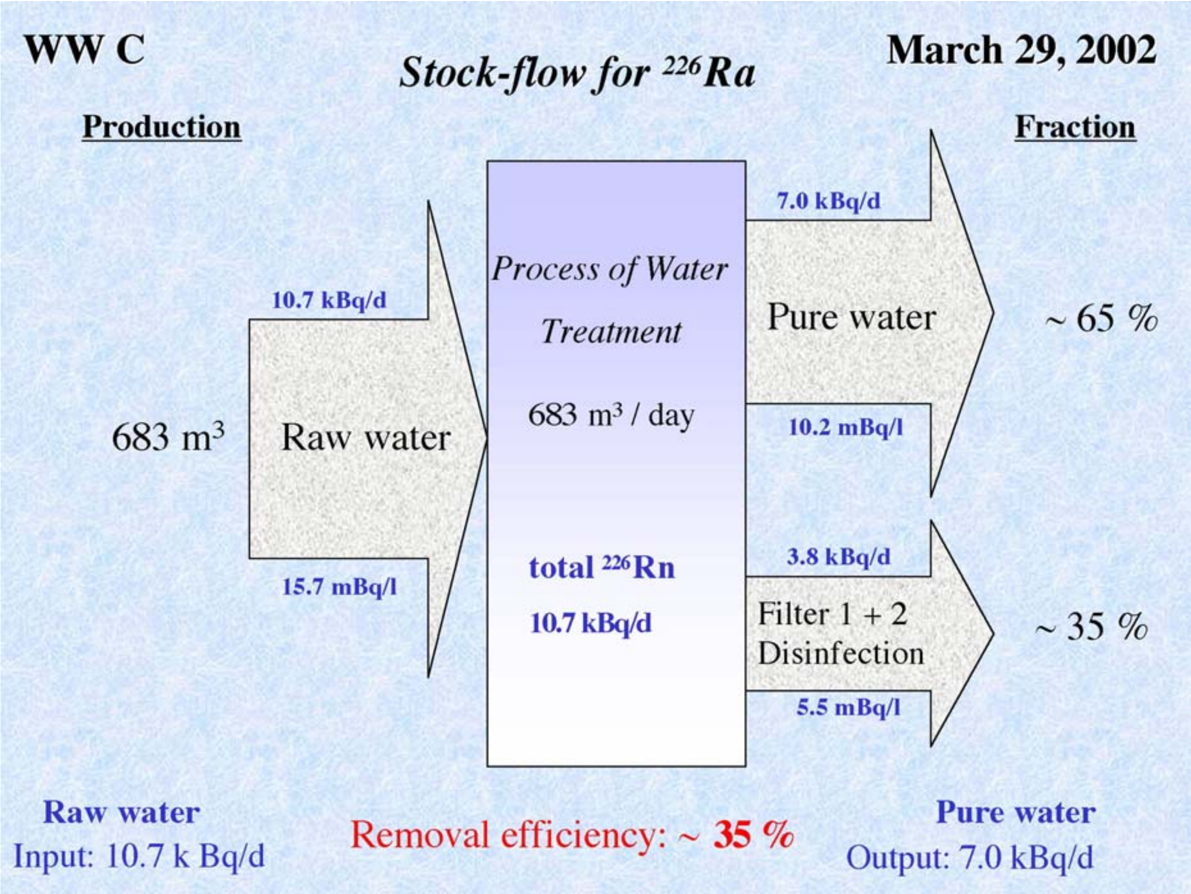


Figure 39: Stock-flow for ^{226}Ra at WW C

Despite the uncertainties from the measurement errors, the calculation of stock-flow was possible and the indicated levels of ^{226}Ra are comprehensive. The removal yield for radium at this facility amounts to approx. 35 % and the abstracted ^{226}Ra concentration is only about 10 kBq per day. In this special case, stock-flow analysis did not lead to any major results and the consideration of the measurement errors leads to overlapping error bars. As a consequence, stock-flow analysis should not be performed at such low levels of natural radioactivity.

9.6.4 Dose Assessment for the Population

The levels of long-lived natural radioisotopes in the waters from WW C are very low and a dose-assessment for the population has not to be carried out explicitly. It is apparent that the TID for the people living in the area is far below the limitation value of 0.1 mSv per year.

9.6.5 Interpretation of Results from WW C, Black Forest, Germany

As expected in the forefront of the investigation, the levels of natural radioisotopes in the waters at WW C are very low. This water treatment facility abstracts low radioactive aquifer waters and the detected levels of radioactivity correspond to geological environment. The present sediments from the Rotliegendes period only contain very little amounts of uranium and other long-lived natural radionuclides.

Unfortunately, stock-flow analysis could only be carried out for ^{222}Rn and ^{226}Ra. The results for ^{222}Rn seem to be coherent and revealed the major sink for this isotope, which is the degassing of volatile radon in the pure water chamber. On the other hand, the calculation of stock-flow for ^{226}Ra is untrustworthy, because of the comparably high measurement errors. Other radionuclides are not present in waters and residues from this facility, which leads to a very low total indicative dose for the local population.

Balancing of radionuclides in the presented waterworks was not applicable to investigate the major pathways of natural radioactive substances. This is due to the very low levels of radioactivity in the investigated waters and sludge.

10 Conclusion

The main intention of this section is to point out the achievements of the investigations described in the experimental part. The main purposes of the experimental part can be summarized as follows:

- **application of radionuclide-extracting planar discs for the radiometry of natural radionuclides in water supply**
- **utilization of stock-flow analysis for quantification of major sources and sinks**
- **first-time balancing of natural radionuclides in water supply**

The application of radionuclide-adsorbing planar discs has proven the excellent reliability and reproducibility of the methods. The entire sampling preparation procedure is fast, simple and efficient, if a few rules and instructions are taken into account. The adsorption yield for radium and uranium is outstanding and amounts to 90 ±5 % and 84 ±5 %, respectively. However, the adsorption efficiency for polonium only amounts to about 60 % and strongly depends on the pH of the respective water sample.

The method using MnO_2-coated discs for radium extraction is applicable for untreated ground- and drinking water samples that have low barium (< 1 mg/l), strontium (< 10 mg/l) and calcium contents only. Otherwise, these competing ions negatively affect the adsorption efficiency or calcium might precipitate onto the surface of the disc. In this case, Na_2EDTA should be poured into the water sample and a dilution with distilled water is recommended for high-mineralized waters, such as thermal waters.

This applies for the uranium-extraction via PAMOX discs as well, because water samples containing ^{238}U concentrations of > 10 Bq/l could not be examined with this procedure. In such as case, special sample pre-treatment, such as dilution with distilled water, should be applied to determine the uranium concentration.

In summary, the investigated MnO_2-coated discs can be used for radium and polonium determination in ground and drinking waters, mostly without any sample pre-treatment. The commercially available PAMOX discs are highly applicable for uranium determination in ground- and drinking waters, which contain uranium concentrations below 10 Bq/l.

Further advantages lie in the reproducibility of the method and the low costs for purchasing radionuclide-adsorbing discs. It has to be emphasized that the determination of adsorption yield can be achieved easily by the subsequent exposition of 2-3 identical discs in the same water sample. Furthermore, the use of an internal standard increases the reliability and reproducibility of the method. It is recommended to spike a ^{209}Po solution into every water sample since the adsorption yield for polonium is not uniform, especially under varying pH-conditions. However, the use of internal standard in radium and uranium containing samples is not essential.

The second main achievement of the experimental part was the first-time application of stock-flow analysis to assess the occurrence of natural radionuclide in water supply. This innovative tool seems to be highly applicable for the calculation of stock-flow in the defined system of water supply. Stock-flow analysis could be utilized to calculate the removal efficiency of water treatment processes and the major sources and sinks for radioisotopes. Work protection and radiological protection for employees can especially benefit from the identification of the pathways of radionuclides.

In this study, stock-flow analysis was feasible at a waterworks in the German Rhine-Nahe-Area. The analysis revealed the main pathways of radioisotopes and discovered that the filter systems are almost exhausted and do not remove dissolved uranium and radium quantitatively. Not only that, it was also revealed that water aeration leads to an enrichment of airborne radon in the waterworks building. The radon concentration in the water aeration chamber is extraordinarily high and amounts to 42 kBq/m^3 in average. As a result, recommendations for the facility management with respect to radiological protection could be given.

Another example for stock-flow analysis was provided for a waterworks in Ontario, Canada. The amounts of radioisotopes were sufficient to calculate stock-flow, but no additional results could be obtained here. This is due to the absence of any water filtration step at this waterworks. Thus, the radionuclides are not removed quantitatively from the raw water and are passing through the waterworks without major changes in concentrations.

In conclusion, a calculation of stock-flow is only feasible if the amounts of radioisotopes present in water supply are explicitly above the LLD of the respective isotopes. Otherwise, the measurement errors do not allow a reliable assessment of the situation in a waterworks. It can be concluded that stock-flow analysis should only be performed if the water treatment facility abstracts medium or high radioactive aquifer waters. In addition to that, different water treatment steps, such as aeration and filtration, should exist.

The third objective of the experimental part was the first-time balancing of natural radionuclide in the entire pathways of water supply. Calculation of stock-flow provided the basics for the balances and the main advantages and restrictions from stock-flow analysis apply here as well. Balances can contribute to identifying the sources and sinks for radionuclides, since a balance has always to be in agreement. The input and output goods (“radioisotopes”) have to be exactly balanced. This is only achievable if the levels of radionuclides in the considered system are sufficiently high enough to allow a defaulting of measurement errors. The radioactive decay of the radionuclides investigated in this study was neglected, since the half-lives of the isotopes are very high in comparison to the duration of the respective cutoff-date. This even applies for ^{222}Rn, because the retention time of radon in a waterworks is comparably low and only amounts to a few hours. However, the delivery of treated water from the waterworks to the consumer takes longer than a few hours. As a consequence, radioactive decay and degassing of ^{222}Rn from water have to be considered.

The balances for the important radioisotope ^{238,234}U, ^{226}Ra and ^{222}Rn were almost exactly in agreement for the waterworks from the German Rhine-Nahe-Area and from Central Ontario, Canada. This especially counts for the isotope ^{222}Rn since the count rates for this particular isotope were comparably high. Furthermore, balancing of radioisotopes at WW A (Rhine-Nahe-Area, Germany) discovered that the residues from water treatment are highly contaminated with long-lived natural radioisotopes, such as ^{238,234}U and ^{228,226}Ra. Unfortunately, the levels of radionuclides present in the waterworks from the Northern Black Forest, Germany, were mostly below the LLDs for the radionuclides of interest. As a consequence, balances could not be provided for all natural radioisotopes.

It can be summarized that stock-flow and balances can only be calculated if the 2-sigma-errors of the measurements are low enough for the calculation of stock-flow. This is only achievable with long measurement times and high count rates, respectively. Otherwise, the calculation of stock-flow and detailed balances appears to be untrustworthy.

11 Possible Problems for Water Suppliers in the European Union

The *European Drinking Water Directive* affects the entirety of the water supply companies within the European Union. Water suppliers will be compelled to determine natural radioactivity in their drinking waters sooner or later, in dependence of the national legislation. This in the first place will result in additional expenses for sampling and measuring. However, enhanced levels of natural radioactivity will only be present in the minority of the tap waters. The main geological areas of risk are almost completely identified, but on the other hand, some ground waters might contain elevated levels of natural radioisotopes even in low background radiation areas.

Radon is not feasible as screening parameter for natural radioactivity present in potable waters. There is no evident correlation between the radon content of a drinking water sample with the levels of long-lived natural radionuclides. It is possible that radon-free water samples contain very high amounts of uranium and radium, respectively. In addition to that, the radon concentration probably decreases quantitatively during the delivery from the waterworks to the consumer due to radioactive decay and degassing.

Gross-alpha and gross-beta activities can only be considered as screening parameters. These parameters are not satisfactory for a compliance with the TID of 0.1 mSv per year. If the total gross-alpha activity of 0.1 Bq/l is only attributed to ^{238}U, the annual TID for babies would be about 2 µSv. On the contrary, 0.1 Bq/l of ^{210}Po corresponds to a TID of 143 µSv/a for babies. This indicates that water suppliers should not confide in the screening parameters only. Since there are no better screening methods available yet, water suppliers have to be satisfied with gross-alpha and gross-beta activities.

Natural fluctuation in radionuclide concentration may occur during the period of a year. In such as case, multiple measurements are required to achieve compliance with the new regulations.

The main concerns for water suppliers can be summarized as follows:

- **Disposal of radioactive waste** arising from water treatment is not yet regulated in all Member States of the EU and could be very expensive in dependence of the levels of long-lived radioisotopes.
- **Radiation Protection** could be necessary to protect employees at waterworks:
    - ***Radon in indoor air at workplaces*** is of major health concern
    - ***Gamma dose rate in the proximity of filters*** may be elevated
    - ***Air-dehumidifiers*** may accumulate high levels of radon decay products and contribute to elevated gamma dose rates
    - ***Handling of contaminated waste*** may lead to enhanced gamma dose rates for workers as well.

- Waterworks in the vicinity of nuclear power plants may **exceed the limitation value for tritium** (100 Bq/l) – especially if surface water is abstracted. A marketable removal method for ^3H from raw water is not available yet
- Expensive **removal processes for radionuclides** may be necessary to fulfill compliance with the new standards
- **Multiple measurements** may be required due to natural fluctuations in radionuclide concentration and the measuring expenditure may be costly
- **Public information policy** may be problematical due to the existing prejudices against radioactivity in general

Detailed recommendations for water supply companies will be provided in chapter 13, page 130.

12 Possible Problems for Water Suppliers in Ontario, Canada

The circumstances for water suppliers in Ontario are quite different compared to the conditions in the EU. Maximum acceptable concentrations are already in force for all the important natural radioisotopes (including long-lived radon decay products) and major exceptions do not exist. The regulations are clearly defined in the *Drinking Water Systems Regulation* and the responsible authorities publish recommendations for affected waterworks regularly. However, the disposal of radioactive residues from water purification is not regulated by any ordinance. On the other hand, only a small fraction of the waterworks in Ontario accumulates residues from ground water treatment. Thus, the vast majority of Ontario's water supply companies will not be negatively affected by the new regulation. However, the obligatory water quality reports have to include parameters of natural radioactivity in the future.

On the contrary, the occurrence of radionuclides in private well waters is not restricted by the new legislation, as long as the water is not served to the public and less than six residences are served. As a consequence, the major concern with respect to natural radioactivity in potable waters lies on the thousands of families that satisfy their water demand via private wells.

13 Recommendations for Water Supply Companies

The recommendations for water suppliers provided in this section represent the opinion of the author and they go further than the requirements of the national legislation. The suggestions introduced in this section are exclusively given for European water suppliers, since the situation in Canada is more transparent than within the European Union.

Unfortunately, detailed recommendations for water suppliers regarding the new legislation in Europe do not exist at this point. In Germany, the radioactivity parameters of the amended *Trinkwasserverordnung* will enter into force in a few months or to be exact in December 2003.

However, the German legislator and the competent authorities have not yet published any regulations or suggestions how to achieve a compliance with the new ordinance. Furthermore, the appropriate sampling and measuring procedures for natural radionuclides are not regulated at this point. This situation is unsatisfactory for water supply companies, especially in areas with high radioactive aquifer waters, such as Erzgebirge, Fichtelgebirge or Black Forest.

Catalogue of recommendations:

The following list provides detailed suggestions for water suppliers with respect to natural radioactivity. The recommendations should be considered for future actions in waterworks regarding radioactivity present in raw and drinking waters.

I. **Application of screening methods**

The geology and hydrochemistry of aquifers may change rapidly over short distances and geological maps are not applicable for an assessment of water quality. Thus, water supply companies should utilize screening methods for natural radionuclides present in drinking waters. This even applies for waterworks in “non-risk areas”, such as Northern Germany or the Netherlands. It is highly suggested to perform screening measurements (gross-alpha, gross-beta activities) before the new legislation is enforced in a few months. As mentioned earlier, screening methods are probably not sufficient but they can provide a first trend. Since the occurrence of the radioisotope $^{3}\mathbf{H}$ is also restricted in potable waters, determination for this isotope has to be performed as well.

II. **Performance of multiple measurements**

Natural fluctuations and variations in radionuclide concentrations of aquifer waters may lead to a miscalculation of the TID for consumers. It is suggested to perform multiple measurements throughout the year to prove the compliance with the new limitation values.

III. Calculation of total indicative dose (in accordance to legislation)

If the screening reveals considerable activity concentrations for gross-alpha or gross-beta, a detailed determination of single radionuclides has to be carried out. The main radionuclides of importance for calculating the TID are:

$$\mathbf{^{238}U, ^{234}U}$$
$$\mathbf{^{228}Ra, ^{226}Ra}$$

The isotopes $\mathbf{^{210}Po}$ and $\mathbf{^{210}Pb}$ should be determined as well because they are of major health concern due to ingestion from drinking water and will be restricted by the legislator sooner or later. The European Commission has recently published recommendations for these long-lived radon decay products and an agreement with these recommendations will be advantageous for water suppliers. This applies for $\mathbf{^{222}Rn}$ as well, since the European Commission recommends a maximum acceptable concentration between 100 - 1,000 Bq/l. For radon concentrations exceeding 1,000 Bq/l remedial action should be taken with respect to radiological protection.

IV. Removal of radionuclides from drinking waters

The adequate treatment techniques for removing radionuclides from raw waters have been introduced in section 7.2, page 51. They should be applied, if the calculated TID violates the new limitation value of 0.1 mSv per year for any age group.

V. Determination of radionuclides in residues from water treatment

The next step has to comprise of the determination of long-lived radionuclides in residues from water treatment. Currently, this point is not of an urgent nature since there exist no official regulations concerning a disposal of wastes from water purification yet. However, measurements of the gamma dose rate in the vicinity of filters and slurry tanks should be performed. This is done to get a first impression of a possible enrichment of long-lived radionuclides in the residues.

VI. Application of stock-flow analysis

This modern procedure is highly applicable for identifying the major sources and sinks for radionuclides and provides important information for the pathways of radioisotopes. Furthermore, radiological protection for workers especially benefits from stock-flow analysis.

VII. Radiological protection for workers at water related workplaces

Radiation protection for employees in waterworks is getting an increased attention. This action includes radon at workplaces in waterworks and enhanced gamma dose rates in the vicinity of filters and air-dehumidifiers. Radon removal from indoor air at waterworks is quite simple and can be achieved by implementing relatively cheap air ventilation systems as discussed in chapter 7.1.1, page 44. Since elevated gamma dose rates are not “removable”, frequent exchange of the filter material may prevent an extraordinary accumulation of long-lived radioisotopes in filters. In addition to that, the duration of stay of workers in the proximity of contaminated filters and air-dehumidifiers should be monitored and restricted, if necessary.

VIII. Application of innovative methods for radiometry

Water supply companies could perform the required measurements themselves, if they own a water analysis laboratory. The introduced methods of using uranium- and radium-adsorbing discs can be a reasonably priced alternative compared to classical radiochemistry. If an analysis within the company is not achievable, only experienced and accredited laboratories should be assigned with the measurements.

IX. Construction of new waterworks

From now on, water supply companies have to definitely consider natural radioactivity when planning to build a new waterworks or when drilling new abstraction wells. Since the geological settings might change rapidly over short distances, it could be reasonable to relocate the wells to an area with low radioactive aquifer waters when necessary.

X. Information policy

Water supply companies with enhanced levels of natural radioactivity in their waters, residues or at workplaces should immediately report to the competent authorities. The authorities will provide more information about radiological protection for workers and will instruct the disposition of contaminated residues from water purification. In addition to that, the actual levels of radionuclides in drinking waters should be included in the water quality reports that are regularly introduced to the public.

The fundamental steps of the suggested procedure for water suppliers are summarized and illustrated in Figure 40.

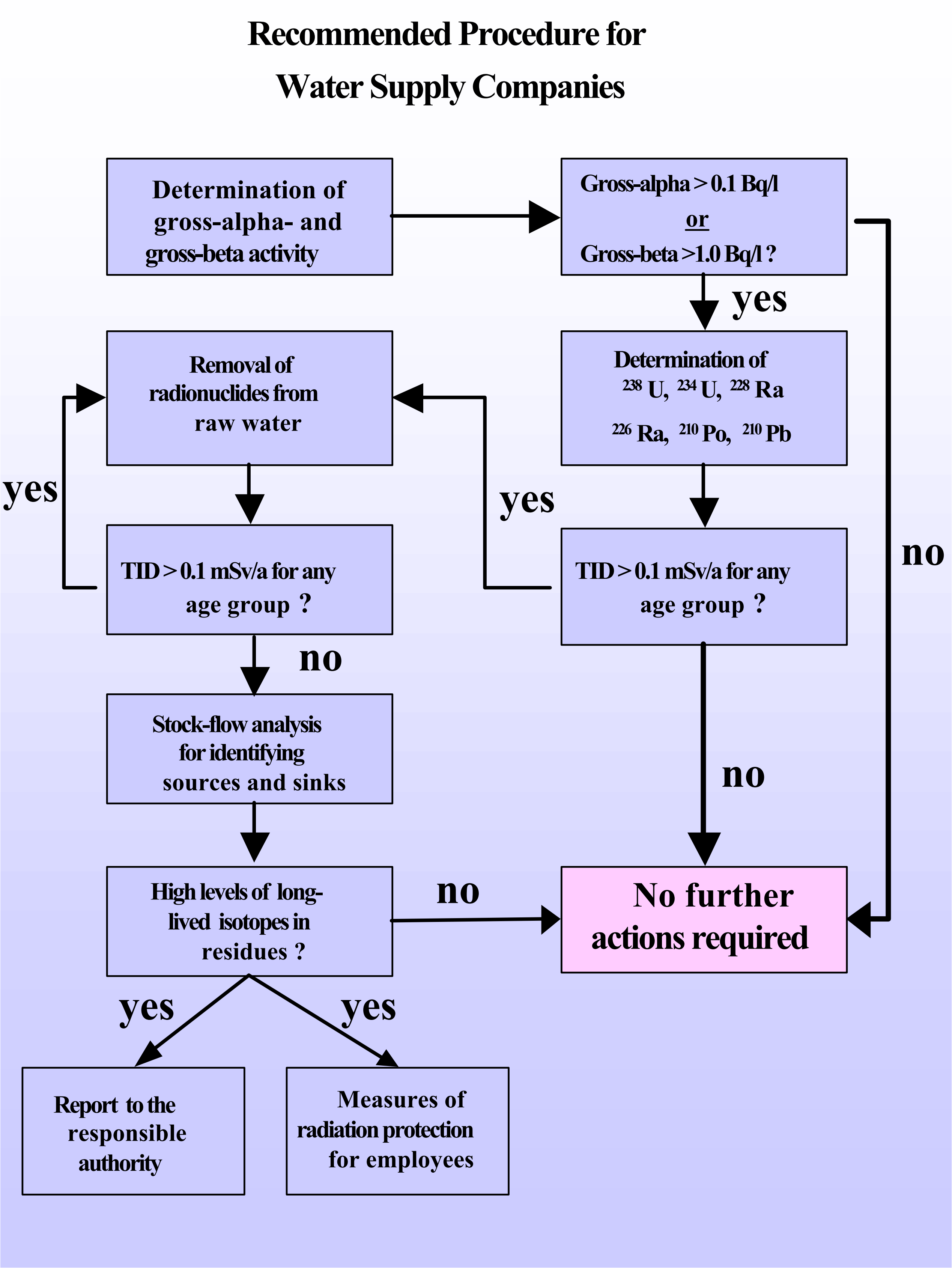


Figure 40: Flow-chart of recommendations for water suppliers

14 Final Thoughts and Prospects

Natural radioactivity now belongs to the parameters of water quality and will obtain increasing attention from the broad public. Water supply companies have to deal with completely new fields, such as radiological protection and removal of radionuclides from drinking waters. As already mentioned, this will result in additional costs for sampling and measuring, which will be shifted to the consumer by an increase of prices for drinking water.

From the perspective of consumer protection it is crucial that possible contaminants will be restricted in the most important human nourishment: drinking water. However, the new limitation values set in the TID seem to be very low compared to the fluctuations of natural radionuclides in the environment. The average effective dose for humans, in dependence of the local conditions, is about 2.4 mSv/a. The levels for external radiation doses range from less than 1.0 mSv to 100 mSv per year on Planet Earth (Michel, 2001). In comparison to these natural variations, a limitation value for the TID of 0.1 mSv/a appears to be questionable.

In addition to that, medical research and epidemiology have not yet found clear connections between increased cancer rates and the consumption of “radioactive” drinking waters. An exemption may be made for uranium, which is undisputedly hazardous due to its chemical properties as a heavy metal. Natural radioactivity has always been present in waters for human consumption and the development of complex organic life took place despite high levels of natural radioactivity.

The problems for water suppliers due to the new legislation are surely manageable after a sufficient transition period. Innovative procedures, such as stock-flow analysis and balances will support water suppliers to tackle the occurring problems with respect to natural radioactivity. Furthermore, simple and cheap measurement procedures, such as the radionuclide extracting discs, will contribute to decrease the costs for the determination of long-lived radionuclides.

There is still a demand for research in the field of radioactivity and water supply. In the first place, contaminated residues from water treatment require additional investigation. The removal of radionuclides from contaminated filter material seems to be an interesting field, since the expenditures for a disposition of radioactive wastes are dependent on the volume of the waste. Another field for future research is the occurrence of ^{228}Ra, ^{210}Po and ^{210}Pb in drinking waters, since there are almost no data available regarding these isotopes. It is well known that these isotopes belong to the most hazardous radionuclides present in the natural environment.

Alternative and affordable removal techniques for long-lived radon decay products in drinking water, such as ^{210}Po and ^{210}Pb, have to be developed and optimized in the near future, since the legislator will surely restrict these isotopes within a few years.

The development of on-line measurement techniques for the most important natural radioisotopes could be a significant objective for further studies. A continous determination of screening parameters, such as gross-alpha and gross-beta activites, would be an important step to assess the fluctuations and variations of radionuclide concentrations in natural waters. A first study regarding on-line monitoring of gross-alpha activity in natural waters was just published during the conclusion of this project (Hughes & DeVol, 2003).

Finally, the introduced measurement procedures utilizing radionuclide-adsorbing discs should be further optimized. It seems to be desirable to reduce the measurement time for the planar discs by any means to achieve low detection limits, since time is the most expensive and most valuable factor in radiometry.

15 Summary

Natural radioactivity present in drinking water has gained an increased attention since medical and biological research discovered that radiation exposure due to the ingestion of radionuclides can be harmful to humans. As a consequence, new regulations were passed in the European Union and the Province of Ontario, Canada. The amended ordinances now include limitation values for the annual total indicative dose (TID). The new legislation leads to additional problems and uncertainties for water supply companies.

This thesis has provided sophisticated solutions and suggestions for affected water suppliers by introducing the first comprehensive catalogue of recommendations for waterworks with respect to natural radioactivity. The list of recommendations includes important steps, such as application of screening methods, removal of radionuclides from drinking waters and radiological protection for employees. These suggestions could be carried out with the detailed investigation of two typical waterworks in Germany and one water treatment facility in Ontario, Canada.

Three new categories for natural radioactivity in ground waters are suggested in this thesis, based on the geological and hydrological settings of the respective areas. This was done to possess a simple tool to classify aquifer waters **only** with regards to the new limitation values for drinking water. The classification does not consider radon and short-lived radon decay products.

The new categories being suggested are:

- ***L****ow* ***R****adioactive* ***A****quifer* ***W****aters (LRAW)*
  Gross-alpha activity < 0.1 Bq/l and gross-beta < 1.0 Bq/l
- ***M****edium* ***R****adioactive* ***A****quifer* ***W****aters (MRAW)*
  Gross-alpha activity 0.1 - 1.0 Bq/l or gross-beta 1.0 - 10.0 Bq/l
- ***H****igh* ***R****adioactive* ***A****quifer* ***W****aters (HRAW)*
  Gross-alpha activity > 1.0 Bq/l or gross-beta > 10.0 Bq/l

As announced in the introduction, the challenging scientific objective of this thesis was the first-time balancing of natural radionuclides in drinking water supply. This difficult goal was entirely achieved by using *stock-flow analysis* for identifying pathways of natural radioisotopes within the system of water supply. Stock-flow analysis is an innovative tool for the quantification of substances, but it has been applied with respect to natural radioactivity for the first time in this study. The application of stock-flow for water supply was very successful and lead to outstanding results. This modern procedure supports the identification of major sources and sinks for natural radioactivity and provides useful results for radiation protection for employees in waterworks.

In this project, stock-flow revealed that filters might represent an additional source for radionuclides, if they are exhausted and as a result the radionuclides are released to the water.

For instance, an iron filter at a waterworks from the German Rhine-Nahe-Area released about 19 MBq of ^{222}Rn to the water on the cutoff-date. This is due to the radioactive decay of ^{226}Ra, which is extraordinarily enriched in this filter. The activity concentration of ^{226}Ra accumulated in the GAC-layer of this particular material is 9.5 ±2.5 Bq/g.

Despite the presence of sampling and measuring errors, detailed balances could be calculated for a waterworks in the Rhine-Nahe-Area, Germany, and a water treatment facility in Ontario, Canada. These balances were almost perfectly in agreement with respect to input and output of radionuclides at these waterworks. On the contrary, the calculation of balances was not achievable for a waterworks located in the Northern Black Forest, Germany, since the levels of long-lived radionuclides in the raw and drinking waters were only in the order of a few mBq/l. Balances seem to be practicable especially for waterworks abstracting medium or high radioactive aquifer waters. In conclusion, balances and stock-flow analysis can only be applied if the levels of the respective radionuclides are significantly above the lower limit of detection (LLD) of the used instrumentation. Otherwise, the measurement errors will not permit the calculation of balances.

Another important objective was the initial utilization of innovative and affordable measurement procedures for a compliance with the new legislation. These methods based on radionuclide-extraction via planar discs were developed within the past years but they have never been tried out before with regards to an application in water supply. The expenditures for determining radionuclides in waters could be decreased if the fairly simple and progressive method using radionuclide-extracting discs is applied.

For instance, MnO_2-coated polyamide discs are highly applicable for determining radium isotopes in drinking waters. The adsorption yield of those discs amounts to at least 85 % and the sampling preparation is relatively simple. Uranium-extracting polyamide-oxime discs showed excellent results with respect to chemical recovery (> 80 %) and energy resolution in alpha-spectrometry. This method is outstanding and is applicable without further sample treatment for ground- and drinking waters containing uranium concentrations of less than 10 Bq/l (U_{nat}). The reliability and reproducibility of these methods for uranium and radium determination has been explicitly confirmed in this study.

Another valuable result of this project is the fact that residues from water treatment can be highly contaminated with long-lived natural radioisotopes, such as uranium and radium. The residues from a waterworks in the German Rhine-Nahe-Area contain significant amounts of long-lived radionuclides of up to 36.5 ±7.5 Bq/g. This enrichment is due to the removal of radioisotopes from ground water by granulated activated carbon (GAC) filtration. The removal efficiencies observed in this study were lower than expected, since some filters were almost exhausted with regards to radionuclide removal. For example, the removal efficiency for radium in the waterworks from the German Rhine-Nahe-Area only amounted to 25 %. A proper disposal of contaminated wastes, such as filter material and sludge, is highly recommended despite the absence of official regulations regarding this issue.

The amounts of radionuclides encountered during the investigations correspond to the respective geology of the areas. The highest concentrations were detected at the waterworks in the Rhine-Nahe-Area, Germany. In fact, the gross-alpha activity of the raw waters at this facility ranges from 0.3 –2.0 Bq/l. This is mainly due to the presence of uranium-bearing rhyolite and the high flow velocity of ground waters in joint aquifers within the Saar-Nahe-Basin.

However, the levels of radionuclides encountered in Ontario, Canada, were below the first expectations. This applies particularly for the Sudbury and Timmins areas of Central Ontario. The reason for this is that the investigated waterworks abstracts ground water from aquifers, which do not contain significant amounts of natural radioactivity. As a consequence, a study of the local geology on a small scale is not sufficient for an assessment of the situation with respect to natural radioactivity present in aquifers. The individual case of a water treatment facility has always to be considered. On the other hand, investigated private well waters from Ontario revealed significant levels of uranium (10 µg/l) and radon (440 Bq/l).

Fortunately, none of the sampled drinking waters from Germany and Canada exceeded the limitation value for the total indicative dose of 0.1 mSv per year. The maximum level of TID was calculated for a drinking water from the German Rhine-Nahe-Area, where babies receive a committed dose of 70 µSv per year via ingested drinking water.

16 References

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17 Annex

17.1 Table Index

17.2 Figure Index

17.3 Equation Index

Curriculum Vitae Sascha Wisser

Date of Birth:	February 04, 1973
Education	1979 – 1983 Primary School in Enspel 1983 – 1992 Highschool (Gymnasium Westerburg)
Military Service	July 1992 – June 1994 Sanitätsbataillon 5, Rennerod
Study	WS 1994 – SS 1997 Philipps-University Marburg WS 1997 – SS 2000 Gutenberg-University Mainz March, 2000: Diploma in Geology
Scholarship	Promotionsstipendium der Friedrich Ebert-Stiftung, Bonn January, 2001 – April, 2003
Employment	ESWE-Institute for Water Research and Water Technology, Wiesbaden, Germany (Head of Radioactivity Department) since May, 2003
Awards	Orden der Radiometrie Schloß Theuern, May 18, 2001
Lectures	*Bilanzierung natürlicher Radionuklide in der Wasserversorgung*. 33. Radiometrisches Seminar, Theuern (Bayern), 18. Mai 2001 *Natürliche Radioaktivität in Wasserwerken*. Vortrag am Zentrum für Strahlenschutz und Radioökologie, Hannover, 05. Juli 2001 *Determination of Uranium-Isotopes in Ground- and Drinking Waters from Ontario, Canada*. 1st Workshop on Natural Radionuclides in Hydrology and Hydrogeology (NuRaHyd-1), Centre Universitaire Luxemburg, September 04-07, 2002 *Natural Radionuclides in Drinking Waters from Ontario, Canada*. ENOR III Conference - Enhanced Naturally Occurring Radioactivity, Dresden, March 03-07, 2003

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