

RADON IN NATURAL WATERS

Analytical Methods; Correlation to Environmental Parameters;
Radiation Dose Estimation; and GIS Applications

Doctoral Thesis

BY

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We made from Water Everything

*This work is dedicated to Walzed; Ula & Fadwa;
& To my Parents*

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LIST OF PAPERS

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals.

Paper I. Determination of ^{222}Rn and ^{226}Ra in water using a large volume ionisation chamber, *J. Environmental Radioactivity*, 48, 235-245, 2000,

Isam Salih, Håkan B.L. Pettersson and Eva Lund

Paper II. ^{222}Rn in coastal waters: onboard analysis of ^{222}Rn depth-profiles and evaluation of non-supported content, *in manuscript*

Isam Salih, Håkan B.L. Pettersson and Jürgen Herrmann.

Paper III. Impact of fluoride and other aquatic parameters on radon concentration in natural waters, *J. Applied Radiation & Isotopes*, submitted

Isam Salih, Mattias Bäckström, Stefan Karlsson, Eva Lund, and Håkan. B.L. Pettersson.

Paper IV. Uranium and thorium series radionuclides in drinking water from drilled bedrock wells: correlation to geology and bedrock radioactivity and dose estimation, *J. Radiation Protection Dosimetry*, 102 (3), 249-258, 2002,

Isam Salih, Håkan B.L. Pettersson and Eva Lund.

Paper V. Spatial correlation between radon (^{222}Rn) in groundwater and bedrock uranium (^{238}U): GIS and geostatistical analyses, *J. Spatial Hydrology*, 2(2), 1-10, 2002

Isam Salih, Håkan B.L. Pettersson, Åke Sivertun and Eva Lund

Paper VI. Chemical character of drinking water from Swedish crystalline bedrock, *J. Environmental Monitoring*, submitted

Mattias Bäckström, Stefan Karlsson, Isam Salih and Håkan B.L. Pettersson.

Description of my contribution to the papers

- Paper I In this paper I took part in the scientific planning, and was responsible for the design, data collection, evaluation and writing the draft
- Paper II In this paper I took part in the scientific planning, and was responsible for the data collection, evaluation and large part of writing
- Paper III In this paper I was partly responsible for the scientific planning and experimental design, and responsible for radon measurements & designs, data evaluation and large part of writing
- Paper IV In this paper I took part in the scientific planning, and was responsible for the sampling & data collection, evaluation and writing the draft.
- Paper V In this paper I was responsible for the scientific planning, evaluation and writing.
- Paper VI In this paper I was responsible for sampling & data collection and geological characterisation of data, and took part in the manuscript review.

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ABBREVIATIONS & KEYWORDS

ABBREVIATIONS:

Bq	Becquerel
CTD	Conductivity Temperature Depth
FWHM	Full Width at Half Maximum
GIS	Geographical Information System
GPS	Global Positioning System
HCl	Hydrochloric acid
HPGe	High Purity Germanium
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICRP	International Commission on Radiological Protection (reports)
IDW	Inverse Distance Weighting
KeV & MeV	Kilo & mega electron volts
LLD	Low Limit of Detection
LSC	Liquid Scintillation Counter
Sv	Sievert
PC	Personal Computer
PCA	Principal Component Analysis
PLS	Partial Least Square
RMSE	Root Mean Square Error
SD (σ)	Standard Deviation
SGU	Geological Survey of Sweden

KEYWORDS:

ATMOSTM, bedrock, bubbling, drinking water, effective dose, fluoride, geology, geostatistics, GIS, groundwater, IDW, indoor air, ionisation chamber, kriging, microbubble, polonium (²¹⁰Po), radium (²²⁶Ra), radon (²²²Rn), salinity, seawater, stable elements, uranium (²³⁸U, ²³⁵U, ²³⁴U).

Linköping University Medical Dissertation No. 820

ABSTRACT

Investigations of radon in natural water and its relation to physical and chemical parameters are outlined in this thesis. In particular, a method for measuring ^{222}Rn in water at low concentrations ($\sim 20 \text{ mBq l}^{-1}$) is described, followed by discussions concerning the design and its application to study both radon and parameters influencing radon levels in natural waters. A topic considered is the impact of fluoride and other aquatic parameters on radon in water. Moreover, variables such as uranium series radionuclides and stable elements in water, bedrock and sediment radioactivity and geology are investigated in two case studies. This was performed by employing radiometric-, chemical-, statistical- and GIS & geostatistical- analyses. The general water chemistry and presence of some elements such as fluoride was observed to influence radon levels in water. Health aspects of radon in drinking water are discussed based on radiation dose assessments. The radiation doses are compared with and added to doses incurred from ingestion of uranium, radium and polonium isotopes in drinking water and inhalation of radon in air in order to estimate total exposures for different age categories. The results may have a potential for future epidemiological studies.

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SCOPE OF THE THESIS

The overall objective of this thesis has been to improve the understanding of the distribution of radon in natural waters by studying physical, chemical and geological parameters control this distribution. To obtain this, interest has been focused on:

- Development of analytical procedures to evaluate radon (^{222}Rn) and radium (^{226}Ra) in waters (paper I)
- Utilising the developed method to investigate ^{222}Rn and ^{226}Ra depth profiles in seawater (paper II)
- Employment of the method to investigate physical and chemical parameters that influence radon transfer to and from water (paper III)
- Evaluation of radon and long-lived uranium-series nuclides in groundwater. This includes also correlation to geology and estimation of radiation dose to man due to water consumption (paper IV)
- Using GIS and geostatistical techniques for spatial analyses of radon in water in correlation to geology and uranium content of the bedrocks (papers IV and V).
- Evaluation of chemical parameters of all groundwater samples used in the study and investigations of their impact on radon (papers VI and III).

RESEARCH APPROACH

To meet the objectives discussed above, a series of controlled laboratory experiments and field protocols was designed and conducted. In these experiments, an approach of continuous radon measurement in a closed circuit was followed using a radon monitor based on alpha detection. Multiple analytical techniques such as gamma ray spectrometry, alpha spectrometry and ICP-MS were used for evaluation of related parameters. These parameters (i.e. uranium-series radionuclides and stable elements) in addition to geological characterisation of e.g. bedrock and sediment and their radioactivity contents were used as background information for radon investigation in waters. The presence of radon in groundwater was studied in relation to water chemistry by investigating about 70 elements. The result of this study was used as an input for developing a controlled laboratory experiments to investigate the most related parameters (e.g. fluoride, carbonates). GIS and geostatistical analyses were used for developing maps of radon in groundwaters and maps of radon inventories in seawaters. These maps were used to obtain correlation of radon to source terms.

Finally, in the summary the major results of this research are summarized. Important accomplishments are highlighted, and areas for future research are identified.

CHAPTER ONE

INTRODUCTION

1.1 General Background

The increased awareness of radon (^{222}Rn) as a significant potential threat to public health has made it necessary to further investigate and expand our understanding of radon in natural water. The main source of indoor exposure to long-lived radionuclides in the uranium decay-series in general, is potable water, whereas ^{222}Rn may enter the indoor environment by direct water transport, by groundwater transport and diffusion to the dwelling by advective transport and diffusion from the ground to the dwelling, or by emanation from building materials. The water transport pathway has been regarded as a less significant contributor to the radon levels found in dwellings. However, recently more attention has been paid to this pathway, especially when considering exposure of infants and children by ingestion of radon in drinking water, and if combined with high levels of U, Ra and Po in drinking water it may constitute a significant public health risk.

Another area of recent interest in radon is in the marine environment. Radon may be used as a trace element to study the processes and source terms affecting the transport and mixing of seawater.

The study of natural radioactivity of the uranium series in water provides useful information for many applications (health, hydrology, geochemistry...etc). Performing such kind of studies require powerful tools and well developed procedures. This is particularly important when dealing with complex systems such as groundwater or seawater where both extremes (high and low levels of radon) exist in addition to many influencing parameters. Each element in the uranium series has its own physical and chemical properties, which also depends on environmental conditions. Although the physical, chemical and thermodynamical properties of these radionuclides are well known under laboratory conditions, their behaviour remain unpredictable under these complex systems. Therefore, if we need to evaluate, for example, the exposure

to Man from natural radioactivity of water, it is necessary to determine each radionuclide separately. The occurrence of natural radioactivity in drinking water has been a subject of extensive studies worldwide during the last years. Most of these studies are focused on investigating places of high levels and evaluating exposure of the population to radiation from the consumption of water, correlation between the levels of these radionuclides in water and other parameters, such as geological structure, radioactivity content of underlying bedrock and disequilibria in the U-series. The variability of water radioactivity addresses the issues associated with research methodology dealing with method developments, further investigating nuclide properties, influencing parameters and applying advanced analytical tools to explore the behaviour and mobilisation of these nuclides in these systems.

Radon (^{222}Rn), being the only gas in the U-series, shows unique chemical and physical properties in the uranium-series.

In studying radon chemistry, for example, investigators have suggested that, in analogy to krypton and xenon complexes, radon may form difluoride (RnF_2) products that hydrolyse in the presence of water molecules. This addresses the issue of radon-fluoride combinations, which may have impact on radon levels in aqueous environments. Performing investigations under typical environmental conditions may help in understanding radon behaviour in waters. Therefore the present work is primarily devoted to radon (^{222}Rn) in natural waters.

Before proceeding, let us first look at the distribution of long-lived uranium series nuclides and radon in natural waters.

1.2 Distribution of Uranium series in natural waters

1.2.1 Uranium, Radium, Radon and progeny in groundwater

The ultimate source of naturally occurring radionuclides is the earth's crust. Among these radionuclides there exists three principal decay series originating from ^{238}U , ^{235}U and ^{232}Th . Being one of the most abundant sources of naturally occurring radioactivity, the ^{238}U series has been widely investigated. A schematic diagram of the uranium-238 decay series is given in Figure 1.1a, showing the members of this series, their half-lives and their decay modes. The decay mode of the gas radon (^{222}Rn) is shown in figure 1.1b.

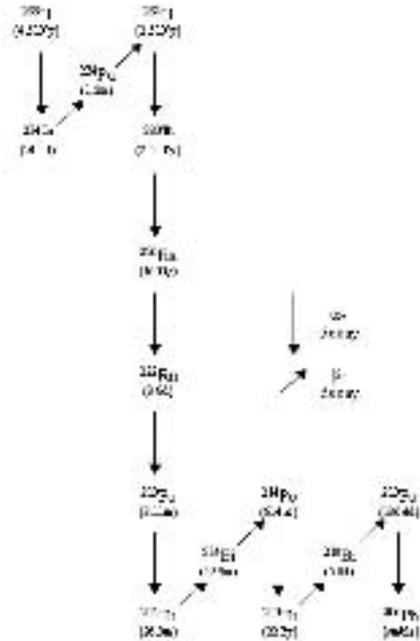


Figure 1.1a: Uranium-238 decay series nuclides

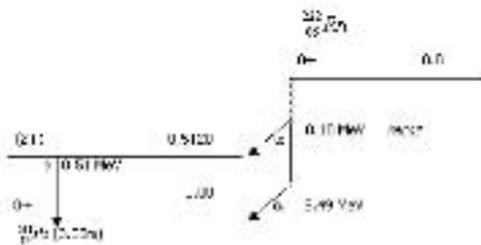


Figure 1.1b: Radon decay mode

The levels of uranium in igneous rocks are typically in the range 0.01-10 ppm and often increase with Si content, and can in extreme cases exceed thousands of ppm (Ivanovich and Harmon 1982).

U-series nuclides are expected to be in secular equilibrium (i.e. having the same activity concentrations) in closed bedrock systems. In groundwater systems significant disequilibria is observed, which indicates that in open systems, rock interactions induce significant elemental and isotopic fractionations (Osmond and Cowart 1992). High natural levels of alpha

radioactivity in groundwater are often associated with areas of granite bedrock (Ortega et al 1996). Although the physical and chemical properties of these elements are well known, it is difficult to predict the behaviour and mobilisation in more complex natural system.

The transfer or disposition of an atom created in this series into groundwater systems depends on many factors involving the physical and chemical properties of the element. In addition to that groundwater systems vary from region to region. Figure 1.2 illustrates the formation and transport of groundwater.

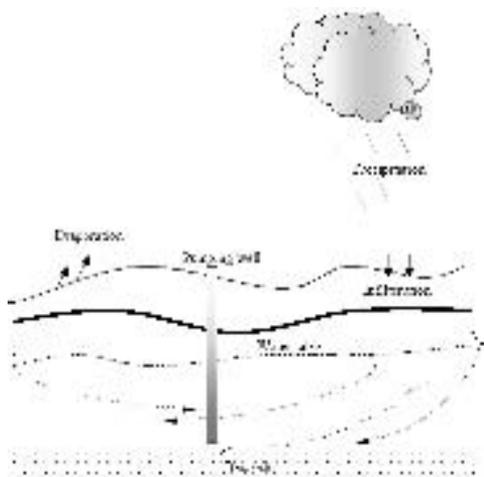


Figure 1.2: Groundwaters

In general the rock porosity and permeability control the behaviour of groundwater. For example igneous rocks, such as granite, have high permeability, resulting from fractures in the rocks that permit faster flow relative to, for example shale.

The general properties of uranium, thorium, and polonium are metallic while radium is an alkaline earth and radon is a gaseous element. Soluble uranium complexes, e.g. uranyl, are readily produced in oxidizing environments, whereas in reducing groundwater environments uranium, and especially the uranyl ion, is readily precipitated or adsorbed on organic compounds (De Vivo et al 1984). Release of radium from rock to water is mainly due to alpha recoil (Sun H. & Semkow 1998). Radium dissolves readily in waters of low pH (e.g. newly formed groundwater) and its concentration is often related to concentrations of total dissolved solids, barium and sulphate.

Radon concentration in groundwater is mainly controlled by the lithology (Misdaq & Elharti 1997) of the aquifer. Radon enters the water phase to form a

metastable clathrate-hydrate with water, $Rn \cdot 6H_2O$. Clathrates are chemical compounds consisting of lattice molecules and inclusions of smaller molecules within the crystal lattice, that traps molecules in its crystal structure without chemical bonding (Lawrence S. 1983). As ^{222}Rn is the direct daughter of ^{226}Ra , a high level of ^{226}Ra in bedrock is expected to generate high levels of ^{222}Rn in water, which then migrates away from the source. Groundwater can carry ^{222}Rn over large distances depending on flow rate, e.g. at flow rates between 0.5-1.0 meter per day Rn could be transported about 20-40 m before it is completely decayed. High concentrations of ^{222}Rn could lead to detectable levels of both ^{210}Pb and ^{210}Po . In aquifers that have elevated ^{210}Po concentrations, normally ^{222}Rn levels are also elevated. However, due to absorption/desorption processes, both the ^{210}Pb and ^{210}Po levels show large variations. In groundwater, as mentioned earlier in this chapter, uranium is not usually in equilibrium with its progeny. The reasons for this behaviour are mainly due to the differences in the mobilisation in groundwater and physical-chemical processes such as physical half-lives of these nuclides, their transport between rock and water systems and their water chemistry (e.g. sorption/desorption processes; ion exchange capacities). Therefore, in order to draw a complete picture about groundwater radioactivity that comes from uranium, it is necessary to investigate each nuclide involved.

1.2.2 Radon in Seawater

There are several processes and sources contributing to ^{222}Rn in seawater; e.g. surface interactions in the water/atmosphere interface, inflow from freshwater bodies, diffusion from seabed sediments, *in situ* production from ^{226}Ra in water seepage from groundwater discharges and hydrothermal vents. In seawater the levels of ^{222}Rn (and ^{226}Ra) are generally low compared to levels in groundwater. Typical values of ^{226}Ra in the southern Baltic Sea are 1.7 – 2.2 $mBq \cdot l^{-1}$ (Kowalewska 1986); in the Bay of Bengal 5.4-29 $mBq \cdot l^{-1}$ with ^{222}Rn levels of 1.3-1.7 $Bq \cdot l^{-1}$ (Ghose et al 2000); in the Black Sea ^{222}Rn and ^{226}Ra

range 22-48 mBq·l⁻¹ and 11 - 56 mBq·l⁻¹ respectively (Karahan et al 2000) and in the Dead Sea the range of ²²²Rn is 4.3-6.3 Bq·l⁻¹ (Al-Bataina et al 1997).

It has been suggested that a microbubble phenomenon enrich natural fluids with ²²²Rn, by carrying ²²²Rn in water from a source towards the surface (Várhgy et al 1992). The microbubble may also mediate transfer of surfactants to water surface. The increase in salinity increases the transfer of these surfactants as observed by Skop et al 1993. In order to draw an overview over the distribution and input of ²²²Rn in seawater, in the present work (paper II) investigation of ²²²Rn content is performed. Excess ²²²Rn inventories are calculated to seek for possible parameters responsible of ²²²Rn distributions at this environment (²²⁶Ra in water & surface sediments, profiles of water salinity and temperature... etc).

CHAPTER TWO

ANALYTICAL METHODOLOGY FOR DETERMINING RADON AND SOME URANIUM SERIES RADIONUCLIDES IN WATER

2.1 Radon Analyses

Evaluation of radon concentration in water, in the present work, is based on two methods: I) a newly developed method (“ATMOS”) and II) gamma ray spectrometry. A third method (Liquid scintillation counting, LSC) was introduced for comparison and also to optimise it to evaluate large number of samples per day for any future investigations. Most of the groundwater analyses (presented in paper IV) are evaluated using gamma spectrometry as it offers low counting and statistical errors for a wide range of concentrations. The “Atmos” method is developed here (paper I) to enable radon measurements at very low concentrations i.e. as low as $20 \text{ mBq}\cdot\text{l}^{-1}$ in ground or sea waters (papers I & II).

2.1.1 “ATMOS” method:

2.1.1a Experimental Set-up

A set-up (subject of paper I) is constructed here to expel radon from a water sample, by bubbling, to air in a confined space and measure its concentration in ion-chamber in a closed circuit. Figure 2.1 shows the experimental set-up including the ionisation chamber system.

2.1.1b Radon gas monitor

ATMOSTM (Gammadata-Sweden, 1997) is originally designed to measure radon content in open air. It operates by pumping the air at rates of 1.4 litres per minute. The air then passes through filters that remove radon daughters before reach an ionisation chamber. The alpha particles emitted from the decay of ^{222}Rn , and the *in situ* produced ^{218}Po and ^{214}Po are detected by the ion-chamber and the spectra are stored in a 256-channel memory as an energy

spectrum (5.49, 6.00 and 7.69 MeV respectively). The resolution of the peaks (FWHM) is about 0.30 MeV.



*Fig. 2.1. Set-up of the detector system
Sketch diagram of the set-up is shown in
paper I.*

The instrument also provides graphical time distribution of the detected radon, calculated from the energy spectrum in 10-minute intervals. The instrument is connected to a pc through a serial board where both energy and time spectra can be loaded in addition to the possibility of providing the instrument with calibration factors and choosing a background ...etc. For more details about the equipment see Atmos 1997.

Some investigators have made constructions of similar detectors. Example of that is a continuous true radon monitor developed by Samuelsson and Pettersson 1984.

In “Atmos” method, the radon level in water (C_W) is obtained through measurement of the radon concentration in the void air (C_A), following the equation:

$$C_W = \alpha(t) \cdot C_A \quad 2.1$$

where $\alpha(t)$ is an empirical factor, which is obtained as result of the system calibration. C_A is obtained by analysing the alpha spectra using the ^{222}Rn and ^{218}Po alpha peaks at 5.49 and 6.00 MeV respectively. A typical alpha spectrum and temporal radon concentration curve are given in paper I.

Calibrations for this set-up are made using traceable ^{226}Ra standard prepared and measured while in secular equilibrium with ^{222}Rn and ^{222}Rn progeny.

2.1.1c Mathematical Analysis of the Set-up

Consider the set-up in figure 2.2, in which radon is transferred from water to air with a transfer factor α_1 and back to the water by the factor α_2 . If the Rn activity at any time t in water is A_w and in air is A_a , the total activity, A_T is:

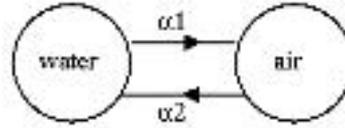


Figure 2.2: sketch diagram of ^{222}Rn transport between air and water

$$A_T = A_w + A_a = \text{constant} \quad 2.2$$

At time $t = 0$,

$$A_T(0) = A_w(0) \quad 2.3$$

At time t :

$$\begin{aligned} A_T(t) &= A_T(0)e^{-\lambda t} \\ &= A_w(0)e^{-\lambda t} \end{aligned} \quad 2.4$$

where λ is radon decay constant

The equation of motion is then;

$$\frac{dA_a}{dt} = \alpha_1 A_w - \alpha_2 A_a - \lambda A_a = \alpha_1 (A_T - A_a) - \alpha_2 A_a - \lambda A_a$$

$$\frac{dA_a}{dt} + (\alpha_1 + \alpha_2 + \lambda) A_a = \alpha_1 A_T e^{-\lambda t} \quad 2.5$$

Introducing exponential factor $e^{-(\alpha_1 + \alpha_2 + \lambda)t}$ gives

$$\frac{d}{dt} (A_a e^{-(\alpha_1 + \alpha_2 + \lambda)t}) = \alpha_1 A_T(0) e^{-(\alpha_1 + \alpha_2)t} \quad 2.6$$

Integration yields

$$A_a e^{-(\alpha_1 + \alpha_2 + \lambda)t} = \frac{\alpha_1}{\alpha_1 + \alpha_2} A_T(0) \cdot e^{-(\alpha_1 + \alpha_2)t} + C \quad 2.7$$

The boundary conditions: at $t = 0$, $A_a = 0$ gives

$$C = \frac{\alpha_1}{\alpha_1 + \alpha_2} A_w \quad 2.8$$

This implies that

$$A_a(t) = \frac{\alpha_1}{\alpha_1 + \alpha_2} A_w(0) \{e^{-\lambda t} - e^{-(\alpha_1 + \alpha_2 + \lambda)t}\} \quad 2.9$$

Which is the homogenous solution of the differential equation (2.5). However, in reality A_a at $t=0$ takes some value due to sample agitation or temperature changes since sampling. Therefore the particular general solution of the differential equation is applied and can be written as;

$$A_a(t) = \frac{\alpha_1}{\alpha_1 + \alpha_2} A_w(0) \{e^{-\lambda t} - e^{-(\alpha_1 + \alpha_2 + \lambda)t}\} + \beta A_w e^{-\lambda t} \quad 2.10$$

Where β is the percentage of radon in the void air.

Fitting of experimental data gives the following empirical values

$$A_a(t) = 0.912 A_w(0) \{e^{-0.000126t} - e^{-0.09272608t}\} + 0.05 A_w e^{-0.000126t} \quad 2.11$$

i.e. $\sim 5\%$ of the radon content in the sample is released to the void air before measurement starts.

Using background measurement (blank), the detection limit (LLD) of the method can be obtained, at 95% confidence level, using the formula (Currie 1968):

$$LLD = \frac{0.00075 + 3.29 \cdot cps}{\varepsilon \cdot V}, \quad 2.12$$

where cps is counts per second, ε is the α efficiency and V is the sample volume. Clearly, increasing the volume reduces the LLD.

2.1.1 Gamma ray spectrometry:

This technique is widely used to investigate many radionuclides (natural or anthropogenic) in different environmental samples. In the present work, radon in water samples is determined at least four hours after sampling, using a low level γ -spectrometry based on an HPGe-detector (42% relative efficiency) situated in a low-level underground laboratory. The detector is surrounded with aluminium bags filled with aged air (in addition to the standard lead shielding) in order to reduce the radon background. These bags were made of foil sheets consisting of 9 μ m aluminium, 12 μ m polyester and 75 μ m low-density polyethylene thickness. Background measurements showed that more than 80% reduction in radon daughter γ -peaks was achieved after introducing these air bags. The radon concentration of water samples is assayed by 1-8 hour counting followed by analysis of γ -peaks from ^{214}Bi (609 keV) and ^{214}Pb (295, 352 keV) using the Ortec GammavisionTM software for evaluating the gamma spectra. Energy and efficiency calibrations are made using a traceable radium standard solution (overall uncertainty $\pm 3.7\%$), prepared in the same sample geometry, while in secular equilibrium between ^{222}Rn & progeny.

2.1.3 Liquid Scintillation Counting:

A low-level Wallac 1415 GuardianTM LS spectrometer is used for evaluating ^{222}Rn concentration in the water sample (Salonen 1993). The system is equipped with a pulse-shape analyser, which separates pulses caused by alpha or beta decay into separate spectra. The alpha spectra are transferred to a PC through RS232 serial interface and analysed.

At the sampling site, three samples of 8 ml each are collected using a pipette into 20 ml bottles, which contain 12 ml OptiPhase 'HiSafe' 3 cocktail solution. Then the samples are shaken to facilitate the transfer of radon into the organic phase and measured with LSC after four hours.

2.1.4 Comparison between Gamma spectrometry, “Atmos” and Liquid Scintillation Techniques for measuring radon in water samples

The following table presents a comparison between the three techniques used in this study for evaluating radon concentration in water, based on measurements performed here:

Table 2.1: Comparison between three methods for determining radon in water

	“ATMOS”	Gamma	LSS
Detection limit [mBq·l ⁻¹]	20-45	1700	30
Best analysis range [Bq l ⁻¹]	0.05 - 1000	> 5.0	0.05 -
No of samples assayed per day	2 – 5	2 – 5	Up to 48
Intercomparison	A-G:	A-L:	G-L:
(Regression coefficient [R ²])*	A=(1.02±0.01) G	A=1.06±0.01 L	G=(1.04±0.02) L
p-value =0.0000 (for each)	R ² =1	R ² =0.99	R ² =0.99

*) The abbreviations: A- “ATMOS”, L- Liquid Scintillation Spectrometry and G- Gamma spectrometry

2.2 Uranium, Radium and Polonium Analyses

For the analysis of these nuclides in waters samples, a pre-concentration procedure is followed as given in paper IV. The activity concentrations of uranium and radium isotopes are obtained by gamma spectrometric measurement while polonium is determined by α -spectrometric counting.

Some few samples were selected for uranium analysis for the purpose of determining the ratios of uranium isotopes in groundwater (disequilibrium) using the precipitates obtained here and applying the procedure described by Nilsson et al. 1989. The results (not included here) showed significant disequilibria in most of the investigated sites.

2.3 Stable elements analyses

Elemental analyses of water samples in this work is performed using *quadrupole* ICP-MS, ELAN[®] 6000 and Agilent 4500. The ICP-MS uses high-temperature argon plasma to generate metal and elemental ions, which are

introduced into a mass spectrometer for separation and quantification. Paper VI presents the chemical analysis of groundwater samples.

In addition analyses of electrical conductivity, anions, alkalinity, total organic carbon, inorganic carbon, anions chloride, fluoride, nitrate and sulphate, Paper VI gives these data and data for most of the stable elements. The elements include Li, Be, B, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Pd, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, W, Re, Hg, Tl, Pb, Bi, Th and U. Statistical analyses were performed to study the impact of these elements on radon in water. Partial least squares showed that uranium, fluoride and to a lesser extent nitrate have a positive impact on the predictive ability of radon concentrations. The radon-fluoride relationship was further investigated by laboratory-controlled experiments.

CHAPTER THREE

INVESTIGATION OF RADON AND OTHER RADIOLOGICAL PARAMETERS IN GROUND AND SEA WATERS

This chapter presents two case studies that were carried out using the methods described in the previous chapter. The main objective was to investigate radon distribution in relation to source terms and influencing parameters in different aqueous environments (groundwater & seawater).

3.1 CASE STUDY I: Investigation of radon and uranium series radionuclides in drilled well water

3.1.1 Data Collections

Groundwater samples were collected from 328 selected sites within the Östergötland and Kalmar counties in southeastern Sweden during the period 1998-2001. The sites were selected based on geological and aero-radiometric map information in order to cover areas with different soil/bedrock composition. Interest has been paid to drilled bedrock wells and in particular granite/pegmatite bedrock areas. Information about the wells (which include water quality production rates, well diameter, total depth, depth in soil, depth in the rocks etc.) was obtained from the national well registry. As a first step, samples were gathered from residential dwellings. At each site water was sampled both close to the well (at the hydrofore, see figure 3.1) and at the kitchen faucets to be analysed by gamma ray spectrometry (and/or Atmos & LSC methods).



Figure 3.1: Typical picture of a hydrofore (left) used to pump water from a well (right), taken during the sampling campaign.

Testing of water at the household tap involved visiting residences where permissions were obtained from household owners to collect about 15 litres water samples. In order to obtain fresh water from the wells, the tap water was allowed to run fully at least 10 minutes before sampling. The bottles were then filled by cold water at minimum flow to minimize radon losses. A sampling reproducibility test, performed by measuring 10 successive samples from one site, did not detect any deviating results. All ten values ± 1 SD in counting statistics agreed with the mean value. The pH of the water was measured at the site using a pH-meter with an accuracy of ± 0.01 . During sampling the locations of the sites were precisely recorded using global positioning system (GPS). Also indoor gamma dose rates were measured in three different rooms (for 237 sites), using a GM-counter based dose-rate meter RNI 10/R IntensimeterTM. The average values of the ambient dose equivalent rates at these locations are plotted versus radon concentration of kitchen waters, presented in figure 3.2a. A sampling protocol is shown in Table 3.1.

Table 3.1: Example of the sampling protocol

SAMPLE CODE	PLACE	Gamma ($\mu\text{Sv/h}$)	X-Y Coordinates GPS data	Temperature ($^{\circ}\text{C}$)	pH	Redox Potential (mV)	Well Depth (m)	Remarks (Filters...)
	Kitchen	0.05	57°59.547		7.05	+10	110	Fe/ sand
XX-001	Bed room	0.11	15°41.483	12				
	Living room	0.12						

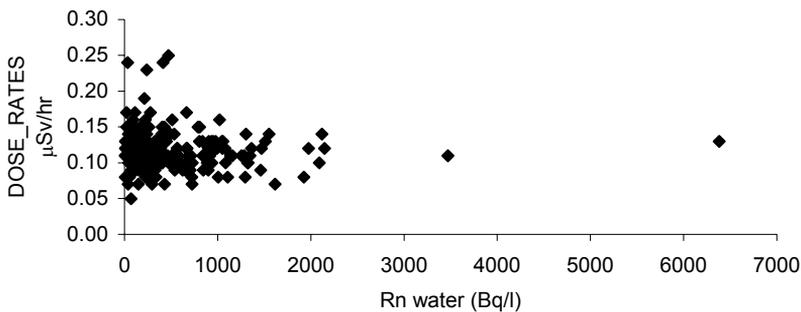


Figure 3.2a: Indoor ambient dose equivalent rates ($\mu\text{Sv h}^{-1}$) versus radon concentration in tap water (Bq l^{-1}) for 237 sites

3.1.2 Results

Uranium series radionuclides in drinking water from 328-drilled wells in southern Sweden are investigated in correlation to source parameters. The distribution of radionuclides, in two counties (Östergötland and Kalmar) displayed a wide range of concentrations. Concentrations ($\text{Bq}\cdot\text{l}^{-1}$) in groundwater samples fall in the range: ^{238}U (<0.027 - 5.3), ^{226}Ra (<0.016 - 4.9), ^{222}Rn (5 - 8105) and ^{210}Po (<0.05 - 0.947). The full result is given in paper IV.

Interestingly, radon concentrations in water from kitchens faucets were well correlated to the corresponding well water ($\text{RnW}=1.09\cdot\text{RnK}$, $R^2=0.94$). Figure 3.2b shows a comparison between radon concentrations in water from wells (RnW) to that from kitchens (RnK) by plotting the $\text{RnW}:\text{RnK}$ ratio versus site numbers sorted in ascending order.

The Z-test against a value of 1.0 returned two-tailed p-value of 0.0073. About 3% of the sites (shown at left part of the graph) have radon removal devices. The ratio RnW/RnK reaches values of up to 120, which corresponds to 99.2% Rn removal efficiency.

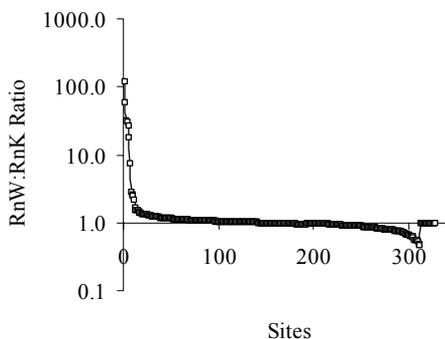


Figure 3.2b: score graph of radon in kitchens to radon in wells ratio versus sampling sites

The graph in Fig. 3.2b indicates that losses of radon from well to kitchen tap are generally insignificant, i.e. the water pipes used in the houses are generally gas tight. Some of the drilled wells (2%) were not accessible due to their constructions (shown at the right part of the graph).

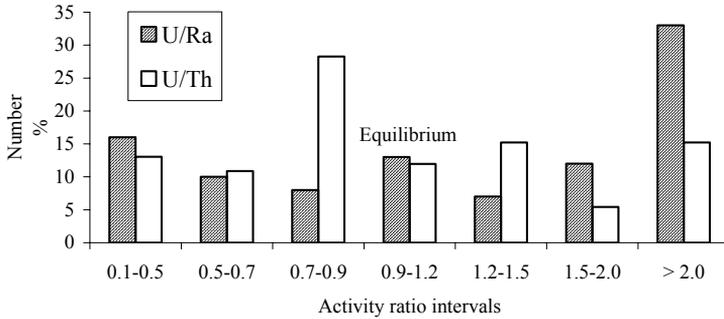


Figure 3.3: ^{238}U : ^{234}Th and ^{238}U : ^{226}Ra activity ratios (AR) for all sites where

In figure 3.3 the frequency distribution of $^{238}\text{U}/^{234}\text{Th}$ and $^{238}\text{U}/^{226}\text{Ra}$ activity ratios for all sites are shown. ^{234}Th concentrations were evaluated by means of gamma energies 63 and 92 keV. The activity relationship of ^{234}Th and ^{238}U and between ^{238}U and ^{226}Ra display significant disequilibria in most of the investigated sites. Only 13% of the sites indicate close to equilibrium status (activity ratios between 0.9-1.2).

As expected, high natural radioactivity concentration in groundwater was found in granite mixtures, especially with pegmatite inclusions. An attempt was made to correlate water radioactivity to bedrock uranium content and geology. In paper IV the results of ^{238}U , ^{226}Ra , ^{222}Rn , ^{210}Po in water relative to uranium in bedrocks are presented in a set of plots. The scatter plots show poor correlations between groundwater and bedrock radioactivity, which indicate great differences in radionuclide release to the groundwater and their transport. The geological map of the study area, synthesised from the Geological Survey of Sweden survey maps, is mostly characterised by granitic formations. The correlation between type of geology and the levels of each of the studied nuclide was performed using simple point-to-point relationship and the result is presented in paper IV. Statistically the distribution of radionuclides in

groundwater was rather uniform, i.e. there was no significant distribution differences across the geological groups.

3.1.3 Statistical Analysis

As the data did not show normal distribution, non-parametric tests were employed. The Kruskal-Wallis test shows no significant differences in concentration distributions between the ten geological groups at $p < 0.05$ for any of the radionuclide investigated. The contribution of each radionuclide to the total radioactivity varies considerably across the sampling sites.

Spearman's rank correlation test applied to the full dataset showed poor relationships between the different nuclide concentration distributions ($R^2 < 0.25$). However, poor inter-correlation is not unexpected since groundwater leach rates and adsorption properties for these radionuclides are different. Descriptive statistics of the studied uranium-series radionuclides is given in Table 3.2.

Table 3.2: Descriptive statistics of concentration of uranium series radionuclides in ground waters from 328 drilled wells.

	²²² Rn	²³⁸ U	²³⁴ Th	²²⁶ Ra	²¹⁰ Po
	[Bq l ⁻¹]	[mBq l ⁻¹]			
Min	4.7	14	20	8.0	0.5
Max	8105.1	5292.9	3539.3	4403.9	947.1
Aritm mean	538.9	187.9	130.5	245.1	34.3
SD	695.2	450.4	309.7	446.2	77.2
Skewness	5.4	7.9	7.6	5.3	8.0
Kurtosis	52.1	80.6	76.2	41.4	88.0
1-st Quartile	126.1	20	20	20	2.8
Geom mean	347.9	73.9	20	113.5	14.2
3-rd Quartile	751.5	202.1	161.5	276.1	39.1

3.2 CASE STUDY II: Investigation of Radon, Radium and Polonium in Baltic Sea water

The main objectives of this study were: 1) to apply *in situ* the method of bubbling that has been developed for measuring low levels of radon in water and 2) to quantify the ^{222}Rn - ^{226}Ra depth profiles for the study of inventories or vertical mixing along the water column of Baltic Sea water.

3.2.1 Data Collection and Analysis

Seawater samples were collected at 19 sites during two GAUSS cruise expeditions in July-August 2000 (GAUSS # 352) and in June-July 2001 (GAUSS # 369). The cruises were organised by the German Federal Maritime and Hydrology Agency. Eight sites, located in the Baltic Proper on the eastern coast of Sweden, were investigated in first cruise. In the second cruise eleven sites were investigated, four sites located on the southern coast of Sweden (Baltic Proper), two sites located on the western coast in the Kattegat and five sites located in the Skagerakk. Water samples were taken at different depths by means of a Niskin water sampler. Salinity, temperature and depth were obtained by a CTD-detector attached to the sampler.

For radon analysis 4.5 litres of water was extracted from the bottles into 5L glass bottles, using a slow flow method, and secured with lids containing two gas tight quick connectors. The samples, then allowed to equilibrate at room temperature, were subsequently measured by bubbling in a closed-loop set-up (paper I, II). In order to analyse radium and polonium, 20-30 litres water samples were drawn from the sampler and acidified to about pH 2. ^{208}Po tracer was added while stirring. Both Ra and Po were co-precipitated with MnO_2 using the procedure described in paper IV.

3.2.2 Results

The results of water column profiles of ^{222}Rn , ^{226}Ra , salinity and temperature from the two cruises are given in a set of plots in paper II. ^{226}Ra was uniformly distributed i.e. there is no significant difference between the investigated areas. ^{222}Rn showed high fluctuation and increased levels (factor of 2) in the Baltic Proper compared to the other regions. The mean radon inventories are about twice the radium inventories in Skagerakk/Kattegat areas and up to five times the radium inventories in the Baltic Proper. The good correlation between radon inventories with depth indicates an effective mixing of radon with depth. Based on the ^{226}Ra and ^{222}Rn data, and using GIS & geostatistical tools, maps of ^{226}Ra and ^{222}Rn in seawater were created (paper II). Because of the few data for plotting at present time, these maps provide only regional estimates of average concentration of these radionuclide inventories. However, differences of the spatial distributions between ^{226}Ra and ^{222}Rn concentrations could be observed.

The ^{226}Ra content of surface sediments were evaluated in samples from the same sites, showing about a ten-fold variation in concentration. However, the surplus and variations in radon inventories in water cannot be explained by these radium concentration variations. It is suggested that the 2-3 times higher radon inventories in water in the Baltic Proper is due to the large influx of radon by river discharges.

CHAPTER FOUR

GIS AND GEOSTATISTICAL ANALYSIS OF RADON IN WATER

This chapter describes results of using the geographical information system (GIS) and geostatistical tools for investigating the spatial distribution of radon in water. Surface maps of radon in groundwater based on measurements of radon (^{222}Rn) in drilled bedrock wells, data presented in chapter three, were constructed and compared with existing bedrock uranium concentration maps (paper V). The goal of these types of analyses is to improve our understanding of radon distribution in water and to explore the possibility of geographical extrapolation of radon concentration data. The geostatistical interpolation techniques include: i) inverse distance weighting (IDW) and ii) kriging interpolators, which are commonly used to estimate values at unmeasured locations using mathematical models (see e.g. Pebesma and de Kwaadsteniet 1997; Astorri et al 2000; Zhu et al 2001). The goodness of interpolation is normally obtained via cross validation processes and the level of interpolation errors, i.e. Root Mean Square Error (RMSE). The produced maps can be used as a first step in identifying areas of possible radon elevation for any future investigations and remedial actions. The following subsections describe the two selected interpolators (IDW and Kriging) and their use in the present study.

4.1. Creation of a grid surface for radon in water using IDW interpolator

The idea is to generate maps that match existing bedrock maps, which was obtained from the SGU. The basic principle of IDW is that points are weighted such that the influence of one point relative to another is a function of inverse distance. Weighting is assigned to points through the use of a weighting power and the radius object. The greater power means that the nearby points have the greater influence. In the present study a fixed radius has been chosen in order to get an idea on how far radon could be transported in water. This method allows changing input value of the radius, which was changed systematically.

At each radius the interpolation was performed and the produced layer (radon in water) was compared with the bedrock uranium layer.

Correlation analysis between the produced maps of radon in water using this method and uranium in bedrock maps varies with respect to input radius value, r . The best correlation coefficient (R^2) was 0.45 obtained at $r=2.7$ km.

One of the drawbacks using this method is that maxima and minima are always among data points since the inverse distance weighted interpolation is a smoothing technique by definition. But on the other hand, it is a powerful interpolation technique that leads to reasonable predictions with no problem with results exceeding the range of meaningful values.

4.2. Creation of radon in water grid surface using Kriging

Kriging is an advanced interpolation procedure that generates an estimated surface from an x-y scattered set of points with z values (radon concentration). It is a weighted moving averaging method of interpolation derived from regionalized variable theory, which assume that the spatial variation of a property, known as a ‘regionalized variable’, is statistically homogenous throughout the surface. Kriging derive weights from the semivariogram that measures the degree of spatial correlation among data points in a study area as a function of distance and direction between data points. The semivariogram controls the way that kriging weights are assigned to data points during interpolation, and consequently controls the quality of the results. The semi-variogram $\gamma(h)$ of a regionalized variable is defined by

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^N [Z(x_i + h) - Z(x_i)]^2 \quad 4.1$$

where x_i+h and x_i are sampling position separated by a vector h , $Z(x_i)$ is a random variable at fixed position x_i , and $N(h)$ is number of data pairs separated by a vector h . Ordinary kriging is a well-known type of kriging interpolation that uses only the sampled primary variable to make estimates. Cokriging allows one or more secondary variables to be included in the model and assuming that the primary and secondary variables are moderately correlated,

the estimation accuracy of the primary variable should increase. Cokriging estimation ensures that the value of a variable estimated, on the basis of the neighbouring values of one or several other variables, is the best possible based on the following criteria: a) the absence of bias between the estimated value and the true one and b) the minimization of the variance of the estimations.

Experimental variograms were created for radon concentration in groundwater in the study area, which is split into two sub areas for the purpose of obtaining good estimation. A variogram displayed in paper V shows the plot of variance relative to distances that separate the pair over one of the sub area. Spherical function presents a good fit.

The plot is characterized by: a zero nugget (the y intercept), a sill value (difference between the maximum value and the nugget) of $\gamma=1.7$ and a range (the distance at which the model reaches the sill) of 4 km.

Using this method a radon map, as an example, is generated and presented in figure 4.1.

The correlation coefficient between this surface and uranium in bedrock surface is very low ($R^2=0.01$). This indicates the complexity of radon transport in geological matrixes and also shows that geographical extrapolation of radon concentrations in water versus U in bedrock is not possible. .

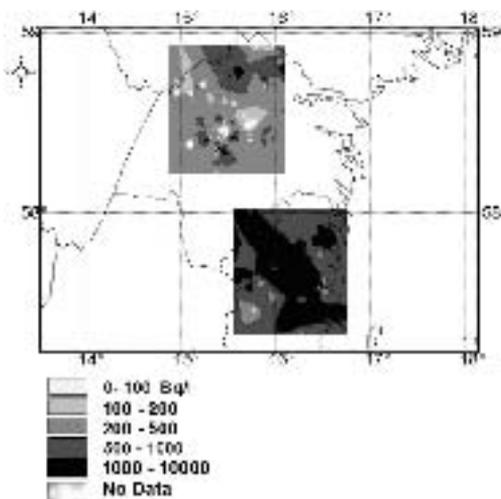


Figure 4.1: Maps of radon in groundwater created using kriging, the area is divided into two regions in order to get good estimations

4.3 Use of Spatial Cluster Analysis

The purpose of this analysis was to group similar concentrations of the studied radionuclides and to perform analysis of clusters in order to make spatial interrelation analysis. Because of the skewness of the data, the concentrations of the nuclides were first log transformed. The analysis was, then, performed by looking at local clusters, simultaneously detecting their location and testing for their significance. This was performed with spatial scan statistics analysis using SaTScan software (Hjalmarsson et al 1996). Information on high rates clusters found for the radionuclides are presented in Table 4.1. The table displays cluster centres, radii and their significance (p-value). Only primary and some of the secondary clusters are presented. The results obtained here (Table 4.1) reflect the lateral differences on the distribution of radionuclides in groundwater. Table 4.1 presents results of purely spatial analysis for clusters of radionuclides concentrations with high rates using the Poisson model.

Table 4.1: Locations of significant clusters of the four radionuclides as found by SaTScan, RA = Relative Abundance

Nuclide	Most likely Cluster				Secondary Cluster			
	Coods	Radius	RA	P-value	Coods	Radius	RA	P-value
U-238	15.3893N	0.06	2.15	0.018	15.5274N	0.25	1.44	0.111
	58.2960E				58.7575E			
Ra-226	15.6505N	0.13	2.05	0.216	15.5409N	0.03	3.87	0.859
	58.7212E				58.5390E			
Rn-222	15.8490N	0.89	1.33	0.002	15.5978N	0.08	4.14	0.766
	57.6003E				58.7904E			
Po-210	16.4506N	0.35	3.94	0.001	16.0931N	0.16	4.02	0.293
	57.5763E				58.8064E			

4.4. Spatial Distribution of ^{222}Rn and ^{226}Ra in Seawater

The concentrations of ^{226}Ra and ^{222}Rn in seawater were used first to calculate the inventories at each site, and then geostatistical tools were used to create gridded surfaces for these concentrations. Because of the few data for plotting at the moment, these maps provide only regional estimates of average concentration of these radionuclides. However, differences of the spatial distributions between ^{226}Ra and ^{222}Rn concentrations could be observed. In paper II we show the map of the concentrations, which was constructed by using the Inverse Distance Weighted (IDW) interpolator. The root mean square error (RMSE) and average standard error for the predictions were 13.2 and 10.4 for the ^{222}Rn map and 5.6 and 5.7 for the ^{226}Ra map respectively.

CHAPTER FIVE

**INVESTIGATION OF SOME PHYSICAL AND CHEMICAL
PARAMETERS OF RADON IN WATER**

5.1 Theory of radon transport

Radon gas (melting point (-71°C), boiling point (-68.8°C), critical temperature (104°C) and critical pressure of 62 atm.) is soluble in cold water (the solubility is about 0.5 at 0°C and decrease to ~ 0.1 at 100°C) and chemically it can form compounds like clathrates and fluorides (Lawrence 1983).

The transfer of radon from rocks to groundwaters is mostly governed by diffusion through crystalline lattices and through and along cracks and along the crystal boundaries. After being generated, ^{222}Rn atoms tend to move away from their original location until their recoil energy is totally transferred to the medium. Water increases the absorption of the recoil energy, thus enhancing the chance that the atom will terminate its recoil within the water.

The transport of radon in water can be considered to be due to the continuous motion of water molecules. This motion gives rise to mobilization of vacancies in the direction of reducing concentration. A steady state diffusion model for the transport of radon in porous media can be a useful to describe this system as well, since the water is an ideal homogenous medium. Radon release into the water phase at a constant flux of ^{222}Rn increases with time according to the equation:

$$A(t) = A_{\max}(1 - e^{-\lambda t}) \quad \dots \quad 5.1$$

A_{\max} is the activity at $t > 5$ half-lives, λ is the decay constant.

The flux density is proportional to the concentration gradient (Fick's law):

$$J = -D \nabla C \quad \dots \quad 5.2$$

where D = diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]

The steady-state diffusion is based on solution of the one-dimensional diffusion equation:

$$\frac{d^2C}{dz^2} - \frac{\lambda}{D}C = 0 \quad \dots 5.3$$

Using diffusion model assumption the variation of transport of radon with the medium depth can be described for an infinite isotropic medium, as:

$$C(z) = C(0)e^{-z/L} \quad \dots 5.4$$

Where $L = \sqrt{D/\lambda}$ is the diffusion length [m], $\lambda =$ radon decay constant [s^{-1}], $z =$ distance from source [m].

5.2 Radon transfer from water to air

Radon transfer from water to air occurs mainly by out-gassing, especially if the water is agitated or heated. The transfer efficiency depends on physical factors such as temperature and pressure or external factors such as bubbling or agitation. By using the “ATMOS” method (described in chapter two and in paper I) we showed that the transfer coefficient (T_f) of radon from water to air reaches 86% if the water is agitated at room temperature. The transfer coefficient, (T_f), increases with increasing water temperature. Experimental verification of the temperature dependence was obtained using the same set-up used in paper I. As shown in figure 5.1, all radon could be removed from water if the temperature is raised to above 42°C.

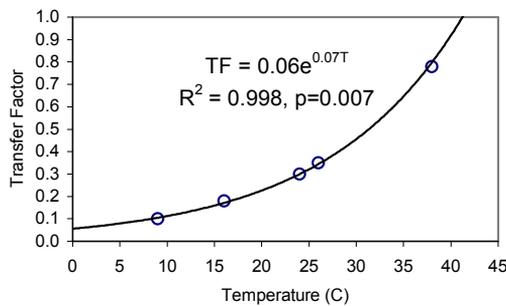


Figure 5.1: Rn transfer from water to air versus water temperature

Under normal conditions in dwellings, the amount of radon transfer from water to air is dependent on many factors that include the way of water use. For

example, in boiling the water or taking a shower most of the radon in water will be released. The transfer coefficient of radon from water to air has been evaluated for single houses by Nazaroff et al 1987 (see also NRC 1999). In their report to the National Council on Radiological Protection (NCRP 1989) they concluded that the ratio of radon in water (Bq/l) to that in air (generated from the water) (Bq/m^3) is about 10^{-4} .

As a part of the case study presented in chapter three (paper IV), radon in indoor air was also determined in order to study the transfer from indoor water usage and for the purpose of evaluating the contribution to the overall indoor exposure. As most of the studied dwellings were constructed of wooden materials the groundwater and soil/rock beneath the house are assumed to be the predominant sources of indoor radon. Solid-state nuclear track detectors (CR39) were distributed to houses for 2-3 months exposure during winter-spring time, and analysed by a certified Rn laboratory (Strålskyddstjänst, Sweden). The exposure period was chosen such as to be representative for the annual average indoor radon exposure.

The concentrations were found to range between 10 and $950 \text{ Bq}\cdot\text{m}^{-3}$ ($m_{\text{ean}} 133 \pm 125 \text{ Bq}\cdot\text{m}^{-3}$ (1 S.D.)). A plot of radon in air versus radon in kitchen tap water is given in paper IV, showing a poor correlation, i.e. there is a large variation in the magnitude of radon escape from water to indoor air in dwellings.

The ratio of Rn in air to Rn in water was found to range from 2.5×10^{-5} to 3.7×10^{-2} with a median value of 3.0×10^{-4} , which is in reasonable agreement with the general value given by the National Council on Radiological Protection (NCRP).

5.3 Impact of Stable Elements on Radon Concentration in Groundwater

This section deals with statistical analysis for studying the impact of stable elements on radon concentration in natural water. More than 70 stable elements were analysed in the same 328-groundwater samples used for radioactivity analysis in addition to conductivity, alkalinity, NO_3 , SO_4 , and total organic carbon. The results of these chemical analyses are summarised in paper VI. The

statistical analysis relative to radon data is based on full data evaluations. Applying univariate statistics to explain the presence of radon from chemical data returned no indication of relationship. However, when using multivariate statistics a possible linkage likely exist. Using partial least squares (PLS), which is a multivariate modelling technique, one can predict parameters from other measured parameters. The parameters involved here are the concentrations of stable elements, which are normalized (divided with the standard deviation) in order to give them an equal impact on the model regardless of their absolute concentrations. Paper III discusses results obtained by using the logarithms of the concentration and also by removing one parameter at time in order improved the model. Several parameters (i.e. pH, nitrate, fluoride, U, Cs, alkalinity, Pb, Chloride, Fe, conductivity, sulphate and Mn) were identified as possible predictors use for Rn. Of these, uranium was found to have a great impact on the predictive ability but also fluoride and caesium. The predictive ability has a R^2 equal to around 0.60 using only 2 PC. Based on this result the relation between radon and fluoride has been investigated experimentally presented in the following subsection.

5.4 The Influence of Fluoride, Carbonates and pH on Radon Transport in Water

The method developed in paper I was modified, here, to enable measuring radon transfer from water to air by avoiding the air to circulate through the water. Radon transfer as a function of water chemistry was measured for sets of demineralised water samples prepared with environmental concentrations of fluoride and carbonates for various pH (paper III). The samples contained known amounts of Ra tracer and the pH was adjusted using HCl and NaOH. The samples were let to stand for 24 hours before counting for 6 hours. The values of radon released, given in paper III, are normalized to the maximum value. The results indicate that high release radon is associated with low fluoride content and vice versa. In order to investigate the details of this relationship a set of samples with different fluoride concentrations and different

pH were prepared. The results (paper III) show a strong radon-fluoride relationship on radon transfer/loss, especially at low pH (e.g. pH3). However, for environmental conditions with pH of water of about 6-9 the effect is less dramatic.

5.5 Transfer of radon from source to fluorinated water

Simulation of radon transfer from a solid source into the water phase was investigated experimentally. A radium source (prepared by co precipitation with MnO_2) was shared between two sets of bottles that were filled with water with different concentrations of fluoride. The first set was closed while the second one left open and both were left to equilibrate for 24 hours. Then a 8 ml sample was carefully taken with a pipette, and mixed with a 12 ml liquid scintillation cocktail, Optiphase HiSafe 3TM, in a 20 ml vial. This was then measured in a liquid scintillation counter, Wallac 1415 GuardianTM, after about four hours. The results (shown in figure 5.2) from both set-ups showed the positive correlation between radon uptake and fluoride.

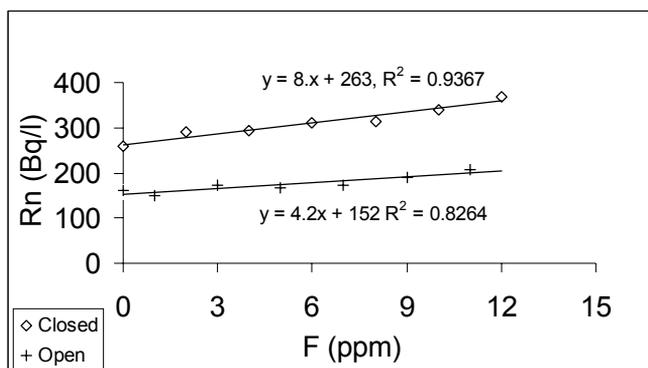


Fig 5.2. Transfer of radon from source to water versus fluoride concentration in water

CHAPTER SIX

**EXPOSURE FROM RADON AND OTHER URANIUM-SERIES
RADIONUCLIDES IN DRINKING WATER; RADIATION DOSE
ESTIMATION**

This chapter presents results of radiation dose calculations of selected radionuclides from the uranium and thorium series in drinking water with special emphasis on radon. The dose (Effective dose) due to the intake of these nuclides for 328 homes, using drilled-well water for drinking, is evaluated for different age categories.

In evaluating the health risks from uranium, we should know that and due to its properties uranium has dual types of effects when ingested: chemical toxicity and radiation exposure. The major health effect of uranium is attributed to the chemical kidney toxicity (Wrenn et al 1985; Leggett 1989; Kurttio et al 2002). The World Health Organization (WHO) recommends the limits of total uranium in drinking water to $2 \mu\text{g}\cdot\text{l}^{-1}$. However, other limits are used e.g. in the US, where the maximum contaminant level is $30 \mu\text{g}\cdot\text{l}^{-1}$ (EPA 2000).

In evaluating the absorbed dose due to radon ingestion from drinking water, the stomach is assumed to primarily receive all the dissolved portion of radon. Before it leaves the stomach some of the radon diffuses into and through the stomach wall (NRC 1999). Then radon (& daughters) passes next to the stem or progenitor cells, which are radiosensitive and also absorbs in blood irradiating the whole body internally, which may later result in cancer development. Children and infants show increased vulnerability due to the fact that they drink more raw water in proportion to their body mass compared to adults.

In order to estimate the radiation dose from drinking water the data presented in chapter three is used. In the present investigations it is observed that about 80% of the sites ($n=328$) have radon concentrations exceeding the recommended exemption level for radon in drinking water of $100 \text{Bq}\cdot\text{l}^{-1}$ (Nordic 2000) and 15% of the sites exceed the action limit of $1000 \text{Bq}\cdot\text{l}^{-1}$.

Similarly, 11.1% of the sites exceed the generally accepted limit of $30 \mu\text{g}\cdot\text{l}^{-1}$ for uranium and 47% of the sites exceed the limit of $185 \text{mBq}\cdot\text{l}^{-1}$ for combined radium ($^{226}\text{Ra} + ^{228}\text{Ra}$) used by many authorities.

In calculating the absorbed dose, assumptions on the rates of ingestion of tap water of $0.6 \text{l}\cdot\text{d}^{-1}$, $0.8 \text{l}\cdot\text{d}^{-1}$ and $1.3 \text{l}\cdot\text{d}^{-1}$ for children aged 1y and 10 y and adults respectively were made according to data from a US survey (Ershow & Cantor 1989). The intake rates include both direct intake of tap water and intake of processed tap water (e.g. coffee, tea, water used in food preparation). Since radon is readily lost from water by heating and bottling, the consumption of interest is that of water directly taken from the tap. Here half of the total intake is considered as derived directly from the tap (NRC 1999). Recent dose conversion factors for ^{238}U , ^{226}Ra , ^{228}Ra , and ^{210}Po ingestion reported by the *International Commission on Radiological Protection* (ICRP 1996) for three age categories: 1 year, 10 years and adults were used in the calculations. In calculating the contribution of dose from uranium, secular equilibrium between ^{238}U and ^{234}U is assumed, bearing in mind that in many ground water environments the ^{234}U may well exceed the ^{238}U levels. For calculating and estimating doses due to radon ingestion, dose conversion factors based on a *National Research Council* (NRC 1999) diffusion model were used. According to their model calculations the dose to the stomach wall predominates the organ doses. For ages 1 year, 10 years and adults these factors are respectively 2.3×10^{-8} , 5.9×10^{-9} , and 3.5×10^{-9} Sv per Bq.

The radiation doses due to radon inhalation were calculated according to the ICRP 1993 assuming an equilibrium factor (the quotient of the Equilibrium Equivalent Concentration to the ^{222}Rn concentration) of 0.4 and assuming 5700 hours spent indoors annually (Westrell C 1984).

The result of the dose calculation is presented in paper IV in association with geological structure from which the drinking water is derived. It should be noted that while the doses are calculated for concentration data for each individual site, they are generic since the well user age categories are not yet

available. The range of total effective doses due to ingestion, for the full dataset, is 0.05 - 20.4 mSv \cdot y⁻¹ and the mean values for the specified age categories, are respectively 1.52, 0.64 and 0.51 mSv \cdot y⁻¹. The contribution of ²²²Rn in water to the total ingestion dose ranged between 2.1 and 99.2% with a mean value of 74.9%.

The effective dose due to inhalation of ²²²Rn in air ranged between 0.2 and 20 mSv \cdot y⁻¹ (mean 1.9 \pm 1.8 mSv \cdot y⁻¹ (1 S.D.)). Categorization of dose by age is not made since reliable differential dose coefficients are not available. However, if based only on inhalation rates at different age, the doses estimated for age 1 y would be slightly lower.

Based on doses from ingestion of water and inhalation of ²²²Rn in air from all sites, the average contribution from inhalation of ²²²Rn in air to the total effective dose (ingestion + inhalation) is calculated. These amounted to 58 \pm 22%, 73 \pm 18% and 77 \pm 16% (1 S.D.) for the age categories 1y, age 10 y and adults respectively. The results show the importance of including the ingestion exposure route when making cancer risk assessment for ²²²Rn exposure in dwellings, especially for the exposure of children.

Risks Estimates

The effective doses received by ingestion of radon and long-lived radionuclides in water and radon in indoors air for the 328 well waters investigated are summarized in Paper IV. In order to estimate the risk of developing cancer from this exposure, risk coefficients obtained from epidemiological studies have to be used. The US National Academy of Sciences (NAS, 1990) report on age dependent lifetime cancer mortality risks (risk per 0.1 Sv effective dose) following acute radiation exposures. In the case of long-term exposure to radon and long-lived radionuclides, i.e. at low dose and dose-rate, the risk is believed to be lower. The ICRP (1990) propose a dose/dose-rate reduction factor of 2, which will be used here. Further, for the calculation the age specific effective doses (1y, 10y, adults) were used (Paper IV), and the NAS (1990) risk

coefficients were calculated for each age category by interpolation. The dose data and risk estimates are given in Table 7.1 for the maximum and median doses obtained from the full dose-data set. For comparison also the estimated lung cancer mortality risks from exposure to radon in indoor air is shown. This risk was estimated based on recent risk assessments made by the US National Research Council (NRC 1999). However, the NRC data refers to a mixed age population of smokers and non-smokers. Thus, the risks given in Table 7.1 assume an age-independence of risk. The cancer risks were calculated for lifetime exposure and exposure between ages 20-70 years of age. It should be noted that the risk data are rather crude estimates given the simplistic calculations. The results show that for the particular study area, the expected cancer risks are generally rather insignificant compared to the overall lifetime cancer mortality risk. However, for the areas of high radon and long-lived radionuclides the excess risk is significant, and more so if including radon in air exposure.

Table 7.1. Estimates of excess lifetime cancer mortality risks from radon and long-lived radionuclide exposure by ingestion of well water. Notation A refers to maximum doses and notation B to median doses estimated for the 328 well waters (Paper IV).

	Effective dose (mSv/y)			Excess lifetime cancer mortality risk	
	Age at exposure			Exposure period	
	1y	10 y	adults	1-70 y	20-70 y
A. Rn in water	16.1	9.0	6.9		
U, Ra, Po in water	4.3	3.5	1.4	3.3%	1.4%
Rn in air	1.6	1.6	1.6	1.8% ^{*)}	1.3% ^{*)}
B. Rn in water	0.45	0.06	0.05		
U, Ra Po in water	0.29	0.17	0.03	0.06%	0.04%
Rn in air	1.43	1.0	1.0	1.6% [*]	0.8% ^{*)}

^{*)} Refers to lung cancer only

CHAPTER SEVEN

CONCLUDING REMARKS

7.1. Summary

In this work, a method for measuring radon at low levels (detection limit, LLD $\sim 20 \text{ mBq l}^{-1}$) has been developed (paper I). This method provides a reliable and specific radiometric procedure for measuring ^{222}Rn in water for a wide range of concentration. It also shows a good potential for indirect analysis of ^{226}Ra in water at environmental levels (LLD $20\text{-}45 \text{ mBq l}^{-1}$).

Compared to established techniques for ^{222}Rn analysis of water, e.g. by LSC and gamma spectrometry, the method is inexpensive, easy to set up and it can be used *in situ*. The method has been tested against gamma ray spectrometry system for measuring radon in natural waters from a set of drilled wells, and against liquid scintillation spectrometry. Good agreement between the methods has been observed with advantages of the developed method for measuring low concentrations.

A regional study to evaluate radon in relation to some influencing parameters has been undertaken. Samples were collected from 328 selected drilled bedrock wells. Long-lived radionuclides of the uranium series, stable elements and other chemical parameters have been investigated.

The results indicate that some variables such as uranium and fluoride in water affect the radon levels. The radon-fluoride relationship has been investigated (paper III) in two ways: a) by investigating correlation between radon and all candidate chemical parameters in natural waters and b) by designing a laboratory experiments using the concept of the method in paper I. This study dealt with the accumulation of ^{222}Rn in water in relation to water chemistry, which has been investigated for 72 natural water samples. Statistical analyses using partial least squares showed that uranium, fluoride and to a lesser extent nitrate have a positive impact on the predictive ability of radon concentrations. The laboratory experiments were based on the method described in paper I with the modification that ^{222}Rn exhalation from the water surface is circulated in the

closed loop set-up without circulation of the gas through the water. This enables measuring the ^{222}Rn transfer from water to air without disturbing the sample. A Box Behnken design was created using three levels for each variable (fluoride, carbonates and pH) and a total of 16 experiments. The results of these experiments showed that the fluoride ions in water, especially at low pH, strongly affect the transport of ^{222}Rn in water, with a decrease in radon transfer/exhalation with increasing fluoride concentrations. As radon is not believed to form chemical compounds under the conditions of which these experiments were performed, physical processes may be responsible for the radon trapping in water. It is therefore suggested that parameters, such as the micro-bubble phenomenon and diffusion are affected by the presence of fluoride, reducing the radon mobility in water with increasing fluorides.

In relation to other parameters, the 328-groundwater sites, which were selected based on geological and aeroradiometric maps, were compared with geology and uranium in bedrock. Uranium contents of the bedrocks were reported to range from <1 to 48 ppm, for bedrocks mainly characterised as granite types, occasionally with pegmatite inclusions.

Radon levels in these groundwater samples ranged between 5 and 8105 Bq l^{-1} (paper IV). It has been shown in paper IV that the levels of ^{238}U , ^{228}Ra , ^{226}Ra , ^{222}Rn and ^{210}Po radionuclides in drilled bedrock wells showed expectedly large variations. In addition, no apparent correlation was found between radionuclide concentrations in tap or well water with bedrock geology. Also the inter-correlation between U series radionuclide concentrations in water was poor, pointing to the complexity of the processes involved in radionuclide accumulation in groundwater.

Radiation dose due to ingestion of these radionuclides in drinking water has been calculated for three age categories; one year, ten years and adults. The dose assessment showed large variation in total (ingestion + inhalation) annual effective doses, ranging between 0.05 mSv and 20 mSv, with the major dose contribution arising from ^{222}Rn . However, both the relative and the absolute contribution to dose from ingestion are significant, especially for infants and

children, an observation that must be considered when designing radon surveys and epidemiological studies.

Employing GIS and geostatistical methods spatially analysis of radon distribution in groundwater in connection to bedrock uranium has been performed (subject of paper V). Two methods: inverse distance weighting (IDW) and kriging were investigated for generating continuous surfaces of radon in groundwater based on measured data. The kriging method produced good estimations at unsampled places (RMSE as low as 232), but showed a weak relation to bedrock uranium ($R^2 < 0.1$). This is attributed to several parameters, including groundwater mobilisation, radon transport and other factors. Simple interpolation methods, such as IDW, with only one or two variables showed to be useful. IDW with fixed radius showed to be useful in obtaining search distance that links between two auto-correlated layers (uranium in bedrock & radon in groundwater). The best correlations ($R^2 = 0.5$) were obtained for input radius between 1 and 2.7 km, i.e. distances far greater than expected for radon transport in water. This implies that there are more parameters involved in carrying radon in groundwater systems that needs investigation.

The distribution in groundwater is mainly controlled by the availability of parent radionuclides in bedrock and also the water chemistry (paper IV & VI). In the 328-groundwater samples, it was found that 28% of the samples exceed the 1.5 ppm fluoride drinking water standard (WHO 1996) and 11% exceed 30 $\mu\text{g/l}$ uranium being the US EPA maximum contaminant level (EPA 2000). In total 49% of the samples exceed one or both of fluoride and uranium. It was found that the major aqueous chemistry (pH and alkalinity) governed the aqueous concentrations of most trace elements. As pH increase the concentration of fluoride increase and uranium showed highest concentration at intermediate pH. As the alkalinity increase uranium increase and fluoride showed highest concentrations at intermediate alkalinity. It has been observed that aqueous chemistry controlled trace elements more than the geology.

As another direct application, the method was utilised for evaluating radon in seawater in relation to source terms (paper II). Nineteen sites at the Baltic Sea have been investigated for depth profiles of radon and radium together with water temperature and salinity measurements. On average, radon concentrations were three times higher than those of radium. Generally the radon levels are comparable with levels found in other semi-enclosed seas (Karahana et al 2000). Inventory calculations suggested indicate close relationship between radon and radium in water with significant excess of radon. The correlation between Rn inventories and water depth indicate effective mixing of radon with depth i.e. diffusion of radon is not the major transport mechanism.

Based on the ^{226}Ra and ^{222}Rn inventory data, and using GIS & geostatistical tools, maps of ^{226}Ra and ^{222}Rn in seawater (raster data) were created.

7.2. Future prospective

The results obtained within this thesis constitute a regional baseline for radon in drinking water and points at the linkage to fluoride in water as well as uranium in bedrock. However, further investigations on the impact of aquatic parameters are needed, in particular to facilitate an improved prediction model, but also to further investigate the possibility of geographical extrapolation of radon data. In order to further explore the radon-fluoride relationship, there is a good potential in using existing regional and national fluoride in water databases/registries, to located areas of highly variable fluoride concentrations in water. By expanding the study there might be a potential for a future study on health effects. Present dose assessment show a great variability in individual doses, but the current data set is too small for a full-scale health effect study. Although several studies to evaluate the relationship between exposure of radon and cancer (lung cancer, childhood leukaemia) have been conducted, they are focussed on radon in indoor air. Thus, there is a need to investigate the water pathway. The design of an epidemiological study needs careful

considerations, and should include a magnitude of exposure issues, like other water contaminants and other possible confounders. A case-control study to assess the causality is a possible future prospective.

The fast development in the field of bio-dosimetry show promising signs of assessing radiation health effect even at low exposure levels by using bio-indicators. Exposure from radon (and other natural radionuclides) in water may be a candidate for a future bio-dosimetric study.

Turning to the marine environment, further studies on radon, as a tracer of seawater mixing processes is needed. Previously such studies have used tracer such as ^3H and ^{14}C . However, these tracers are not suitable for obtaining information on water exchange on short time-scales. Although the levels of radon in seawater are very low, it can now be evaluated *in-situ*, thus opening doors for future expanded studies on seawater processes.

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