SAHLGRENSKA ACADEMY

Accumulation of ^{63}Ni, ^{106}Ru and ^{125}Sb in phytoplankton

Master's thesis in Medical Physics

Yusuf Ali

Thesis:	30 hp
Program:	Medical Physics
Level:	Second Cycle
Semester/year:	Spring 2022
Supervisor:	Klara Insulander Björk, Rimon Thomas
Examiner:	Magnus Båth

It is with genuine gratitude that I dedicate this work

to my Ayeeyo **Khadiija Gure**.

Dear ayeeyo, I wish you were here in this world to see how far I have come. It means a lot to me that you were there for me when I needed someone the most. The fact that you were already thinking about me when you were just coming out of a coma has made me the person I am today. I want to express my sincere gratitude to you for having you in my life, but I can not find suitable words to describe it. You are simply the definition of an irreplaceable gift to me and I will be forever indebted to you. May God reward you with Jannatul Firdaus and shower you with the wonderful things in it, Amen!

Master's thesis 2022

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Abstract

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Background: Nuclear Power Plants (NPPs) release small amounts of radionuclides which contribute with a low radiation dose to the environment as well as humans and animals. In this context, marine ecosystems are critical, since most NPPs in Sweden are located by the sea. The *Concentration Factor* (CF) is a model parameter that is used to study the transport and uptake of these radionuclides. However, the published CF values for many elements range across several orders of magnitude.

Aims: The aim of this project was to experimentally determine phytoplankton CF for some of the radionuclides released from various nuclear facilities in Sweden, in order to improve their uncertainties and to enable a more realistic dose assessment. The elements analyzed in this study were *nickel*, *ruthenium* and *antimony*.

Materials and Methods: Seawater samples from two separate stations (Anholt E and Karlsödjupet) near NPP in Sweden, were collected by SMHI. Phytoplankton were then cultured in these seawater samples with addition of relevant radionuclides and nutrients. The cultures were filtered when the phytoplankton concentration reached around $1{\cdot}10^6$ cells/mL. A HPGe-detector was used to measure the activity of the filtrates and filters from ^{106}Ru and ^{125}Sb. Likewise, a liquid scintillation counter (LSC) was used to measure the activity of the samples containing ^{63}Ni.

Results and Discussion: The mean calculated phytoplankton dry weight were 33 $\pm$ 8 and 26 $\pm$ 4 pg for Anholt E and Karlsödjupet, respectively. The phytoplankton growth rates and dry weights in the different seawater samples were not significantly different. The mean calculated phytoplankton CF for the respective elements were as follows: 4000 and 3800 L/kg for Ni; 15000 and 20000 L/kg for Ru and 250 and 700 L/kg for Sb. The obtained values are in good agreement with published data.

Conclusion: The phytoplankton CF for the elements studied were as follows: 4000 and 3800 L/kg for Ni; 15000 and 20000 L/kg for Ru and 250 and 700 L/kg for Sb. The CF obtained in this study, had a smaller variation compared to the literature data, thus the uncertainties in the CF have been improved considerably. These CF will therefore provide a more realistic dose assessment.

Keywords: concentration factor (CF), phytoplankton, phaeodactylum tricornutum, uptake, radioactive releases, nickel, ruthenium, antimony, gamma spectroscopy, liquid scintillation counting.

Contents

1

Introduction

1.1 Radioactive releases

During normal operation, Nuclear Power Plants (NPPs) and other nuclear facilities release small amounts of radioactive elements (radionuclides). These radionuclides contribute with a low radiation dose to the environment as well as humans and animals. However, this dose is generally far below the limiting values specified by the *Swedish Radiation Safety Authority* (SSM) [1, 2]. Generally, these releases are reported as activity expressed in Becquerel (Bq), but since the activity itself says very little about the effect of the released radionuclides, the corresponding radiation dose is expressed in millisievert (mSv). In Sweden, SSM states that the consequences of the releases shall be less than a radiation dose of 0.1 mSv per year to the so-called "representative person"[1] [3].

Among the most dose relevant radionuclides that are released to the air and marine environment are: ^{3}H, ^{14}C, ^{51}Cr, ^{54}Mn, ^{58}Co, ^{60}Co, ^{65}Zn, ^{90}Sr, ^{99m}Tc, ^{110m}Ag, ^{125}Sb, ^{131}I, ^{134}Cs, ^{137}Cs and ^{152}Eu [4]. In addition, Ringhals (nuclear power plant in Sweden) expects that the importance of nickel (Ni) will increase in connection with the decommissioning of two of the current reactors. Furthermore, ruthenium (Ru) is of importance when doses are calculated for a hypothetical conservative case where leaking fuel rods are considered. There are large uncertainties regarding the transport and uptake of some of these radionuclides into the marine environment, which means that their effects on health and the environment are uncertain. This is partly due to the complexity of the environment and the different uptake pathways in the food web (plankton - fish - humans), but also large uncertainties in some of the *Concentration Factors* (CF). CF are also used for dose calculation in connection with other releases such as nuclear reactor accidents or nuclear bomb detonations.

Although radiation doses during normal (and controlled) releases are far below regulatory limits, the large uncertainties and lack of knowledge present in the transport and uptake of radionuclides will be a major concern during unplanned releases. Thus, quantification of the radiation dose is necessary. In this context, marine ecosystems are critical, since most nuclear facilities in Sweden are located at the sea.

[1] The "representative person" is a hypothetical group of people who, through their proximity to NPP and other nuclear facilities, receives the highest radiation doses.

Therefore, the focus in this project was to study the uptake of some of the dose-relevant radionuclides in the primary producers of the marine food chain, namely the phytoplankton; particularly *Phaeodactylum Tricornutum* species which is common in marine ecosystems in Sweden [5].

1.2 Phytoplankton

Diatoms are the most common type of phytoplankton and thus the basis of the marine food web [6]. They are generally found as a unicellular eukaryotic organisms with a diameter of 20 - 200 μm [7]. The marine diatoms are said to be among the world's most successful organisms and perhaps the world's most important primary producers. This is due to their ability to live in freshwater, as well as marine and terrestrial environments [8]. Furthermore, they are the main producers of O_2 and consumers of CO_2 in the oceans [9]. Phytoplankton has a significant impact among organisms living in the hydrosphere of the environment, as a primary producer it can transform inorganic elements into organic elements through photosynthesis. Inorganic elements are matter that does not come from living organisms, for example, natural minerals and metals. Through this conversion process, e.g. the oxygen that we breathe in, is in fact extracted from carbon dioxide (which is an example of an inorganic elements) by the autotrophs such as phytoplankton [10, 11].

1.2.1 Ecosystem models

It is important to study the transport of radionuclides through the various trophic levels to humans and in the environment. A common methodology is to use a model parameter called *Concentration Factor* (CF), which relates the concentration of an element in a medium (e.g. seawater) relative to the concentration in the organism under equilibrium conditions. CF are expressed in the unit L/kg. Furthermore, CF are not isotope-specific; for example, the CF for Ni applies to all Ni-isotopes. Both the ICRP and the IAEA have published recommended CF values for different elements in different organisms [12, 13]. However, the published CF values for many elements in these reports range across several orders of magnitude. This is partly due to the various chemical compositions of the water used in the uptake studies, but also because the CF values were established under different, and in some cases unknown experimental conditions. Furthermore, certain elements have been subject to a limited number of investigations, while for other elements, there are no publications (or not found to our knowledge) at CF for several organisms. Uncertainties in the CF may in turn contribute to significant uncertainties in modeling results [14].

The IAEA has compiled CF for many different elements in the report TECDOC-479 [12], and some CF vary over several orders of magnitude. Attempts were made to find additional sources for CF apart from the IAEA report, in order to identify CF that had a limited investigated data (e.g. Sb), but also to identify elements whose CF require a proper determination.

1.3 Previous data

1.3.1 Nickel

Nickel-63 (^{63}Ni) has a half-life of 100 years and decays by β^--emission into the stable isotope Copper-63 (^{63}Cu). Among the Ni isotopes, ^{63}Ni is considered to be one of the main isotope of concern for a variety of environmental reasons [15]. Despite this, only three investigated samples were found in the literature, in which Ni-CF ranged from 160 to 1400 L/kg fresh weight [16, 17]. This corresponds to 900 - 7 800 L/kg dry weight, using IAEA's recommended conversion factor of 0.18 dry weight to fresh weight [12].

1.3.2 Ruthenium

The radioactive isotope ^{106}Ru is also a pure β^- emitter with a half-life of 371.5 days. Again, only three CF data points are reported in IAEA TECDOC-479 [12]. Furthermore, these phytoplankton CF values vary from 54 to 10000 L/kg fresh weight; which approximately corresponds to 300 – 55500 L/kg dry weight using the same conversion factor as above [12]. In another study on the uptake of ruthenium by phytoplankton in seawater, a CF-value of ∼300 kg/L dry weight at equilibrium was obtained [10].

1.3.3 Antimony

Antimony-125 (^{125}Sb) has a half-life of 2.8 years and emits β- and γ-radiation. In a previous publication IAEA-TECDOC-211, only one CF data point of 1000 L/kg was found, although it is not clear whether this CF value refers to fresh weight or dry weight [18]. Antimony is an interesting element from a nuclear waste management perspective since it is a fission product and thus found in nuclear wastes [19]. It is also classified as a pollutant of priority interest both by the *U.S. Environmental Protection Agency* (USEPA, 1979) and the *European Union* (Council of the European Communities, 1976). In spite of its potential toxicity, very little is known about its behavior and uptake mechanisms in marine ecosystems [20].

1.4 Aims

The aim of this project was to experimentally determine phytoplankton concentration factors (CF) for some of the radionuclides released from various nuclear facilities in Sweden, in order to improve their uncertainties and to enable a more realistic dose assessment [4]. The elements analyzed in this study were *nickel*, *ruthenium* and *antimony*.

2

Theory

2.1 Gamma spectroscopy

Gamma spectroscopy is a technique used to identify various gamma emitting radionuclides in a sample. Many radioactive elements emit photons with specific energies when they decay. By measuring the energy of the photon that is emitted, one can identify the existing radionuclides in the sample since each energy is a "fingerprint" on which radionuclide is present in the sample. This can be accomplished using semiconductor detectors [21].

2.1.1 Semiconductor Detectors

Semiconductor detectors are solid-state radiation detectors consisting of e.g. silicon (Si) or germanium (Ge) atoms in a crystal structure, where the atoms are bound by covalent bonds. When incident ionizing radiation hits the detector and interacts with the detector material, so-called electron-hole pairs are produced where the electrons are excited due to added radiation energy, as shown in Figure 2.1. The vacancy left in the valence band acts as a positive charge carrier. In a semiconductor detector, approximately 3 eV is required to excite an electron to the conduction band [23]. By applying a voltage over the detector crystal, these charges are caused to move towards the poles and thus can be detected as an electric current. The measured current pulse (signal) is proportional to the deposited photon energy in the detector [23, 21]. The semiconductor detector used for this project is a High Purity Germanium (HPGe).

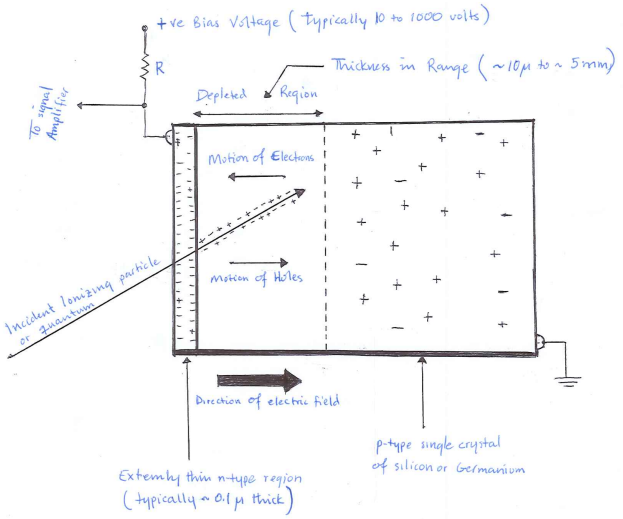


Figure 2.1: Schematic diagram of a semiconductor detector. Redrawn from [22].

2.1.2 Spectrum analysis

Using an integrated *Analog-to-Digital Converter* (ADC) and *Multichannel Analyzer* (MCA), the incoming signals from the HPGe detector were digitalized and transferred to a computer in the form of a gamma spectrum, where the obtained pulses were sorted into channels by their size. The gamma spectrum was then analyzed in *GammaVision* software to study the peaks to obtain the net area (A_n) used for calculation of the activity. The background (B) for each peak were subtracted by fitting a Gaussian distribution, see Figure 2.2. Net peak areas and their associated uncertainties were calculated by *GammaVision*.

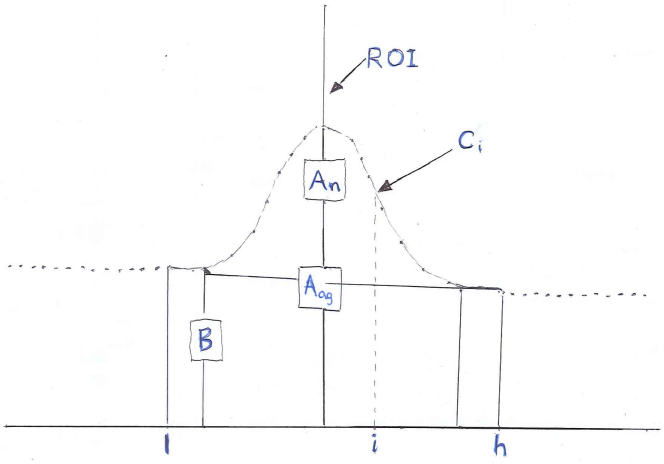


Figure 2.2: Calculation details for Net peak area. A_n and A_{ag} are the net- and gross area. B is the background area, l and h is the Region of Interest (ROI) low- and high limit, respectively; and C_i is the number of counts registered for each channel i. Redrawn from [24].

The measured ^{106}Ru and ^{125}Sb activity, A, in Bq is given by:

$$A = \frac{A_n}{\varepsilon \cdot \Upsilon \cdot t} \tag{2.1}$$

where A_n is the net pulse counts from the respective radionuclide, ε is the detector efficiency, Υ is the radiation yield and t is the measurement time for respective sample in seconds

2.1.3 Detection of ^{106}Ru using gamma spectroscopy

The radioactive isotope ^{106}Ru is a pure β^--emitter and decays to the ground state of ^{106}Rh which has a half-life of 30.1 seconds, and is therefore in secular equilibrium with ^{106}Ru after a short time. As ^{106}Rh in turn decays to ^{106}Pd, its decay is followed by emission of γ-rays from de-excitations of its daughter nucleus (^{106}Pd), as shown in Figure 2.3. By detecting the γ-rays from ^{106}Rh, ^{106}Ru can be detected indirectly using gamma spectroscopy [25].

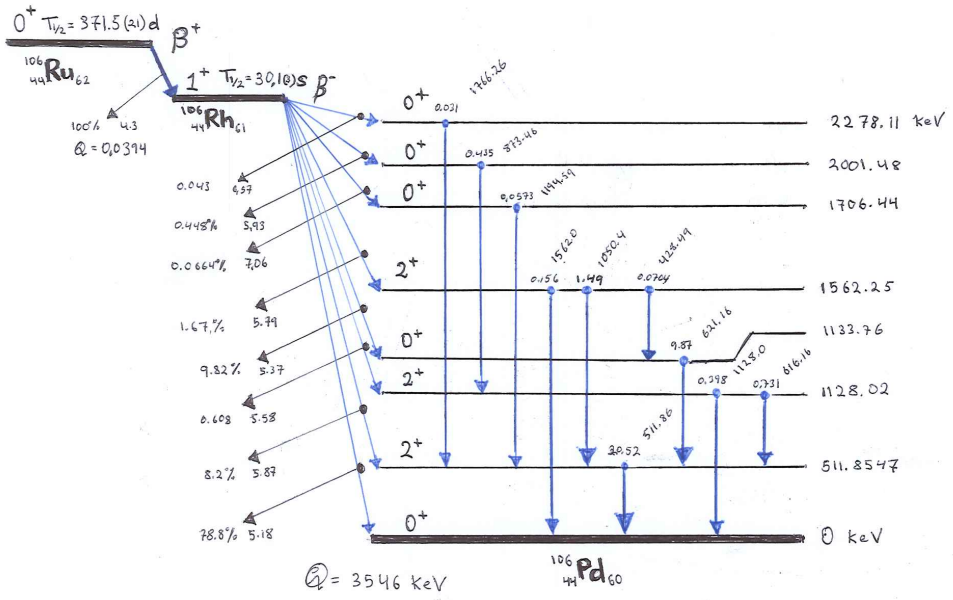


Figure 2.3: Simplified decay scheme for ^{106}Ru. Redrawn from [26].

2.2 Liquid Scintillation Counting

A liquid scintillation counter (LSC) is a detector system that uses a liquid as a scintillator material for detecting particles with low penetration such as α and β. When a particle passes through the scintillator medium, it excites the molecules and a scintillation light pulse is emitted. The light pulse is collected and converted into an electric pulse by a photomultiplier tube by means of a photocathode, while the pulse is amplified by a dynode chain and eventually detected by the electronics, see Figure 2.4. The light emitted (light intensity) is proportional to the deposited energy by the incoming particle [23, 28]. A background measurement (blank sample) with no radionuclides added, was made in an identical manner to the samples containing radionuclides. The registered number of counts was then subtracted from the measurement of the samples. In that manner, any light sources that were not related to the actual scintillation or due to background radiation could be excluded from the measurements. The typical efficiency that can be achieved in a modern LSC (in the absence of significant quenching) is about 60% and 90% for ^{3}H and ^{14}C, respectively [29].

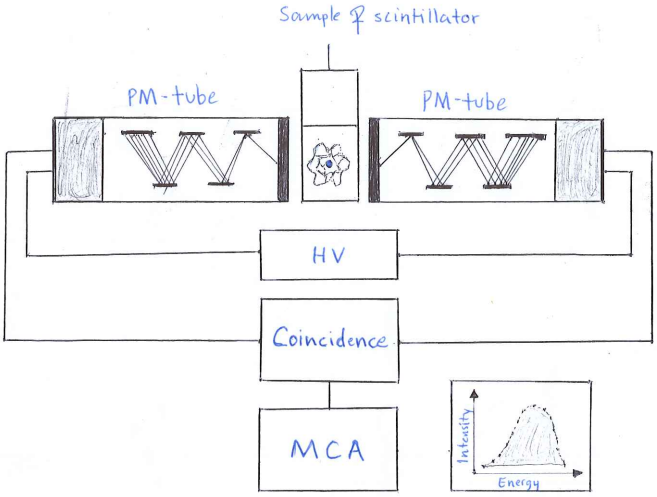


Figure 2.4: A principle schematic sketch showing the sequence of events in a LSC detection system. Redrawn from [27].

The activity of the radioactive samples A was calculated according to the following:

$$\mathrm{A} = \frac{\mathrm{R} - \mathrm{B}}{\varepsilon} \tag{2.2}$$

where ε is the efficiency (obtained from the calibration in CPM per Bq)[1], R is the measured count rate (counts per minute) and B is the background radiation (counts per minute).

2.3 Concentration factor calculation

The Concentration factors for the different elements in seawater was calculated according to the following:

$$\mathrm{CF} = \frac{\left(\frac{\mathrm{A_{plankton}} - \mathrm{A_{control\ filter}}}{\mathrm{m_{plankton}}}\right)}{\left(\frac{\mathrm{A_{filtrate}}}{\mathrm{V_{filtrate}}}\right)} \tag{2.3}$$

where $A_{plankton}$ is the radioactivity on phytoplankton filters, $A_{control\ filter}$ is the average radioactivity adsorbed on the phytoplankton-free control filters[2], $m_{plankton}$ is the dry weight of the phytoplankton in kg, $A_{filtrate}$ is the radioactivity in the medium (i.e. the filtrate) and $V_{filtrate}$ is the volume of the filtrate in L (which was subject to measurement).

[1] see equation 3.3

[2] see section 3.4. Filtration

3

Materials and Methods

3.1 Seawater sampling

Seawater samples from two separate stations near the Ringhals and Oskarshamn NPP, were collected by the Swedish Meteorological and Hydrological Institute (SMHI). These samples were collected in February 2022 at the cline, i.e. at a depth of 50 and 80 meters, sequentially from Anholt E (in Skagerrak; 32.86‰ salinity) and Karlsödjupet (in the Baltic Sea; 10.03‰ salinity). The location of the seawater sampling stations and associated data is shown in Table 3.1.

Table 3.1: The geographic location of the seawater sampling stations.

Sampling station	Sampling platform (code)	Sampling depth [m]	Latitude	Longitude
Anholt E	77SE	50	56° 40.1142′ N	12° 6.6258′ E
Karlsödjupet		80	57° 7.0302′ N	17° 40.1238′ E

3.2 Phytoplankton cultures

The culture process started with the seawater samples being sterile filtered through a 0.2 µm polycarbonate membrane filter (*Cytiva Whatman*^{TM} *Cyclopore*^{TM}), in order to remove any dirt or living organisms from the seawater. The phytoplankton were then cultured in these filtered seawater samples with addition of the relevant radionuclides and nutrients in proportions according to (Guillard, 1975), under controlled light and temperature conditions [30]. The samples were exposed to 12 hours of light daily through cold white LED illumination (6000 K) with an intensity of 200 $\mu Em^{-2}s^{-1}$ [31]. The temperature fluctuated with the light; ranging from approximately 20 °C to 25 °C during the dark- and the light periods respectively.

Cultures consisted of 29 mL of sterile filtered seawater and 1 mL of phytoplankton culture, cultured in 50 mL polystyrene cell culture flasks with vented caps from (*Thermo Scientific*^{TM} *Nunc™ EasYFlask*^{TM}, *Nunclon*^{TM} *Delta surface plasma treated*). Identical control samples were prepared with the same addition of radionuclides and nutrient concentrations, but with 30 mL of seawater without phytoplankton. The

idea was to be able to observe if any radioactivity was sorbed to the control filters or the culture flasks after filtration.

Radionuclides studied in this thesis were selected based on either large uncertainties or limited investigations. The literature search included both the IAEA report and other sources. The radionuclides ^{106}Ru and ^{125}Sb were in the form of dissociated chloride salts with an activity concentration of 500 kBq/mL in a 6 M HCl solution (*Eckert & Ziegler Strahlen- und Medizintechnik AG, Berlin, Germany*). ^{106}Ru was diluted to 2.5 kBq/mL. ^{63}Ni with an activity concentration of 60 kBq/mL with a 0.5M HCl solution was obtained from Chalmers University of Technology. It was originally supplied with a radionuclide purity of 99.9% of ^{63}Ni (*PerkinElmer Life and Analytical Sciences 549 Albany Street, Boston*). There were a total number of 36 samples (including control samples) in the experiment, as shown in Table 3.2 below. The pH value of the radionuclide solution containing ^{125}Sb was about 2, therefore 63 µl of a 6M NaOH solution was added to the cultures to maintain neutral pH, i.e. identical to the seawater prior to the radionuclide addition. The pH values were estimated (readout) with pH indicator paper sticks (***Fisher**brand*®*, pH Indicator Paper Sticks, pHix 0-14*).

Table 3.2: An overview of the experiment with additional data on the radionuclides used. A_c is the added activity concentration, N_s and N_c are the number of experiment- and control samples, respectively. Three replicates were used for each experiment.

Radionuclide	Sampling station	Initial A_c [kBq/mL]	N_s	N_c
^{63}Ni	Anholt E	60	3	3
	Karlsödjupet			
^{106}Ru	Anholt E	2.5		
	Karlsödjupet			
^{125}Sb	Anholt E	500		
	Karlsödjupet			

3.3 Phytoplankton growth

An automated cell counter (*Countess*^{TM} *II FL Automated Cell Counter*) was used to evaluate phytoplankton concentration and growth at regular intervals. Counting was performed at approximately 24-hour intervals, until plankton growth reached a concentration level of $1{\cdot}10^6$ cell/mL. An aliquot of 100 µL was taken from each culture flask and fixated with 2 µL of Lugol's solution (Iodine 99.5%, Resublimed p.a., *Thermo Scientific*^{TM}) in an eppendorf tube before counting. Lugol's is a strong solution composed of potassium-iodide and iodine, and can be used as an antiseptic agent [32]. From the prepared 100 µL aliquots, 10 µL were taken and pipetted twice into a Countess chamber slide (*Countess*® *II FL Hemacytometer*), and inserted it into the instrument (Automated Cell Counter). The device then displayed the concentration of algae in the culture in cells/mL. Note that the instrument works

according to the principle that it counts both live- and dead cells before reporting the average cell size in the sample; and the cell counting is performed at the central location of the counting chamber slide. To avoid the risk of contamination from residual samples, the chamber slides were cleaned with a 75% denatured alcohol disinfectant (DAX Ytdesinfektion 75+) before and after use.

3.4 Filtration

After the phytoplankton had grown to a concentration of approximately $1{\cdot}10^6$ cells/mL, the phytoplankton cultures were filtered using a polycarbonate membrane filter with a filter diameter of 25 mm and a pore size of 1 µm (*Cytiva Whatman*^{TM} *Cyclopore*^{TM}). A vacuum pump was used to apply a transmembrane pressure of 17 kPa. Following filtration of the cultures, the phytoplankton was rinsed twice with 5 mL of filtered seawater. The containers were weighed both after filtration and rinsing to enable dilution and geometry corrections at activity measurement. Control samples were filtered and rinsed in the same way as the phytoplankton samples.

3.5 Phytoplankton dry weight determination

The same filtration procedure as described above was applied to determine the dry weight of phytoplankton. However, the filters were rinsed twice with 5 mL of ammonium formate solution (NH_4HCO_2) (*Ammonium formate 99%, Acros Organics*) instead of seawater. NH_4HCO_2 was used since it evaporates when heated to 60 °C and thus does not contribute any extra mass that could adhere to the filters. The cultures were dried in an oven at 60 °C for a period of approximately 24 hours. The dry weight of phytoplankton was determined by weighing the filters before filtration and again after drying. The mass difference corresponded to the total phytoplankton dry weight of all cells, with the number of cells obtained from the cell counter. The equivalent dry weight per cell could then be determined by dividing the mass difference obtained by the total number of cells in each culture (based on the latest calculated phytoplankton concentration values).

A salinity of 10‰ means that 10‰ (by weight) of the seawater is composed of sodium chloride (NaCl). Since the molar mass of NaCl (M_{NaCl}) is known, its molar concentration (C_{NaCl}) can be calculated according to the following:

$$C_{NaCl} = \frac{s}{M_{NaCl}} \tag{3.1}$$

where s is the salinity of the respective seawater.

Using the calculated C_{NaCl} relative to the respective salinity (32.86‰ and 10.03‰) from equation 3.1, the ammonium formate mass needed could then be determined as follows:

$$m_{NH_4HCO_2} = C_{NaCl} \cdot M_{NH_4HCO_2} \cdot V \tag{3.2}$$

where $M_{NH_4HCO_2}$ is the molar mass of ammonium formate, V is the desired volume of ammonium formate solution, while the remaining notations used is that described in the text above.

3.6 Activity measurements

3.6.1 Gamma spectroscopy

A HPGe detector (Ortec GEM 50P4) with an energy resolution of 1.65 keV at 1.33 MeV and a relative efficiency of 50% (*Ametek, Inc., Oak Ridge, TN, USA*) was used to measure the activity of the filtrates and filters from ^{106}Ru and ^{125}Sb [33]. The filtered seawater and filters containing phytoplankton were placed in cylindrical plastic containers with lids (*Nolato Cerbo, Sweden*) with a known mass and geometry. The detector had shielding consisting of Pb with a layer of Cu and Cd to reduce background radiation. The spectra obtained were analyzed using *GammaVision* software as described in section 2.1.2 (Spectrum analysis). The same HPGe detector was also used to measure any radioactive elements that may have sorbed to the wall of the culture flasks; where the amount of radioactivity sorbed onto the walls was found to be negligible. The measurement was performed until the uncertainty in the main γ-peak area was less than 3%. Background measurements were also performed to exclude noise and background radiation in the energy spectra. Geometric efficiency corrections were made using *EFFTRAN version 4.2* to transfer efficiencies from a calibration source measured with containers identical to those used in this study (i.e. cylindrical plastic containers) [34].

3.6.2 Liquid Scintillation Counting

A LSC (Packard Tri-Carb® 2100TR) with an energy range of 0 - 2000 keV was used to measure the activity of the samples containing ^{63}Ni and to analyze the obtained spectrum. The samples containing 5 mL of the filtered seawater sample with ^{63}Ni and 15 mL of the liquid scintillation cocktail (ULTIMA GOLD^{TM} AB) were mixed in a plastic vial and then analyzed in the LSC. In order to calculate the activity concentrations of the radioactive samples, the counting efficiency in that particular sample must be known. Therefore, corrections for different efficiencies were made when measuring the filtrate and the samples with filters (both with and without plankton). This measurement contained three different variants (only seawater, filters without plankton and filters with plankton) with known ^{63}Ni activity. It was accomplished by mixing the solution of the known activity together with the same liquid cocktail as described above in a plastic vial and analyze it in the LSC. Furthermore, a series of samples with different known activities was measured, and it was concluded that efficiency was constant (linear) for the different count rates (R), see Figure 3.1.

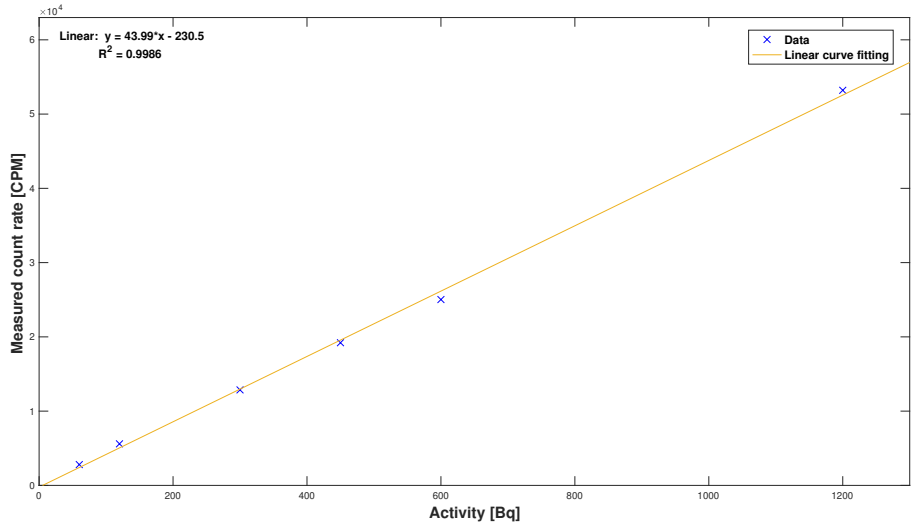


Figure 3.1: A known activiy as a function of the count rate (R) to investigate the detector efficiency.

The efficiency calibration factors were calculated as following:

$$\begin{cases} \varepsilon_{\text{filter}} = \frac{\text{R}_{\text{filter}} - \text{B}}{\text{A}_*} \\ \varepsilon_{\text{filtrate}} = \frac{\text{R}_{\text{filtrate}} - \text{B}}{\text{A}_*} \end{cases} \tag{3.3}$$

where A_* is the known activity in the samples, B is the background contribution, R_{filter} and $R_{filtrate}$ is the measured count rate (counts per minute) by the LSC on the filter and filtrate, respectively.

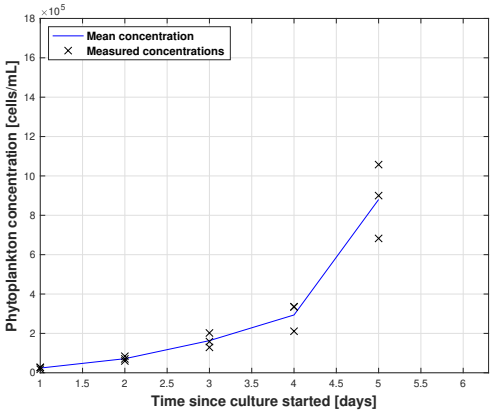
These efficiencies (ε_{filter} and $\varepsilon_{filtrate}$) were later used for the activity determination in equation 2.2. The detected activities in the control filters, plankton filters and filtrates were used to calculate the CF using equation 2.3.

4

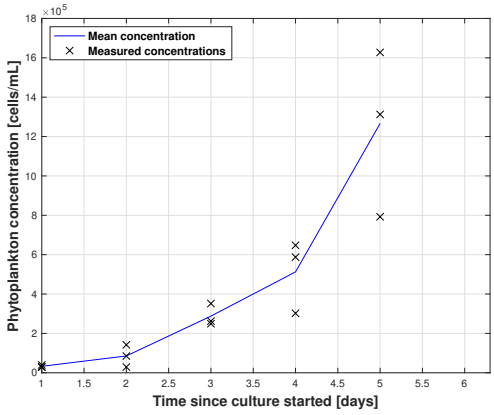
Results and Discussion

4.1 Phytoplankton growth

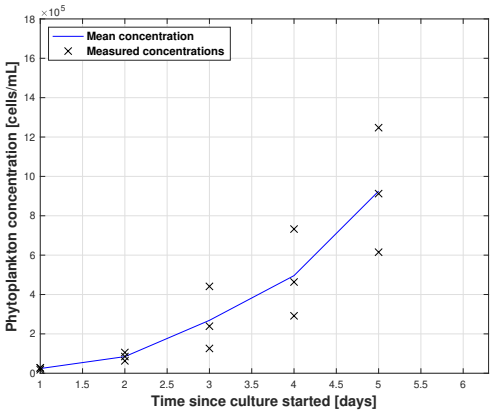
Sub-figures (a), (c), and (e) in Figure 4.1 shows the phytoplankton growth for samples where ^{63}Ni, ^{106}Ru and ^{125}Sb were added to the seawater from Anholt E sampling station while sub-figures (b), (d), and (f) show the corresponding data for seawater from Karlsödjupet sampling station. The fitted line is an interpolation between the points which was made by MATLAB. The plankton concentrations at day 5 were similar for all experiments (for the different radionuclides), when considering the range of the measured concentrations. Which also indicates that the experiments are reproducible and that the methodology is robust. There was no visible difference in terms of phytoplankton growth rate in the seawater from Anholt E and Karlsödjupet; although for samples with addition of Ni and Ru, the algae had already grown to approximately 10^6 cells/mL after 5 days, in contrast to Sb which grew after 6 days as shown in Figure 4.1.



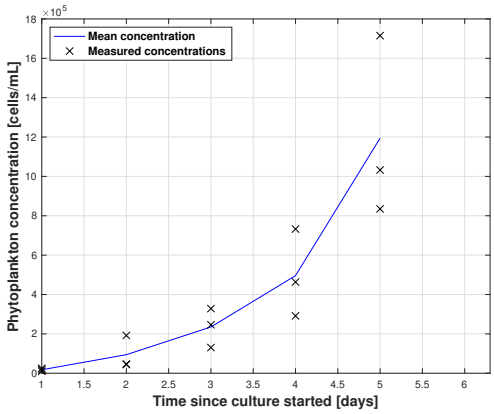
(a) PT growth in water from Anholt E with ^{63}Ni addition.



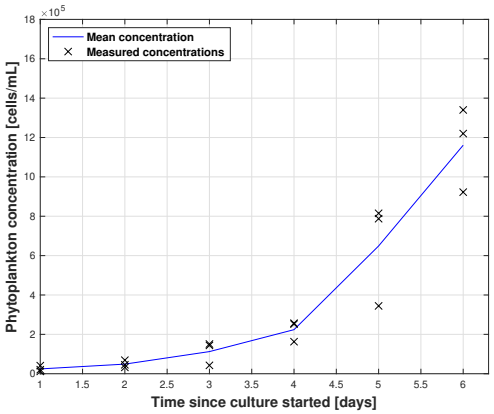
(b) PT growth in water from Karlsödjupet with ^{63}Ni addition.



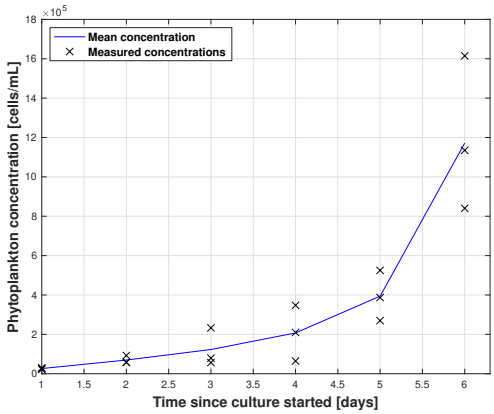
(c) PT growth in water from Anholt E with ^{106}Ru addition.



(d) PT growth in water from Karlsödjupet with ^{106}Ru addition.



(e) PT growth in water from Anholt E with ^{125}Sb addition.



(f) PT growth in water from Karlsödjupet with ^{125}Sb addition.

Figure 4.1: *Phaeodactylum Tricornutum* growth with addition of ^{63}Ni, ^{106}Ru and ^{125}Sb in seawater from Anholt E and Karlsödjupet, respectively.

4.2 Dry weight of phytoplankton

Table 4.1 shows phytoplankton dry weight values from the two seawater sampling stations. The dry weight was measured 5 days after cultivation and three replicates were used to calculate the average weight. The uncertainty was calculated as the standard deviation between the replicates. The dry mass of *P. Tricornutum* is slightly lower than the 35 pg/cell that can be calculated from the data reported by Fábregas et al. (1996) [35]. The organic mass according to Cresswell (2010) is 23 pg/cell for *P. Tricornutum*, which seems to imply that the results with respect to the phytoplankton dry weight are reasonable [36].

Table 4.1: Measured phytoplankton dry weight

Sampling station	Replicates	Average dry weight [pg]
Anholt E	3	33 ± 8
Karlsödjupet	3	26 ± 4

4.3 Concentration factors

Equation 2.3 was used to calculate the CF for each sample separately. The average and uncertainty was calculated from the three replicates. The calculated CF for the different elements (Ni, Ru and Sb) in phytoplankton in seawater from Anholt E and Karlsödjupet, respectively is presented in Table 4.2. Raw data used in the calculation of CF can be seen in Table A.1 in appendix A.

Table 4.2: Calculated concentration factors for Ni, Ru and Sb in *P. Tricornutum*. All CF values determined refer to dry weight.

Element	Sampling station	Natural element concentration [nM]	Averaged CF [L/kg]	Literature CF [L/kg]
Ni	Anholt E	83 ± 5	4000 ± 1200	900 - 7800 [12]
	Karlsödjupet	43 ± 2	3800 ± 500	
Ru	Anholt E	3 ± 1	15000 ± 1100	300 – 55500 [12]
	Karlsödjupet	48 ± 7	20000 ± 8000	
Sb	Anholt E	13 ± 1	250 ± 200	1000 [18]
	Karlsödjupet	< 0 ± –	700 ± –	

There were large variations in the literature CF presented in Table 4.2. Furthermore, it was observed that a lower algae concentration resulted in a higher activity per algae cell. This might be related to the algae's effect on their chemical environment and specification, since the algae in this study grew to much higher concentrations in the culture flasks than they do in their natural environment (in the sea). In this manner, they have an opportunity to influence both the chemical composition of the seawater (culture filtrate) and the speciation of the added radionuclides in different

ways. On the other hand, a lot of the variation could also be due to the plankton dry weight mass used in the CF calculation, which was difficult to measure with high precision. Therefore the uncertainty in the determination of the total algae mass ($m_{plankton}$) is large. So this is something that should be investigated more closely in future studies. There was no statistically significant difference between the CF measured in seawater from Anholt E compared to Karlsödjupet.

4.3.1 Nickel

The mean calculated nickel CF in phytoplankton in seawater samples from the Anholt E and Karlsödjupet were 4000 and 3800 L/kg dry weight, respectively, as shown in Table 4.2. This approximately corresponds to 700 L/kg fresh weight for the respective sampling stations using IAEA's recommended conversion factor of 0.18 dry weight to fresh weight [12]. The CF values obtained in this study are within the range of previously published values, namely 160 - 1400 L/kg fresh weight [16, 17].

4.3.2 Ruthenium

The mean calculated ruthenium CF in phytoplankton in seawater from Anholt E and Karlsödjupet were 15000 and 20000 L/kg dry weight, respectively; which approximately corresponds to 2700 and 3600 L/kg fresh weight, respectively using the same conversion factor as described above. The obtained CF-values lies within the wide range of previously reported literature data, (300 – 55000 L/kg dry weight) [12].

4.3.3 Antimony

The mean calculated antimony CF in phytoplankton in seawater from Anholt E and Karlsödjupet were 250 and 700 L/kg, respectively. However, the CF value determined in the seawater from Anholt E is much lower than those reported in the literature (1000 kg/L), although it is unknown whether the published CF refers to fresh weight or dry weight [18]. There were large uncertainties in this CF (1000 kg/L) for Sb, partly due to that it was an estimated value for different types of plankton (which could be phytoplankton, zooplankton, etc.), and thus not specific to phytoplankton. Furthermore, no details are provided regarding how these CF were obtained. Therefore, it is not entirely unexpected that the CF value obtained in this study could be different. It should be mentioned that on one of the triplicates, the activity concentration was about four times higher (although the triplicates were near identical to each other). This data point was considered to be an outlier and was therefore excluded and hence standard deviation could not be calculated on the CF data due to insufficient measurement data. This regards to the calculated antimony CF in phytoplankton in seawater from Karlsödjupet presented in Table 4.2.

5

Conclusion

In this study, dose relevant CF were experimentally determined for Ni, Ru and Sb for phytoplankton (*Phaeodactylum Tricornutum*), in sea water samples collected from the Baltic sea and Skagerrak sea. The CF for the elements studied were as follows: 4000 and 3800 L/kg for Ni; 15000 and 20000 L/kg for Ru and 250 and 700 L/kg for Sb. All CF values determined refer to dry weight for phytoplankton CF in Baltic sea and Skagerrak sea, respectively. Phytoplankton growth rates and dry weights are in good agreement with those found in the literature. In addition, the CF obtained in this study, had a smaller variation compared to the literature data, thus the uncertainties in the CF have been improved considerably. These CF will therefore provide a more realistic dose assessment. Furthermore, there are various phytoplankton species that have yet to be investigated. Likewise some dose-relevant elements (e.g. Eu, Sb, etc) for phytoplankton in the marine ecosystem. So this is something that could be good to study more closely in future studies, to reduce the uncertainties in CF.

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A

Appendix

Table A.1: An overview of the experiment with the data obtained. A_i is the activity on the plankton filters and A_c is the activity concentration in the filtrate.

Element	Sampling station	Algae cells [pcs]	Algae mass [mg]	Filtrate volume [ml]	$A_{c\text{filter}}$ [MBq/kg]	$A_{c\text{filtrate}}$ [kBq/L]	Sample CF [kg/L]
Ni	Anholt E	57 326 882	1.9	25.8	711 246.7	191 240.8	3719.1
		37 002 625	1.2	24.8	1 262 723.5	236 100.8	5348.2
		51 596 390	1.7	24.3	686 483.0	228 697.8	3001.7
	Karlsödjupet	792 500	0.5	26.0	1 555 711.6	356 626.3	4362.3
		1 312 500	0.9	25.8	1 324 826.8	395 254.5	3351.8
		1 627 500	1.1	26.1	1 212 272.0	322 307.2	3761.2
Ru	Anholt E	33 320 625	1.1	26.7	49.8	4.4	11318.6
		27 429 677	0.9	30.1	53.6	4.0	13467.5
		18 692 876	0.6	30.4	103.4	2.8	37489.1
	Karlsödjupet	48 042 158	1.2	28.0	56.9	4.0	14306.6
		23 767 373	0.6	28.5	104.0	2.9	35463.0
		28 864 281	0.7	28.0	97.5	3.4	28379.8
Sb	Anholt E	25 760 739	0.9	32.2	386.7	808.4	478.4
		38 122 893	1.3	30.8	86.6	800.3	108.3
		31 791 882	1.1	32.7	130.0	854.4	152.1
	Karlsödjupet	28 174 014	0.7	24.8	342.5	189.1	1811.6
		40 864 216	1.1	25.3	206.8	1 206.8	171.4
		20 950 373	0.5	24.9	1 866.3	180.5	10340.8

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