

University of Bremen Faculty of Environmental Physics Postgraduate Environmental Physics Program



Master Thesis

Depth distribution of ¹³⁷Cs in soil profiles in two locations of Northern Germany



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Abstract

This work focuses on the investigation of ¹³⁷Cs vertical distribution in the soil of two different undisturbed sampling sites in Northern Germany in 2014, contaminated by the Chernobyl and global weapons fallout. Additionally, re-examination is implemented by comparing the recent activity distributions with respect to earlier measurements obtained at the same locations in the 1990s.

Soil cores of 72 cm and 82 cm depth are examined from each spot, the soil of which was earlier characterized as orthic podsol and umbric gleysol respectively. In total, 77 samples are measured by gamma spectroscopy in high purity Germanium detectors of 50 % relative efficiency and analysed with the help of a gamma spectrometry software system.

Furthermore, modelling of the physical processes controlling the migration of ¹³⁷Cs is attempted with the use of the convection - dispersion equation in one of the sampling locations. Simulations for both old and recent profiles are done, allowing us to examine the reproducibility of old modelling results.

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Introduction

Radioactive ¹³⁷Cs is an artificial radioisotope produced by fission reactions. It has a relatively long half-life and decays with the release of beta (and in most cases subsequent gamma) radiation. These are mainly the reasons for its significance in the environment along with its bioaccumulation by organisms [Evangeliou et al., 2013]. ¹³⁷Cs was deposited in the Earth's surface globally due to nuclear weapons fallout (1945 - 1981) and concerning Europe its levels were later increased after the Chernobyl accident (April 1986). Fukushima disaster (March 2011) also contributed to that increase, but only by a minor amount [UNSCEAR report 2013].

¹³⁷Cs enters the soil by dry deposition and precipitation scavenging and depending on its migration rate it can be available for plant uptake and/or groundwater contamination. Its vertical profile knowledge, hence, is crucial in examining its migration behavior into the soil and predicting its transfer in human food chains.

Several studies have been made regarding ¹³⁷Cs activity concentrations in soil profiles [Almgren and Isaksson, 2006, Bossew and Kirchner 2004, Kirchner, 1998]. Less exist though regarding re-examination of vertical soil profiles [Schimmack and Schultz, 2006].

In this study, the objective is the re-examination of ¹³⁷Cs vertical distribution originating from the Chernobyl accident and nuclear weapons fallout at undisturbed soils in two regions of Northern Germany sampled first in 1992 [Kirchner, 1998] and 1994 (Kirchner, unpublished data) and later in 2014 at the exact same locations. The fact that the regions under investigation are undisturbed allows for the vertical soil profile of the radionuclide to be observed, not influenced from other than physical - chemical - biological processes, and studied again after all the years since the Chernobyl accident and weapons fallout soil contamination.

The first goal is to retrieve ¹³⁷Cs soil profiles and thereafter compare these results with the ones of the respective older cores as well as compare the results between the two regions.

At a second step, a mathematical model based on the convection-dispersion equation is fitted to the data for one of the regions. The comparison between profiles taken at different times, is an important factor contributing to the model assessment.

Finally, selected samples (related to one of the regions) were measured by Paul Kaiser in the course of his Bachelor thesis [Kaiser, 2016]; these samples are measured again in this work and cross - checking is done to compare the measurement and analysis results obtained in the two different laboratories.

During this study, the following tasks took place:

- Preparation of soil samples (77 in number).
- Calculation and grouping of efficiencies related to different geometries.
- Measurement and analysis of samples by gamma spectroscopy.
- Derivation of the convection dispersion equation and of its solution.
- Retrieval of soil profiles, data processing.
- Work on older soil profiles, older data processing.
- Model application to the old (model reproduction) and to the new data of Sandkrug.

Attempts on model application on Fischerhude data were made but the special features of its profile in combination to the limited amount of time made it difficult to complete and present results in this study.

• Presentation of the work, updated at each case, in two different conferences, namely 2nd International Conference on Radioecological Concentration Processes in Seville, Spain (6th to 9th of November 2016) and the DPG (Deutsche Physikalische Gesellschaft) spring meeting in Bremen, Germany (13th to 17th of March 2017).

Last but not least, this project was a team work; hence it is important to mention that sampling and part of the preparation of the samples (during both of which I was not yet involved with the radioactivity group) were done by other group members.

The outline of this work is:

- Firstly, a theoretical background is presented regarding the principles of radioactivity, radioactivity in soil and gamma spectroscopy.
- Secondly, a detailed description of the study area follows.
- The experimental tasks are explained at a next step.
- Afterwards, the modelling part is introduced.
- The results of the experimental measurements and of the modell application follow.
- Conclusions and outlook are thereafter presented.
- Finally, the references and the appendix follow with analytical datasets used in this study.

Chapter 1

Radioactivity

1.1 Radioactive decay

Radioactive decay is a spontaneous process through which certain nuclides (called radionuclides) approach energy state stabilization by emitting particles or radiation or both due to an adjustment of their internal structure.

The activity of a radionuclide is quantified as the number of disintegrations per second and is measured in Bq (1 Bq corresponds to 1 disintegration per second), while earlier than that Ci was the unit used for many years (1 Ci corresponds to $3.7 \cdot 10^{10}$ disintegrations per second).

Radioactive decay has three main modes: the alpha, beta and gamma decay.

Alpha decay

This kind of decay is mostly related to heavy nuclei with $Z \ge 82$ [Lilley, 2001], which emit a Helium nucleus (α -particle), while decaying. This process can be represented as follows:

$$^{A}_{Z}X \rightarrow ^{A-4}_{Z-2}Y + ^{4}_{2}He + Q$$

where, X is the parent nucleus,

- Y is the daughter,
- A is the mass number,
- Z is the atomic number and
- Q is the mass difference of the parent isotope and the daughter isotope/s which is converted into kinetic energy shared between the emitted particles.

Alpha particles have discrete energies which depending on the parent isotope range from 3 to 9 MeV.

Beta decay

This kind of decay is mostly related to nuclei with neutron (for β^- decay) or proton (for β^+ decay and electron capture) excess.

<u> β decay</u>: In this type of decay, a neutron within the nucleus is transformed into a proton with the emission of an electron and an electron antineutrino:

 $^{A}_{Z}X \rightarrow ^{A}_{Z+1}Y + e^{-} + \bar{v}_{e} + Q$

where, e⁻ is the electron and

 \bar{v}_e is the electron antineutrino.

<u> β^+ decay</u>: A neutron-deficient nucleus is unstable to β^+ decay, hence a proton within it, is transformed into a neutron with the emission of a positron and an electron neutrino:

$${}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Y + e^{+} + v_{e} + Q$$
 Eq. 1.3

where, e^+ is the positron and

 v_e is the electron neutrino.

Beta particles share the energy together with the electron neutrinos or antineutrinos; hence they have a continuous energy spectrum from zero to some maximum value (E_{max}) that ranges from 10 keV to 4 MeV and is characteristic of the specific parent nuclide.

Eq.1.1

Eq.1.2

<u>Electron capture:</u> In this case, a proton in the nucleus captures one of the surrounding electrons:

$${}^{A}_{Z}X + e^{-} \rightarrow {}^{A}_{Z-1}Y + \nu + Q \qquad \qquad Eq. \, 1.4$$

Both Alpha and Beta decay result in the creation of a new nuclide in the products, which might still be in an excited state, hence radioactive.

Gamma decay

It refers to the transition of an excited nucleus to a lower energy state or to the ground state by emitting gamma radiation (photons), thereafter it is not considered as a process of disintegration, but de-excitation. This type of radiation is usually emitted in combination to beta or alpha decay in which nuclei are usually left in an intermediate energy level, as mentioned above.

 $A_Z^A X^* \to A_Z^A X + h v$ Eq. 1.5

where, ${}^{A}_{Z}X^{*}$ is the excited nucleus and hv is a gamma-ray photon.

The energy of the emitted gamma rays is monoenergetic, characteristic for the parent isotope and may range from some keV to some MeV.

A process competing to gamma ray emission is the internal conversion, where the energy available is transferred to an inner shell electron. This electron is then ejected from the atom and the created vacancy, is filled by a higher shell electron. This rearrangement of the atomic electrons following internal conversion (but also electron capture) results in the emission of electromagnetic radiation, called X-rays which is monoenergetic and may appear in gamma spectra. There are also several other decay modes such as delayed neutron/proton emission and spontaneous fission, where a heavy nucleus spontaneously splits into two large fragments. The following graph (figure 1.1) is the chart of nuclides, where each point represents an isotope of a chemical element by type of nuclear decay.



Figure 1.1: Nuclide chart with possible decay modes [Audi et al., 2003].

1.2 Basic Formulas

There cannot be exact knowledge on when a radioactive nucleus will decay, but the probability that it decays in a specific time interval dt can be specified as [Tavernier, 2010]:

 $P = \lambda \cdot dt$

where, λ is the decay constant which is characteristic for a particular radionuclide.

The rate of decay expresses the number of nuclei disintegrated per unit time and is proportional to the number of parent nuclei. Alternatively, this rate is called activity and is expressed as:

$$A = \frac{dN}{dt} = -\lambda \cdot N Eq. 1.6$$

where, dN/dt is the rate of decay or activity (A),

N is the number of parent nuclei.

Another important quantity is the half-life $T_{1/2}$, which is the time duration when half of the number of the initial-parent nuclei has decayed.

If equation 1.6 is further processed:

$$\frac{dN}{dt} = -\lambda \cdot N \to \frac{dN}{N} = -\lambda \cdot dt \to \int_{N_o}^{N_t} \frac{dN}{N} = -\lambda \cdot \int_{t_o}^{t} dt \to \ln N_t - \ln N_o = -\lambda \cdot (t - t_o)$$

where, N_o is the initial number of nuclei at time t_o and N_t is the number of nuclei at time t.

Finally, if $t_0 = 0$, what comes out is the **radioactive decay law**:

$$N_t = N_o \cdot e^{-\lambda \cdot t} \qquad \qquad Eq. \, 1.7$$

This, if multiplied with λ , can alternatively be expressed in terms of activity as:

$$A_t = A_o \cdot e^{-\lambda \cdot t} \qquad \qquad Eq. \, 1.8$$

From the radioactive decay law one can easily deduce the relation between half-life and decay constant:

$$T_{1/2} = \frac{\ln(2)}{\lambda}$$
 Eq. 1.9

1.3 Sources of radioactivity

Radioactivity in the environment is a result of both natural and man-made sources. Natural radiation sources, though, are principally the ones that - under normal circumstances - contribute the most to human exposure. In the following pie chart (figure 1.2) the contribution of different sources of radiation is presented, including both natural and man-made ones.



Figure 1.2: Pie chart showing the percentage contribution of natural and man-made sources to radiation exposure [(1) world-nuclear]

Natural sources

There are two natural sources of radioactivity, the first is the cosmic radiation and the second is the terrestrial radiation.

Cosmic radiation refers to extraterrestrial origin, either galactic or solar. Cosmic rays mainly consist of protons, Helium and other heavier nuclei.

Terrestrial radiation is related to radionuclides which exist on the Earth from the time of its formation, called primordial radionuclides. Some of them are 40 K, 232 Th, 238 U, 235 U and 87 Rb. Apart from 40 K and 87 Rb, the remaining three are the starting points for decay chains, which can be seen in figure 1.3. Moreover, cosmic radiation contributes to the terrestrial sources of radiation by interacting with the Earth's atmosphere, biosphere and lithosphere and producing cosmogenic radionuclides such as 7 Be, 3 H and 14 C.

Man-made sources

The most important sources of man-made radioactivity are nuclear accidents, nuclear power plants, nuclear research and medicine [Cooper et al., 2003]. Due to these human activities, artificially produced radionuclides such as ¹³¹I, ¹³⁷Cs, ²⁴¹Am and ⁹⁰Sr have been released in the environment.



Figure 1.3: Decay chains of ²³⁸U, ²³²Th and ²³⁵U [(2) world-nuclear]

1.5 Radioactive ¹³⁷Cs

¹³⁷Cs is a radioactive isotope of cesium and a product of fission reactions, an example of which is shown in figure 1.4. In such a reaction, ²³⁵U can have more than 200 fission products; ¹³⁷Cs is, though, of a primary concern from an environmental point of view, due to the significant amount that is produced and to its relatively long half-life. Its importance is also related to the fact that its chemical and biological behavior is similar to potassium and rubidium and once it enters the body it is distributed in tissues and cells [Evangeliou et al., 2013].



Figure 1.4: ²³⁵U fission [(3) geigercounter].

 137 Cs was firstly released in the environment during nuclear weapon tests, which induced a global release of 948 PBq (1 PBq = 10^{15} Bq) [UNSCEAR 2000 report]. Nuclear accidents also contributed to that with the most important being the Chernobyl accident in April 1986 and Fukushima disaster in March 2011.

After Chernobyl - with a total release of 85 PBq [UNSCEAR 2013 report] - a large European area of about 200 000 km² was contaminated by more than 0.04 MBq of 137 Cs/m² [IAEA, 2006].

Following Fukushima, the total emission of ¹³⁷Cs was calculated to be on average about 20% of the estimated Chernobyl emission [UNSCEAR 2013 report]. Of this total fallout, only 1.9% was deposited on land areas other than Japan [Stohl et al., 2012].

In Germany, deposition densities in soil from the weapons fallout were at approximately 5-6 kBq m⁻² (estimated value for Northern Germany latitudes) [UNSCEAR 2000 Report], while from the Chernobyl accident of about 6 kBq m⁻² (average value for German soils) [Yablokov et al., 2009]. Fukushima's contribution to these radioactivity levels was negligible [Pittauerova et al., 2011].

¹³⁷Cs Decay

The radioactive decay of 137 Cs is represented in the form of a decay scheme as can be seen in figure 1.5.



Figure 1.5: Decay scheme of ¹³⁷Cs [(4) nucleonica].

According to this scheme, 137 Cs, with a half-life of 30.08 years, decays by 94.7% (branching ratio) to 137m Ba - excited state.

$${}^{137}_{55}Cs \to {}^{137m}_{56}Ba + e^- + \bar{\nu} + Q \; (\sim 514 \; keV) \qquad \qquad Eq. \, 1.10$$

This in turn decays through gamma emission to the ground state 137 Ba with a half-life of only 2.55 min and an emission probability of 85.1%.

$${}^{137m}_{56}Ba \to {}^{137}_{56}Ba + hv \ (\sim 662 \ keV)$$
 Eq. 1.11

In 5.3% of the times ¹³⁷Cs decays directly by β^{-} radioactive decay to stable ¹³⁷Ba state.

$${}^{137}_{55}Cs \to {}^{137}_{56}Ba + e^- + \bar{v} + Q \;(\sim 1176 \; keV) \qquad \qquad Eq. \, 1.12$$

Chapter 2

Terrestrial radioactivity

2.1 General information on soils

Soil consists of mineral and organic matter, water and air arranged in a complicated physicochemical system [Eisenbud and Gesell, 1997], a representation of which can be observed in figure 2.1



Figure 2.1: A representation of soil [(5) fao].

Inorganic constituents of soil are a result of weathering of various rock types. The final soil particles can have various sizes mainly distinguished in three categories namely sand, silt and clay. Soil particles, 0.1 to 2 mm in diameter, are called sand, 0.002 to 0.1 mm are called silt and less than 0.002 mm are called clay and in figure 2.2 their relative size comparison can be seen. Sand particles are generally chemically inert and because of their large sizes water travels through them with ease [Cooper et al., 2003]. Silt particles are smaller and have larger surface areas, while clay particles are the ones with the largest surface area per unit mass and are able to retain greater amounts of water than sandy soils. In reality, many soils have no dominant particle size, but contain a mixture of sand, silt and clay.



Figure 2.2: Relative size comparison of sand, silt and clay [Hillel, 2004].

The organic material of soil consists of residues of animal, plant and microorganism origin. These residues can be present both in their primary form (non-humic) and in different decomposition stages (humic). The concentration of organic matter differs depending on the region and although it represents a small proportion of the total soil mass, it affects physical and chemical soil properties.

Soil vertical profiles reveal horizons (which might be divided in further sub-horizons) with different physical characteristics. These horizons, might differ from soil to soil and also in cases where there is soil accumulation from wind or water deposition.

Some of the most important **physical properties** of soil are described below:

Soil structure, refers to the arrangement of soil particles (sand, silt and clay) into stable units named aggregates and affects aeration, water movement, conduction of heat, plant root growth and resistance to erosion.

Soil texture, is determined by the relative percentage of the components of sand, silt and clay in a soil mass and affects its retention capacity for nutrients and water.

Soil color, is determined by organic matter content, drainage conditions, the degree of oxidation and it distinguishes boundaries within a soil profile. Generally, a dark color reflects poor drainage, high organic content and low annual temperatures.

Porosity, refers to the pore space available - the open space of the bulk soil volume which is occupied by either air or water and allows the movement and storage of water and dissolved nutrients. Porosity depends upon other physical properties of the soil.

Permeability, refers to transmission of water and air through soil and is connected to other soil physical properties such as soil texture and structure. It is important as it affects the supply of root-zone air, moisture and nutrients for plant uptake.

Consistency, is the ability of the soil to stick together and resist to fragmentation.

Dry bulk density, is the mass of solids per unit volume of the soil and it is dependent on the structure of the soil with high bulk density indicating either compaction of the soil or high sand content.

One among other important **chemical properties**, connected to radionuclides behavior in soil, is:

Cation exchange capacity, is the maximum quantity of total cations that a soil is capable of retaining at a given pH, available for exchange with the soil solution. For example, clay minerals and organic matter have negatively charged sites on their surfaces which adsorb and hold cations such as Cs^+ .

2.2 Behavior of radionuclides in soil

Radionuclides' behavior in soil is mainly dependent on the physical and chemical soil properties, the chemical properties of the radioelement, the existence of microorganisms and fungi, the amount of rainfall, the temperature and soil management.

When a soluble radionuclide comes in contact with soil, it can be adsorbed onto the reactive coatings on particles, undergo ion exchange, be complexed with organic compounds, or remain in ionic form. The movement of the radionuclide through the soil is hence determined to a large extent by these partitioning processes [Cooper et al., 2003]. These processes are affected by the pH and cation concentration of the soil. Additionally, the downward movement into the soil profile is determined by the soil water content, the dynamics of which together with the texture and structure of soil, directly affect the radionuclide speciation [Pöschl and Nollet, 2007].

When radionuclides are transported with water and sorption takes place, the rate of movement of the radionuclide is reduced relative to the rate of movement of the water. For most ions, adsorption is reversible. In order to quantify this process - for modelling purposes - in case of equilibrium (rate of sorption equals the rate of desorption), the distribution coefficient kd is introduced [Shaw, 2007]:

$$k_{d} = \frac{Activity \ concentration \ in \ solid \ phase \ \binom{Bk}{kg}}{Activity \ concentration \ in \ liquid \ phase \ \binom{Bq}{l}} \qquad Eq. 2.1$$

Transport mechanisms

The most important processes governing the mobility of radionuclides in soil are:

Transport of solute by flowing water, which describes the passive movement of dissolved substances and is referred to as advection or convection.

Dispersion due to spatial variations of microscopic convective velocities, which leads to unequal solute movement in the direction of flow.

Diffusive movement within the fluid, which is of molecular or ionic origin and is an important mechanism for solute transport in soils especially in regions where there is little or no water flow. This net transfer of molecules occurs from regions with higher to lower concentrations.

The penetration depth of the radionuclide into the soil profile, is dependent on the migration rates, the radionuclide's half-life, the fallout history and the land use.

Radioactive ¹³⁷Cs in soil

¹³⁷Cs is the most common artificial radionuclide that contaminates soils world-wide. Once it reaches the Earth's surface, either through dry deposition or precipitation scavenging, it can migrate downwards (or in other directions) in the soil-water system mainly by diffusion and

convection. It can also be sorbed to the soil by a reversible process or it can be strongly bound-fixed in soils containing clay minerals and in such soils it has low vertical mobility.

Figure 2.3 resumes the different pathways that ¹³⁷Cs might follow after being emitted to the atmosphere, transported to the landscape and finally being transferred between vegetation, soil and water. In figure 2.4 the effects of some important soil parameters on the mobility of ¹³⁷Cs are shown.



Figure 2.3: ¹³⁷Cs environmental pathways [Ritchie and Roger McHenry, 1990].

	Cs				
Similar ions	K, Rb, NH ₄				
Chemical form in soil	Cs ⁺				
Changes in RN	mobility and plant availability if				
pH-value decreases Clay content decreases Sand content decreases Humus content low	↑ ↑ ↓ ↔				
CEC decreases $K_{\rm d}$ -value (1 kg ⁻¹)	↑ 10 ² -10 ³				

(Key: ↑ increased mobility; ↓ decreased mobility;
 ⇔ no clear effect)

Figure 2.4: Influence of certain soil properties in the mobility of ¹³⁷Cs in soil [Shaw, 2007].

2.3 Plant uptake

Soil-to-plant transfer is one important pathway leading to human ingestion of radionuclides and is quantified by the transfer factor (equation 2.2). For radionuclide concentration in soils, the loss by plant uptake can be considered negligible [Ritchie and McHenry, 1990].

$$TF = \frac{Radionuclide \ concentration \ in \ plant \ tissue \left(\frac{Bq}{kg}\right)}{Radionuclide \ concentration \ in \ soil \left(\frac{Bq}{kg}\right)} \qquad Eq. 2.2$$

Chapter 3

Gamma spectroscopy

3.1 Interaction of gamma radiation with matter

In this research the identification of 137 Cs is obtained through detecting isotope specific gamma rays emitted subsequent to its radioactive decay. Gamma rays, unlike α - and β -particles, can interact with matter by three different procedures and they transfer their energy to electrons which are detected by the ionization they create as they move through matter.

The three main processes by which gamma rays can interact with matter are the Photoelectric effect, the Compton effect and the Pair production.

Photoelectric effect

In this process, the atomic electron completely absorbs the energy of the incident photon and is thereafter ejected from the shell.

This kind of interaction is mostly dominant for low energy photons.



Figure 3.1: Photoelectric effect [Gilmore, 2008].

Compton effect

In this process, the incident photon is not completely absorbed, but scattered by an atomic electron. The latter, having absorbed part of the photon energy, is ejected from the shell.

This mechanism is mostly dominant in intermediate energies.



Figure 3.2: Compton effect [Gilmore, 2008].

Pair production

During this process, the incident photon encounters the electric field of an atomic nucleus and it creates an electron and a positron.

This can only take place in high energies of at least 1.02 MeV that is the sum of electron and positron rest mass.



Figure 3.3: Pair production [Gilmore, 2008].

3.2 Experimental set up

Gamma radiation has a long range in matter, which in combination to the fact that the emitted radiation is characteristic for each nucleus, makes it ideal for the identification of gamma-emitting radioisotopes in bulk samples. This identification is obtained through gamma spectroscopy, by analysing the spectrum produced in a gamma-ray spectrometer, the basic idea of which is shown in figure 3.4.



Figure 3.4: Scheme of gamma-ray spectrometer.

On the whole, the radioactive source emits photons which - in the detector - ideally interact with matter with Photo effect. The emitted electrons, after having transferred their energy to secondary and tertiary electrons, are collected as charge. The identification of a specific radionuclide is based on the fact that the height of each generated pulse is proportional to the energy of the incident photon, which is characteristic of the emitter. In reality, though, many photons undergo Compton instead of Photo effect, resulting in partially transferring their energy in the detector and consequently no identification can be done.

Detector

There are mainly three kinds of detectors used in gamma-ray detection, gas-filled, scintillation and semiconductor detectors. In this study, high purity Germanium semiconductor detectors of 50 % relative efficiency are used.

Semiconductor detectors are built from either elemental or compound single crystal materials which act as semiconductors (figure 3.5). Such detectors have a p-i-n diode structure in which the intrinsic (i) region is created by depletion of charge carriers when a reverse bias is applied across the diode. When the incident radiation-photons interact within this depletion region, hole and electron pairs (charge carriers) are created which are thereafter collected by charged electrodes with the electrons migrating to the positive and the holes to the negative electrode, creating thus, a charge.



Figure 3.5: Left: HPGe detector with lead shielding attached to LN_2 reservoir. Right: Semiconductor band structure [(6) astro].

Ge photon detectors have a small band gap of 0.74 eV [(7) Canberra], which signifies the temperature sensitivity of the material, meaning thus that these detectors have much lower maximum operating temperatures. Practically, hence, they need to be cooled in order to reduce noise - that would result from thermal charge carrier generation (electrons being able to jump the small band gap) - to acceptable levels. Detectors are cooled at around -200 $^{\circ}$ C by staying in thermal contact with the cooling material used - liquid nitrogen (LN₂) - which is

inserted into a container (Dewar). In order to avoid the natural radioactive environment interfering to the measurement of the samples, Pb shielding of 10 cm thickness surrounds the detectors, as can be seen in figure 3.5.

Preamplifier and amplifier

In the same housing with the detector, there is the preamplifier where the detected charge is firstly amplified and converted to a voltage pulse with amplitude proportional to the initial photon energy. The signal is afterwards shaped and further amplified in the amplifier.

ADC and MCA

The analog signal is afterwards converted to digital - pulse - in the ADC (analog to digital converter) and is then recorded in the MCA (multichannel analyser). MCA has a digital memory consisting of thousands channels, each one of which corresponding to a specific pulse height range/energy, which increases with channel number. When a pulse enters the MCA, is analysed for its amplitude and translated into one count in the respective channel.

Spectrometry software and spectrum

The resulting spectrum of detected pulses is displayed in a computer system with - in the case of our laboratory - Genie 2000 Analysis Software. An example of a gamma-ray spectrum as displayed with Genie is presented in figure 3.6.



Figure 3.6: Gamma-ray spectrum of a soil sample related to one of the sampling regions.

This is an example of an analysed gamma-ray spectrum concerning a soil sample. In the x axis, energy is represented and in the y the number of counts. One can distinguish photo peaks related to radionuclides that are common in such a spectrum.

The most prominent natural radionuclides here are 212 Pb at 238.6 keV, 214 Pb at 351.9 keV, 208 Tl at 583.1 keV, 214 Bi at 609.3 keV and 40 K at 1460.8 keV. 40 K is a primordial radionuclide, while all the others are members of thorium and uranium series, shown in figure 1.3.

The artificial radionuclide ¹³⁷Cs, is also distinguished at 661.6 keV.

Another recorded peak is the positron - electron annihilation peak at 511 keV. This peak originates from the collision of a positron and an electron which results in their annihilation and the subsequent release of two gamma-ray photons, each one of them with energy equal to the rest energy of the electron or positron (511 keV).

The blue and red color, differentiate between types of located peaks, with blue denoting multiple (usually double) and red single peak identification. A multiplet peak might result from gamma-ray emission by radionuclides at about the same energy region.

3.3 Principles of samples' software processing

In this chapter, basic principles are presented related to the resulting gamma spectrum, the form of the peaks and the further proceeding until quantitative results are deduced.

Peak shape

The recorded peak is approximated by a Gaussian curve (for large number of events) which occupies a number of successive channels and is characterized by the energy at the center, the Full Width at Half Maximum (FWHM) and the total number of counts.

Calibration

Energy calibration is a fundamental procedure since the resulting spectrum recorded in Genie is expressed as counts versus channel number of the MCA. Therefore it is necessary that channel number can be correlated to energy, taking into account that linear amplifiers are used in which channel number is proportional to the height of the respective pulse.

Energy calibration can be practically implemented through using a certified radioactive source with more than one well-known gamma lines, locating the maximum of the peaks with respect to the channel number where they were recorded.

The linear relationship connecting counts and energy is:

$$E = a \cdot ch + b \qquad \qquad Eq. 3.1$$

where, E is the energy of the gamma ray,

- ch is the channel number where the respective energy is recorded,
- *a* is the gradient and
- b is the offset.

Therefore, the energy versus channel number can be directly read out in the computer screen via Genie software.

Efficiency calibration is a crucial procedure prior to quantitative measurements which takes into account that depending on geometrical reasons such as sample size, density, distance from the detector and self-absorption in the sample, not all the photons emitted - from the radionuclide source - can reach the detector. What is taken into account (and is related to the detector's properties), additionally, is the fact that even when the photons reach the detector, not all of them interact and even if they do, only a few of them interact with Photo effect.

The efficiency varies with energy and hence it is different for each radionuclide plus it varies as being foretold for different geometries and different detectors. In the end, each sample is analysed with respect to a specific efficiency calibration file. An example of curves presenting the efficiency versus energy for different sample geometries (the most used ones for soil samples) is shown in figure 3.7.

The efficiency curves were implemented via ISOCS/LabSOCS which uses Monte Carlo calculation techniques. A prerequisite for that, is building the specific geometries through the Geometry composer, a special tool and part of Genie Software.



Figure 3.7: Efficiency curves for a specific detector related to the 0.5 l plastic bottle with two different filling heights of 30 and 70 mm and to the 0.5 and 1 l Marinelli beaker.

The detection efficiency can be expressed in terms of the number of counts, measuring time, emission probability and activity.

$$\varepsilon(E) = \frac{N}{t \cdot f \cdot A} \qquad Eq. 3.2$$

where, $\varepsilon(E)$ is the efficiency with respect to a specific energy,

t is the measuring time,

f is the emission probability and

A is the activity.

Background

In the resulting gamma-ray spectrum, the recorded photo peaks are located on a background originating from the natural radioactive environment, cosmic radiation or from the continuum due to the Compton instead of Photo interaction. This background (as counts versus channel number or energy) needs to be subtracted during the analysis. An example of a background spectrum is shown in figure 3.8, where one can see apart from the annihilation peak, other peaks discussed before, originating from natural isotopes such as 214 Pb, 214 Bi and 40 K.



Figure 3.8: Typical background spectrum.

Detection limits

Detection limits related to a specific peak, are normally defined by setting a threshold that the counts in the peak should exceed in order for detection to be stated. The threshold is chosen so that the smallest level of activity can be detected with 5% probability of detecting radioactivity when in reality it is not present and a 5% probability of not detecting radioactivity even if it is present.

Uncertainty of the result

Nuclear events follow a Poisson distribution (which as mentioned before, is resembled by a Gaussian distribution in the spectrum analysis software); hence the uncertainty connected to the total number of counts is expressed as their square root. In order for the uncertainty of the final activity concentration (activity per unit mass) result to be found, error propagation has to be implemented taking into account the uncertainty of all factors included in it, which are time, efficiency, total under the peak area counts and background connected counts, emission probability and mass. The final result together with its uncertainty is directly provided via Genie 2000 software.

Chapter 4

Study area

4.1 Sampling regions

The two sampling regions are Sandkrug (N 53.04; E 8.26) and Fischerhude (N 53.11, E 9.04) around 45 km west and 30 km east of Bremen respectively, shown in figure 4.1. Both sampling sites are flat areas used as pastures and they remained undisturbed until 2014 (the recent sampling date).



Figure 4.1: The two sampling sites [(8) openstreetmap].

From the 2014 sampling campaign, the following observations were made with respect to the soil of the two locations:

In Sandkrug the first approximately 40 cm are composed of softer and grey sand and below that until about 45 cm, soil has almost the same color but becomes harder. After 50 cm depth, new browner soil layer arises.

In Fischerhude the first soil layers are dark brown. Between about 26 until 40 cm, sandy soil layers appear, while bellow 40 cm, soil becomes dark brown again.

In the following figure, the soil vertical profile of Sandkrug (with obvious layering) and of Fischerhude are presented.



Figure 4.2: Soil profiles of: Sandkrug (left) and Fischerhude (right).

The majority of soils in Bremen region originate from older glacial drift areas and the resulting characteristic soils are Cambisols, Podsols, Gleysols, Luvisols and Histosols [(9) eusoils].

The two types of soil were classified in a former study in Ehlken and Kirchner (1996) as Orthic Podsol for Sandkrug and as Umbric Gleysol for Fischerhude and their physical and chemical properties can be seen in figure 4.3.

Depth (cm)	Horizon	Density $(g \ cm^{-3})$	Grain size distribution			Pore	pН		Organic	Exchangeable cations				Cation
			Sand (%)	Silt (%)	Clay (%)	volume (%)	H ₂ O	CaCl ₂	matter (%)	Na	K (m	Mg eq kg ⁻¹)	Ca	exchange capacity
Umbrie	c Gleysol													
0-35	Ă.	0.88	88.4	8.6	3.0	65	4.8	3.9	13-1	1.3	2.2	5-1	30.9	112
> 35	G _{0(r)}	1.42	91.1	6.6	2.3	45	5.6	4.4	2.4	0.9	0.5	0.9	15.7	38
Orthic	Podsol													
0-30	Ap	1.40	93.9	4.9	1.2	46	5-2	4.2	4.3	0.9	1.8	2.8	30.8	87
30-40	A.	1.56	94.4	4.6	1.0	42	5.5	4.2	2.4	1.2	1.0	2.1	16.5	66
40-48	Bh	1.42	94.8	4-2	1.0	46	4.7	3-6	2.6	1.0	0-5	3.2	24.7	105
48-56	В.	1.34	91.9	7.1	1.0	50	4.8	3.7	1.9	0.9	0.5	0.9	4.7	76
> 56	c	1.61	97.8	1.6	0.6	38	5.3	4.1	0.3	1.0	0.4	0.4	0.3	31

^aND: not detected, NA: not analysed.

^bTaken from Baumgartner et al. (1990).

Figure 4.3: Physical and chemical properties of the two sampled soils [Ehlken and Kirchner, 1996].

Chapter 5

Experimental part

5.1 Experimental procedure

Sampling technique

For both regions, a big hole of about 70 x 70 cm was dug by colleagues of the radioactivity group and the soil profiles were afterwards sampled with the use of a shovel ($20 \times 15 \times 2 \text{ cm}$), a glass plate (as can be seen in figure 5.1) and a meter scale.

In each region two soil profiles were sampled of 72 and 82 cm depth (separated in 2 cm thick soil layers) connected to Sandkrug and Fischerhude respectively.

After being sampled, the individual soil layers were placed in plastic bags (figure 5.1) and they were properly named/coded.



Figure 5.1: Sampling technique (left) and soil sampling plastic bags (right).

Due to time restrictions in the course of this Master thesis and also due to limited detector measuring time availability, the original plan of measuring two profiles from each region could not be achieved. However, enough samples completing one soil core from each location were processed allowing us to study the ¹³⁷Cs vertical distribution profiles.

Drying - Sieving - Milling

Soil profiles, after transported in the radioactivity laboratory, they were dried at 105 °C until constant mass and sieved in order to remove roots and leaves and to obtain a homogenized sample. Soil samples with bigger consistency particles, were additionally milled since by sieving only a bigger quantity of soil was being excluded.

Measurement

Detector measuring time varied depending on the sample's depth, as in deeper soil layers the ¹³⁷Cs concentration is lower and therefore longer measurement time was needed for the radionuclide to be detected with a relatively low uncertainty. More specifically, measuring times varied from several hours for the top soil layers to six days for the deepest ones. There were cases however that detection was not possible within the obtained measuring time; hence detection limits were identified for these samples.

Next step was the creation of the efficiencies (analytically explained below) used for the analysis of samples.

Geometries and creation of efficiencies

As shown in figure 5.2, there are two different geometries used in this study, the 0.5 1 Marinelli beaker and the 0.5 1 plastic bottle.



Figure 5.2: Geometries: 0.5 l plastic bottle (left) and 0.5 l Marinelli beaker (right) filled up with soil sample.

The criterion for the choice of either geometry was done by comparing the efficiencies related to each one of them for the energy of around 662 keV (where 137 Cs gamma photo peak is detected). Marinelli beaker has a hole on the bottom side allowing it to surround the detector and making it ideal for the measurement of bulk samples (see figure 3.7).

- For samples with volume of about $V \ge 300 \text{ cm}^3$, Marinelli beaker geometry was used. This volume accounts for Marinelli filling heights of at least equal to the height of the Marinelli's hole.
- For all the other samples with $V < 300 \text{ cm}^3$, plastic bottle geometry was used.

In the next table, efficiencies linked to Marinelli beaker and plastic bottle geometries of a specific density (1.5 g cm⁻³) soil sample are presented.

Table 5.1: Efficiency values for plasric bottle and Marinelli beaker related to the same volume.

	Plastic bottle	Marinelli beaker				
	$(\rho=1.5 \text{ g cm}^{-3}, h=78 \text{ mm}, V=300 \text{ cm}^{-3})$	$(\rho=1.5 \text{ g cm}^{-3}, h=80 \text{ mm}, \text{ V}=300 \text{ cm}^{-3})$				
Efficiency	0.0147 ± 0.0008	0.026 ± 0.002				

Even in the case of samples being measured in the same container (i.e Marinelli or plastic bottle) the detection efficiency may differ as a result of varying filling heights or samples' densities. For each case, a different efficiency calibration could be built, something that would be time taking (due to the big amount of samples) and unnecessary as seen below.

The idea is to group soil samples in subcategories depending on the filling height and the density and by checking how much the change of each factor (while the other stays unchanged) influences the resulting efficiency.

The evaluation was done through **efficiency testing**, an example of which is shown in figure 5.3. In this figure, curves corresponding to different filling heights of 0.5 l Marinelli beaker with stable density value are shown. Each point has an uncertainty (1 standard deviation), the magnitude of which covers a certain efficiency range. Efficiency creation was implemented as described in subchapter 3.3.



Figure 5.3: Efficiency versus energy curves for different filling heights of a 0.51 Marinelli beaker.

In the next figure, the same graph as before is shown focusing in the energy range where ¹³⁷Cs emits gamma rays.



Figure 5.4 Efficiency versus energy curves focused on the 137 Cs energy range for different filling heights of a 0.5 l Marinelli beaker.

From figure 5.4, three cases would be distinguished:

- Firstly, efficiency values being almost the same to each other (for filling heights from 88 to 93 mm).
- Secondly, differing efficiency values with overlapping error bars (100 and 110 mm filling heights).
- Finally, differing efficiency values with error bars which overlap the efficiency values of the other points (100, 105, 110 mm filling heights).

In this study the grouping was made based on the final case. This way of grouping obtains the coverage of all efficiency ranges without any gaps in between.

The same procedure was done also by varying densities while keeping filling height unchanged.

Additionally, efficiency testing was also performed with the same way described above for the plastic bottle geometry.

Results of efficiency testing:

Evaluating all the above mentioned, the final groups of efficiencies are created like this:

Marinelli

Case 1 (ρ = stable, h changes): Groups of efficiencies of 5 mm filling heights were made.

Case 2 (ρ changes, h = stable): Only one group of 1.5 g cm⁻³ was used for the majority of samples (with densities ranging from 1.4 and 1.7 g cm⁻³ and for such discrepancies, the efficiencies were almost identical to each other). Only in the case of two samples having quite different densities (0.7 and 1.0 g cm⁻³), two new efficiencies were built for them

In total for 0.5 l Marinelli beaker, 8 different efficiency groups were built with respect to one characterized detector of the radioactivity laboratory. Since efficiency changes for different detectors, the created efficiencies had to be transferred to the respective detectors where measurement was implemented. Finally, around 25 efficiency files were built.

Plastic bottle

Case 1 (ρ = stable, h changes): Similarly like for the Marinelli beaker, groups of efficiencies of 5 mm filling heights were made.

Case 2 (ρ changes, h = stable): In that case, the discrimination was done by 0.2 g/cm³ density.

In total, taking into account efficiency transfers, about 30 efficiency files were built.

Analysis

Finally, the analysis (the basic principles of which are described in chapter 3) and the subsequent identification of 137 Cs follow. The final result, in our case, is given as a value of activity concentration (Bq kg⁻¹, dry mass) together with its 1 standard deviation uncertainty.

Chapter 6

Modelling of radionuclides in the terrestrial environment

6.1 Introduction to the concept of modelling

When radionuclides enter the environment, they can be subject to different processes, follow different pathways and reach people. Taking all these into account, mathematical models have been developed and have become a valuable method for simulating the transport and behavior of radioactivity in the environment [Cooper et al., 2003].

Modelling of the environment, in general, is used from simply describing the state of the environment to predicting its future state either as a result of a specific incident or not. Models can be used to assess the impact of possible future practices that may lead in radioactive releases and also in the analysis of scenarios that will thereafter be taken into account in policy and decision making. In cases of a nuclear accident, for instance, where decisions have to be made in early stages when no sufficient data might be available, the use of models enables the estimation of future concentration of radionuclides and doses, helping thus for proper decisions to be made [Scott, 2003].

Apart from some of the advantageous applications of modelling mentioned above, there are also some limitations. One of them, first of all, is that the application of models is based on assumptions for simplification and therefore a manageable description of the situation (the one to be modelled). As soon as this is achieved, the model's output quality is related to a number of factors, such as the approach and scientific background, but also to the input data which can be unavailable or incomplete.

Whether a model is good or not depends on a number of factors. First of all, a model should be as simple as possible so that its implementation is more feasible. Apparently, a model should also be realistic, valid, reliable, accurate, precise and reproducible.

The three main stages in the development of a model are design and conceptualization, estimation (or calibration) and verification (or validation). After having specified the situation that needs to be studied, the development of the conceptual model is the next step. At this point, the appropriate environmental processes that have been considered together with the parameterization systems should be introduced [Scott, 2003]. Afterwards, this whole concept should be represented mathematically in a series of equations. At the estimation stage, unknown parameters are estimated, a process known as calibration. Additionally, model fitting needs to be performed, which is actually composed of three steps, the model prediction, the comparison of model prediction to the data and the determination of the best fitting parameter. Finally, in the verification stage, one has to check how the model behaves and how good it represents the real situation of interest.

The reliability of a model is related to the uncertainties it contains and their magnitude. Uncertainties are introduced in all stages of the building of a model. More specifically, there could be measurement, conceptual, modelling and parameter value uncertainty. Therefore, an uncertainty analysis needs to be done, so that the total uncertainty of the model's output is quantified.

6.2 Modelling the vertical distribution of ¹³⁷Cs in soil

The fallout radionuclide ¹³⁷Cs is the subject of this study and regarding its transport several studies have been made [Almgren and Issaksson, 2006, Bossew and Kirchner, 2004, Kirchner, 1998, Kirchner et al., 2009, Schuller et al., 1997]. In this direction, hence, different models have been built and used.

Time dependent models take physico-chemical processes into account to describe migration of radionuclides in soil. Additionally, due to the fact that ¹³⁷Cs is strongly adsorbed to cation exchange sites, movement in soils due to chemical and biological processes is limited [Ritchie and McHenry, 1990]. Hence, physical processes play a major role in describing its vertical migration in soils and models dependent on such processes should be used especially for undisturbed sites [Kirchner et al., 2009].

In this study a physically based model dependent on the convection - dispersion equation is used that takes into account convection, dispersion and sorption phenomena in soil. For a solute transported in the z depth - direction of a homogeneous soil, the 1 dimensional convection - dispersion equation is described as [Kirchner, 1998]:

$$\frac{\partial C(z,t)}{\partial t} = D \frac{\partial^2 C(z,t)}{\partial z^2} - u \frac{\partial C(z,t)}{\partial z}$$
 Eq. 6.1

where, C

u the effective transfer rate (cm y^{-1}) and

D the effective dispersion coefficient ($cm^2 y^{-1}$).

the total volumetric concentration (Bq cm^{-3}),

The first term of equation 6.1 describes the rate at which cesium concentration changes with time, the second and third one represent the dispersion and convection term respectively in the vertical direction.

The main simplifications considered are [Bossew and Kirchner, 2004]:

- The model is one dimensional in space, meaning that only the vertical component of transport is being considered.
- The model parameters u and D are considered as constant over the soil column and over time.
- Only two phases of ¹³⁷Cs are considered, the mobile one which is the cesium fraction that migrates downward in soil solution and the sorbed one which is the cesium fraction that is sorbed to soil by a reversible process.
- Linear sorption equilibrium is assumed to exist between the ¹³⁷Cs adsorbed and the one in solution.
6.3 Analytical derivation of the CDE and of its solution

Derivation of the CDE

First of all, the model is based on the diffusive-convective transport equation, on the continuity equation and the linear equilibrium sorption equation [Bossew and Kirchner, 2004]:

$$J = -D'\frac{\partial C_L}{\partial z} + u'C_L \quad Diffusive - convective \ transport \qquad Eq. 6.2$$

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial z} - \lambda C \quad Continuity \qquad \qquad Eq. 6.3$$

$$C_s = k_d C_L$$
 Interaction (linear sorption) Eq. 6.4

$$C = C_s + wC_L$$
 Connection between C_s and C_L Eq. 6.5

where, J expresses the flux (Bq $m^{-2}y^{-1}$),

 C_L the concentration in the liquid/sorbed phase (Bq m⁻² cm⁻¹),

- Cs the concentration in the solid phase (Bq $m^2 cm^{-1}$),
- C the total volumetric concentration (Bq $m^{-2} cm^{-1}$),
- D' the dispersion concstant (cm² y⁻¹),
- u' the interstitial water flow velocity (cm² y⁻¹),
- λ the radioactive decay constant (y⁻¹),
- kd the partition coefficient (dimensionless),
- w the water content (cm^3 water/ cm^3 soil).

Note: J, C, Cs, and C_L are z and t dependent.

By 6.4 and 6.5:

$$C = C_L(k_d + w) = R C_L$$

with R being the retardation factor which expresses the retardation of a radionuclide in a porous medium and is dependent on the partition coefficient (which is described in subchapter 2.2) and the water content.

This if combined with 6.2:

$$J = -\frac{D'}{R}\frac{\partial C}{\partial z} + \frac{u'}{R}C$$

If effective dispersion constant and effective dispersion velocity are introduced:

 $\mathbf{D} = D'/\mathbf{R}$ and $\mathbf{u} = u'/\mathbf{R}$, then this ends up:

$$J = -D \frac{\partial C}{\partial z} + u C \qquad \qquad Eq. 6.6$$

and in combination to 6.3:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \lambda C \quad Convection - dispersion - decay \qquad Eq. 6.7$$

A change of dependent variable to $W = C e^{\lambda t}$ (W is as C, dependent in z and t) leads to an equation without the decay term and then applying in 6.7:

$$\frac{\frac{\partial W}{\partial t}e^{\lambda t} - We^{\lambda t}\lambda}{(e^{\lambda t})^2} = \frac{D}{e^{\lambda t}}\frac{\partial^2 W}{\partial z^2} - \frac{u}{e^{\lambda t}}\frac{\partial W}{\partial z} - \frac{\lambda W}{e^{\lambda t}}$$
$$\frac{\partial W}{\partial t} = D\frac{\partial^2 W}{\partial z^2} - u\frac{\partial W}{\partial z}$$
 Convection – dispersion equation (CDE) Eq. 6.8

Solution of the CDE

Initial and boundary conditions are:

- Zero initial concentration, $C(z, 0) = C_0(z) = 0$ and hence $W_0(z) = 0$,
- Semi-infinite space and time, hence 0 ≤ z ≤ ∞ and 0 ≤ t ≤ ∞, with a finite solution, meaning lim_{z→∞} C = 0 and consequently lim_{z→∞} W = 0,
- Pulse like inputs described by a delta function in a flux type inlet condition: $Q'_{o}\delta(t) = \left| -D \frac{\partial W}{\partial z} + u W \right|_{z=0}$ [Butkus and Konstantinova, 2008] where $Q'_{o} = Q_{o}e^{\lambda t}$ is the initial deposition density and has the units of Bq/m².

Laplace transform will be used for the solution, according to which the Laplace transform $\hat{f}(s)$ of a function f(t) is defined as [Jury and Roth, 1990] :

$$\hat{f}(s) \equiv L(f(t)) \coloneqq \int_0^\infty f(t) \exp(-st) dt$$

for $0 \le t \le \infty$ and for values of the conjugate variable s where the integral exists.

Laplace transform of boundary condition gives: $\widehat{W}_{\infty} = 0$.

La place transform of inlet condition:

$$\int_{0}^{\infty} D \frac{\partial W}{\partial z} \exp(-st) dt = D \frac{\partial \widehat{W}}{\partial z}$$

$$= \int_{0}^{\infty} uW \exp(-st) dt = u\widehat{W}$$

$$= \int_{0}^{\infty} Q'_{o}\delta(t) \exp(-st) dt = \int_{0}^{\infty} Q_{o} \exp(\lambda t)\delta(t) \exp(-st) dt = Q_{o}$$

Therefore:

$$Q_o = \left| -D \frac{\partial \hat{W}}{\partial z} + u \hat{W} \right|_{z=0} \qquad \qquad Eq. 6.9$$

La Place transform will be evaluated in equation 6.8:

$$\int_{0}^{\infty} \frac{\partial W}{\partial t} \exp(-st) dt \xrightarrow{\text{Integrating by parts}} Wexp(-st)|_{0}^{\infty} + s \int_{0}^{\infty} Wexp(-st) dt =$$

$$= W_{\infty} \exp(-s\infty) - W_{0} \exp(-s0) + s\widehat{W} = s\widehat{W}, \widehat{W} \text{ is } z \text{ and } s \text{ dependent}$$

$$= \int_{0}^{\infty} D \frac{\partial^{2} W}{\partial z^{2}} \exp(-st) dt = D \frac{\partial^{2}}{\partial z^{2}} \left(\int_{0}^{\infty} Wexp(-st) dt \right) = D \frac{\partial^{2} \widehat{W}}{\partial z^{2}}$$

$$= \int_{0}^{\infty} u \frac{\partial W}{\partial z} \exp(-st) dt = u \frac{\partial}{\partial z} \left(\int_{0}^{\infty} Wexp(-st) dt \right) = u \frac{\partial \widehat{W}}{\partial z}$$

Hence by the Laplace transform of equation 6.8, we end up with:

$$s\widehat{W} - D\frac{\partial^2 \widehat{W}}{\partial z^2} + u\frac{\partial \widehat{W}}{\partial z} = 0 \qquad \qquad Eq. 6.10$$

Solutions to equation 6.10 are of the form: $\widehat{W} = \exp(mz)$, with m being a constant. If this is inserted into 6.10 and after a small rearrangement:

 $exp(mz)(s - Dm^2 + um) = 0$, this should be true for all z.

$$\to (s - Dm^2 + um) = 0 \to m = \frac{-u \pm \sqrt{u^2 + 4Ds}}{-2D} = \frac{u}{2D} \left(1 \pm \sqrt{1 + \frac{4Ds}{u^2}} \right)$$

The general solution is:

$$\widehat{W} = Aexp\left[\frac{uz}{2D}\left(1 - \sqrt{1 + \frac{4Ds}{u^2}}\right)\right] + Bexp\left[\frac{uz}{2D}\left(1 + \sqrt{1 + \frac{4Ds}{u^2}}\right)\right]$$

In order for $\widehat{W}_{\infty} = 0$, B should be zero. **Hence:**

$$\widehat{W} = Aexp\left[\frac{uz}{2D}\left(1 - \sqrt{1 + \frac{4Ds}{u^2}}\right)\right] \qquad \qquad Eq. \, 6.11$$

If Equation 6.11 is inserted into 6.9:

$$\begin{aligned} \left| -DAexp\left[\frac{uz}{2D}\left(1 - \sqrt{1 + \frac{4Ds}{u^2}}\right)\right] \cdot \frac{u}{2D}\left(1 - \sqrt{1 + \frac{4Ds}{u^2}}\right) + uAexp\left[\frac{uz}{2D}\left(1 - \sqrt{1 + \frac{4Ds}{u^2}}\right)\right] \right|_{z=0} &= Q_o \\ \rightarrow -DA\frac{u}{2D}\left(1 - \sqrt{1 + \frac{4Ds}{u^2}}\right) + uA = Q_o \rightarrow A = \frac{2Q_o}{u\left(1 + \sqrt{1 + \frac{4Ds}{u^2}}\right)} \end{aligned}$$

Hence:

$$\widehat{W} = \frac{2Q_o}{u\left(1 + \sqrt{1 + \frac{4Ds}{u^2}}\right)} exp\left[\frac{uz}{2D}\left(1 - \sqrt{1 + \frac{4Ds}{u^2}}\right)\right]$$
$$\rightarrow \widehat{W} = \frac{2Q_o}{u\sqrt{\frac{4D}{u^2}}\left(\frac{1}{\sqrt{\frac{4D}{u^2}}} + \sqrt{\frac{u^2}{4D} + s}\right)} exp\left(\frac{uz}{2D}\right) exp\left(-\frac{z}{\sqrt{D}}\sqrt{\frac{u^2}{4D} + s}\right) \qquad Eq. 6.12$$

At this step the goal is to transform from $\widehat{W}(z,s)$ to W (z,t)

For this reason the following shifting theorem through inverse Laplace transform will be used [Jury and Roth, 1990]:

$$L^{-1}(\widehat{f_{(as+b)}}) = \exp\left(-\frac{bt}{a}\right)L^{-1}(\widehat{f_{(as)}})$$

Where, α corresponds to 1 and

b corresponds to $u^2/4D$

By applying this into 6.12 we end up having:

$$L^{-1}\left[\frac{2Q_o}{u\sqrt{\frac{4D}{u^2}}\left(\frac{1}{\sqrt{\frac{4D}{u^2}}} + \sqrt{\frac{u^2}{4D}} + s\right)}\exp\left(\frac{uz}{2D}\right)\exp\left(-\frac{z}{\sqrt{D}}\sqrt{\frac{u^2}{4D}} + s\right)}\right] = \frac{2Q_o}{u\sqrt{\frac{4D}{u^2}}}\exp\left(\frac{uz}{2D}\right)\exp\left(-\frac{u^2t}{4D}\right)L^{-1}\left(\frac{\exp(-z\sqrt{s}/\sqrt{D})}{\sqrt{u^2/4D} + \sqrt{s}}\right)} \qquad Eq. \, 6.13$$

The last factor of 6.13 will be calculated based on the general formula mentioned below [Jury and Roth, 1990]:

$$L^{-1}\left(\frac{\exp(-z'\sqrt{s})}{\sqrt{s}+a}\right) = \frac{1}{\sqrt{\pi t}}\exp\left(-\frac{z'^2}{4t}\right) - a\exp(at^2 + az')\operatorname{erfc}\left(\frac{z'}{2\sqrt{t}} + a\sqrt{t}\right)$$

where, z' corresponds to z/\sqrt{D}

$$\alpha$$
 corresponds to $\sqrt{u^2/4D} = u/2\sqrt{D}$ and

erfc is the complementary error function,
where
$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_{z}^{\infty} e^{-t^{2}} dt$$
.

Hence and after a small rearrangement:

$$L^{-1}\left(\frac{\exp(-z\sqrt{s}/\sqrt{D})}{\sqrt{u^2/4D} + \sqrt{s}}\right)$$
$$= \frac{1}{\sqrt{\pi t}} \exp\left(-\frac{z^2}{4Dt}\right) - \frac{u}{2\sqrt{D}} \exp\left(\frac{u^2t}{4D} + \frac{uz}{2D}\right) \operatorname{erfc}\left(\frac{z}{2\sqrt{Dt}} + \frac{u\sqrt{t}}{2\sqrt{D}}\right) Eq. 6.14$$

Taking equations 6.13 and 6.14 into account and by rearranging, the total solution is:

$$W = Q_o \left[\frac{\exp(-(z-ut)^2/4Dt)}{\sqrt{\pi Dt}} - \frac{u}{2D} \exp(uz/D) \operatorname{erfc}\left(\frac{z+ut}{2\sqrt{Dt}}\right) \right]$$

Turning back to C (C=W exp($-\lambda t$)), we end up in the final solution of the CDE:

$$C = Q_0 e^{-\lambda t} \left[\frac{\exp(-(z-ut)^2/4Dt)}{\sqrt{\pi Dt}} - \frac{u}{2D} \exp(uz/D) erfc\left(\frac{z+ut}{2\sqrt{Dt}}\right) \right]$$

Since there are two sources of ¹³⁷Cs considered (Chernobyl and Weapons fallout):

$$C(z,t) = \sum_{i=1}^{2} \left\{ \underbrace{Q_{oi}}_{i} \underbrace{e^{-\lambda t i}}_{A \in \mathbf{B}} \left[\underbrace{\frac{e^{-(z-ut_i)^2/4Dt_i}}{\sqrt{\pi Dt_i}} - \frac{u}{2D} e^{u z/D} erfc\left(\frac{z+ut_i}{2\sqrt{Dt_i}}\right) \right] \right\} \qquad Eq. 6.15$$

The final solution is dependent upon the depth of the sample and time and is expressed in Bq $m^{-2}cm^{-1}$. The main characteristics of the solution are the dependence on:

- The initial deposition density (term A).
- The term that describes the exponential decay of the pulse (term **B**)
- The coupled convection dispersion term (C).

As an example of what this solution implies is shown in figure 6.1, where the coupled convection - dispersion - decay of a solute pulse at three different times is presented. As time passes, the pulse travels downwards, spreads out and its total integral decreases due to the radioactive decay.



Figure 6.1: Example of the solution of the convection - dispersion equation concerning the 137Cs activity concentration in the soil profile 10, 30 and 80 years after the initial deposition. Graph produced in R studio.

6.4 Model fitting

Non-linear least square fitting

R statistical environment was used for the application of non-linear least square fitting of the model to the data. The intention was to minimize the residual sum of squares:

$$RSS = \sum_{i=1}^{n} (f(x_i) - d_i)^2 \qquad Eq. 6.16$$

where, $f(x_i)$ is dependent on the x_i independent variable and is the equation to be fitted to the data d_i .

In this study, $f(x_i)$ corresponds to the equation 6.15, where u and D are used as free parameters, the values of which will be estimated by the fitting procedure and these values should be the ones that lead to the least deflection of the fitted curve from the data, meaning to the minimum RSS.

The minimization technique is based on an iterative method of improving a trial solution by a reduction of the goodness-of-fit parameter [Hughes and Hase, 2010], in this case the RSS.

Algorithms

Two algorithms (iterative approaches) were used for the fitting procedure, namely the Gauss-Newton, the Levenberg-Marquardt in order to achieve validation of the results.

Gauss-Newton: This algorithm is used in non-linear regression problems with the advantage that second derivatives are not required. It presumes that the least squares function is locally quadratic and it finds the minimum of the RSS by finding the minimum of the quadratic.

Levenberg-Marquardt: This algorithm combines two methods, when the parameters are far from their optimal value, it acts like a gradient descent method according to which the RSS is reduced by updating the parameters in the steepest-descent direction, while when the parameters are close to their optimal value it acts like the Gauss-Newton method [Gavin, 2016].

6.5 Methods

From activity concentration in Bq kg⁻¹ to Bq m⁻² cm⁻¹

is the activity concentration and

Results of ¹³⁷Cs activity concentration as directly deduced from the analysis procedure are given in Bq kg⁻¹ and in this unit the vertical soil profiles are visualized and compared. For the modelling procedure, though, a change of unit to Bq m⁻² cm⁻¹ needs to be done, since in this unit the solution of the convection - dispersion - equation is given. The conversion is done by using the density of the soil as precisely characterised in the past study and mentioned in Ehlken and Kirchner (1996). Hence, the applied formula is:

$$a\left(\frac{Bq}{m^2 cm}\right) = a\left(\frac{Bq}{kg}\right) \cdot \rho\left(\frac{kg}{m^2 cm}\right) \qquad Eq. 6.17$$

where, a

 ρ is the density.

Inventories

The ¹³⁷Cs inventory refers to the total radionuclide activity in the soil profile per surface area and in this study it is calculated as [Poreba and Bluszcz, 2007]:

$$Cs-137_{inv} = \sum_{i=1}^{n} Cs_i \cdot \rho_{di} \cdot d_i$$
where, $Cs-137_{inv}$ is the cesium inventory in Bq m⁻²,
i is the sample index,
n is the deepest sample with detectable ¹³⁷Cs,
 Cs_i is the activity in the i-th soil sample in Bq kg⁻¹,
 ρ_{di} is the dry bulk density of the soil in kg m⁻² cm⁻¹ and
 d_i is the thickness of the i-th sample in cm.

Separation of two cesium fractions

From the ¹³⁷Cs activity concentration values, separation between Chernobyl and weapons fallout related cesium was implemented in the 1990s soil profiles. It was done with the use of ¹³⁴Cs data (which were no longer detectable in 2014 since this artificial isotope of cesium has a shorter half-life of about 2 years) and by taking into account the ¹³⁴Cs:¹³⁷Cs activity ratio of the Chernobyl fallout of 0.528 ± 0.008 [Kirchner and Noack, 1988] at the time of deposition. The applied formula is:

$$Cs - 137_{Chernobyl} = \frac{Cs - 134}{\left(\frac{Cs - 134}{Cs - 137}\right)_{86}} e^{(-\lambda_{134} + \lambda_{137})t} \qquad Eq. 6.19$$

where, Cs -137 _{Chernobyl}	is the Chernobyl fraction of ¹³⁷ Cs as measured for the older
	cores,
<i>Cs</i> -134	is the ¹³⁴ Cs measured value in the 1990s,
$\left(\frac{Cs-134}{Cs-137}\right)_{86}$	is the cesium fractions as measured in May 6, 1986,
$e^{(-\lambda_{134}+\lambda_{137})t}$	is the decay correction factor from 1986 to the 1990s referring to
	the abovementioned fraction with,
λ_{134} , λ_{137}	being the decay constants of ¹³⁴ Cs and ¹³⁷ Cs respectively and
t	being the time between 1986 and the 1990s.

The weapons fallout fraction is then calculated as:

$$Cs - 137_{weapons} = Cs - 137_{measured} - Cs - 137_{Chernobyl} \qquad Eq. 6.20$$

Initial deposition densities

Initial deposition densities (Bq m⁻²) were used as fixed values determined by decay correcting the inventories related to Chernobyl and weapons fallout.

Chernobyl related inventory was calculated from Chernobyl related ¹³⁷Cs data of the 1992 work, with the use of ¹³⁴Cs vertical profile as described above.

Two cases were considered for weapons related inventory. In the first case it results from a single fallout event and in the second case it results from more than one fallout events as seen in table 6.1. In both cases the total deposition density referring to a specific date was taken from Kirchner's previous work who calculated it based on the weapons related ¹³⁷Cs data.

Year	¹³⁷ Cs (% of the total deposition activity				
	relative to a reference date)				
1958	9.50				
1959	9.50				
1960-1962	13.84				
1963	25.86				
1964	11.89				
1965	10.82				
1966-1968	7.13				
1969-1973	6.24				
1974-1978	4.08				
1979-1983	1.13				

Table 6.1: Analytical deposition history of weapons fallout events taken from Kirchner's older study.

Uncertainty analysis

Uncertainty connected to the separation of cesium fractions (without considering any uncertainty in the decay constant and the time t) was calculated with error propagation formula. According to this, for a function f(x,y) its standard deviation is calculated as (neglecting correlations):

$$\sigma_f = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 \cdot \sigma_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \cdot \sigma_y^2}$$

Chapter 7

Results

7.1 Experimental results and discussion

Distribution of ¹³⁷Cs within the soil profiles

• Sandkrug (orthic podsol)

Experimental depth distributions of ¹³⁷Cs are presented in figure 7.1 for Sandkrug both for the recent and old sampling campaigns. In the same graph, the measured (in 1992) profile of the short-lived ¹³⁴Cs is plotted. Logarithmic scale is used in the y axis so that the characteristics of the whole soil profile are visible. With vertical dashed lines, the different soil layers as observed in 2014 sampling campaign and mentioned in subchapter 4.1 are distinguished.



Figure 7.1: ¹³⁷Cs vertical profile (Sandkrug) in 1992 and 2014 together with ¹³⁴Cs data as measured in 1992. Horizontal and vertical error bars refer respectively to the thickness of the soil layer and the one standard deviation of the activity concentration.

The next graph (figures 7.2, linear y axis) demonstrates again the old vertical profile together with the calculated cesium fractions related to the Chernobyl accident and global weapons fallout (this separation was done as described in subchapter 6.5). The two fractions of 137 Cs are shown until the depth (12 cm) where 134 Cs was detectable in the profile; below this depth all activity concentrations are accounted to the weapons fallout.



Figure 7.2: Total ¹³⁷Cs vertical profile together with its Chernobyl and weapons fallout fractions for Sandkrug, 1992. Error bars are as described in figure 7.1.

1992: From figure 7.1 one can see that there are two peaks distinguished in the past ¹³⁷Cs distribution, one near the surface of the soil and another one at around 20 cm depth. From figure 7.2, it is evident that Chernobyl related ¹³⁷Cs accounts for the surface peak, showing diffusion like transport. The deeper peak is connected to the weapons fallout, revealing that its migration was dominated by a convective process, as firstly mentioned by Kirchner (1998).

2014: In 2014 (figure 7.1), the maximum activity concentrations still lie near the soil surface. Unlike in the older core, distinction of two peaks is not obvious. The region though at around 12 cm depth, triggers interest whether connected with the overlap of Chernobyl and weapons fallout related cesium and whether the weapons source is connected to the activity concentrations measured in the region from 12 to 25 cm.

• Fischerhude (umbric gleysol)

Similarly as before, experimental depth distributions of ¹³⁷Cs are presented in figure 7.3 (logarithmic y scale) for Fischerhude both for the recent and old sampling campaigns. In the same graph, the measured (in 1994) profile of the short-lived ¹³⁴Cs is presented. With vertical dashed lines, the different soil layers as observed in 2014 sampling campaign and mentioned in subchapter 4.1 are distinguished.



Figure 7.3: ¹³⁷Cs vertical profile (Fischerhude) in 1994 and 2014 together with ¹³⁴Cs profile as measured in 1994. Error bars are as described in figure 7.1.

The next graph (figure 7.4, linear y axis) demonstrates the old vertical profile with the cesium fractions related to the different fallout sources. The two fractions of ¹³⁷Cs are shown until the depth where ¹³⁴Cs was detectable in the profile; below this depth all activity concentrations are accounted to the weapons fallout (as mentioned also above for the other sampling site).



Figure 7.4: Total and separated - in Chernobyl and weapons fallout fractions - ¹³⁷Cs vertical profile (Fischerhude) in 1994. Error bars are as described in figure 7.1.

1994: Depth distribution (figure 7.3) in the core sampled in 1994 reveals one prominent peak not near the surface, but at a depth of around 15 cm which from figure 7.4 is visible that is connected to the Chernobyl fallout. Cesium concentration stays at a level of about 10 Bq kg⁻¹ between 23 and 28 cm depth which is connected to the weapons fallout (figure 7.4) and it starts decreasing at deeper soil layers.

2014: Twenty years later (figure 7.2) one peak, 5 cm deeper, at around 20 cm depth is observed which is possibly connected to the Chernobyl fallout. However, no proof can be provided for that, due to the lack of 134 Cs data in 2014. Directly below 20 cm depth, cesium activity concentration shows a steep decrease until about 30 cm depth to a level of around 0.1 Bq kg⁻¹. This decrease coincides with the existence (at that depth range) of a sandy layer.

In both cores of Fischerhude, there is cesium uniform distribution in about the first 10 cm of the soil, where organic and peaty soil was observed.

A general comment for both regions is the decrease of 137 Cs concentration as depth increases, which is expected since it is an artificial radionuclide deposited in soil and not initially existent in it.

Vertical profiles are totally different between the two sampling sites, something that would be partly expected since as described in subchapter 2.2 behaviour of a radionuclide in soil is not only dependent on the radionuclide itself but also on the type of soil and the processes taking place.

More specifically, the two different ¹³⁷Cs fractions show dissimilarities between the sampling spots:

Chernobyl fallout peak in Fischerhude in 1994 (figure 7.3) is located in a notable different depth in comparison to the respective one in Sandkrug in 1992 (figure 7.1), with the former one showing greater migration (about 13 cm deeper) within the soil over almost the same time period (from 1986 to the 1990s).

Weapons related cesium in Fischehrude (1994) is relatively uniformly distributed from the surface of the ground until about 28 cm depth, in contrast to the respective one in Sandkrug which demonstrated an evident peak. Landis et al. (2016) measured weapons fallout profiles (in different types of soils though), and among one of them, a similar uniform distribution was observed.

The general knowledge presented in chapter 2 for radionuclides in soil and different factors affecting their migration even if being helpful for understanding the background of all different processes, is not enough for a definite interpretation of the profiles.

Inventories

Activity levels decrease from the 1990s to 2014, in both regions, and this shift can be mainly attributed to the radioactive decay of 137 Cs as can be seen below. In table 7.1 the inventories in Bq m⁻² are presented related to both sampling sites and to both sampling dates.

Table 7.1: ¹³⁷Cs inventories for Sandkrug and Fischerhude referring to the 1990s (decay corrected to 2014) and to 2014.

Sampling site	Year	¹³⁷ Cs (Bq m ⁻²)	
Sandkrug	1992 (decay corrected)	~ 4100	
	2014		
Fischerhude	1994 (decay corrected)	~ 5800	
	2014	~ 3500	

• Sandkrug

¹³⁷Cs inventory of 2014 coincides relatively well with the one from the 1992 decay corrected value, which shows that cesium content is consistent in the soil throughout the years (as expected for flatlands like the one studied here), without any significant loss or gain.

Both in the 1992 and 2014 core, around 73% of the total inventory is present in the first 12 cm of the soil (where Chernobyl related cesium was mostly identified in 1992). In the old core, 95% of the total inventory is present from the surface up until about 30 cm, while for the new core 95% lies at the first 25 cm, which implies that the recent profile is somewhat compressed with respect to the old one.

• Fiscerhude

¹³⁷Cs inventory of 2014 differs by about 40% from the decay corrected value of 1994, which does not coincide with other inventory discrepancies of about 25% (as mentioned for instance in Bossew et al., 2004) for closely located sampled soils.

¹³⁷Cs plant uptake from soils was roughly calculated depending on transfer factor data from Ehlken and Kirchner (1996) (transfer factor equation is mentioned in chapter 2, equation 2.2). For this type of soil, depending on the season and the frequency of harvesting, transfer factors of about 1 to 8 were measured. In addition, the average activity concentration for the uppermost 10 cm of soil (this depth range was mentioned in the 1996 study) in the old core is ~37 Bq kg⁻¹ (dry mass). With an approximate density of harvested grass of 0.5 kg m⁻² (dry mass), activity in plants of about 18 to 148 Bq m⁻² are calculated. Plant uptake thus, is indeed negligible (as also mentioned in subchapter 2.3) with respect to the inventory discrepancy observed.

This discrepancy would not be expected for a flatland; therefore ⁴⁰K profiles are also plotted in order to provide some extra information about the soil profile and inventory. This radionuclide with a half-life of about 1.2 billion years is natural and a typical one existent in soils.



Figure 7.5: ⁴⁰K profiles in Fischerhude, in 1994 and 2014.

As can be seen, 40 K profiles between the two sampling dates differ a lot especially in the deeper soil layers, something that raises question marks whether some properties or dynamics changed in the soil or another factor that is not known up to now. Inventories also differ by about 55 %, with the 1992 one being ~196700 Bq m⁻² (no decay correction is needed due to the much longer half-life of 40 K in relation to the time between 1994 and 2014), while 2014 being ~85075 Bq m⁻² (for the 0-70 cm, the respective measured depth range in 1994).

If the respective 40 K profiles are compared for Sandkrug (next figure) one can see that they are more consistent between the 1990s and 2014, with inventories differing by about 10%, being around 83500 for 1992 and 94800 Bq m⁻² for 2014 for the respective measured depths.



Figure 7.6: ⁴⁰K profiles for Sandkrug, in 1992 and 2014.

7.2 Modelling results and discussion

• Sandkrug - Old core fitting

Fitted curves of the convective - dispersive model to the old soil core regarding Chernobyl and weapons fallout ¹³⁷Cs for Sandkrug, are presented in figures 7.7 and 7.8. These were obtained in Kirchner's published work in 1998 and were recalculated in this study. In table 7.2 the resulting parameter estimates from the past and recent fitting are shown.

For the Chernobyl fallout (1.5.1986) initial input of 4763.12 Bq m^{-2} was used (from Kirchner's work in 1992)



Figure 7.7: Fitting of the convective-dispersive model to the Chernobyl related ¹³⁷Cs data (presented with triangle symbols) in Sandkrug 1992. Solid and dashed line relate to the past and recent fitting respectively. Error bars are as described in figure 7.1.

For the weapons fallout fitting, two cases were examined, firstly a single fallout event as initial deposition and secondly an analytical deposition history (as described in subchapter 6.5). Contamination density referring to the 1.1.1964 is 4435.7 Bq m^{-2} and is taken from

Kirchner's previous work on the same dataset (an extensive deposition history was also considered for the 1992 fitting).



Figure 7.8: Fitting of the convective-dispersive model to the weapons related ¹³⁷Cs data (presented with triangle symbols) in Sandkrug, 1992. Solid line is the result of past work. Dashed and thick solid lines refer to recent work with deposition history and single fallout as input event respectively. Error bars are as described in figure 7.1.

Cesium fractions of the 1992 profile	u (cm y ⁻¹)	$D (cm^2 y^{-1})$	RSS	Study
¹³⁷ Cs, Chernobyl	0.12 ± 0.08	0.59 ± 0.19	20552	Kirchner 1998
	0.12 ± 0.08	0.58 ± 0.19	20337	This study (G-N, L-M)
	0.73 ± 0.04	0.99 ± 0.29	16716	Kirchner 1998
¹³⁷ Cs, weapons	0.72 ± 0.04	0.98 ± 0.27	16545	This study (G-N, L-M) (deposition history)
	0.70 ± 0.04	1.24 ± 0.29	16529	This study (G-N, L-M) (single fallout)

Table 7.2: Parameter values and residual sum of squares (RSS) from fitting the model to the depth profile of 1992 (Sandkrug). G-N and L-M account for the Gauss-Newton and Levenberg-Marquardt algorithms respectively.

The curves of Chernobyl related ¹³⁷Cs in 1992 (figure 7.7) reveal a good agreement between the older and recent fittings. This agreement is also obvious by looking at the estimated parameters and RSS values in table 7.2.

From figure 7.8 consistency between the solid and dashed line (older and recent weapons related 137 Cs fitting) is observed. Both of these curves refer to an analytical deposition history input. The respective estimated parameters (table 7.2) differ only by less than 1 %.

The alternative of using **single event** as the form of initial deposition for weapons fallout, also examined here, provided a slightly different fitted curve (figure 7.8, thick solid line). Comparing the fitted parameters for the old and this (single fallout event) fitting, RSS values and effective velocities do not differ much (about 1 % for RSS and 4 % for u). The biggest difference is observed between the effective dispersion constants which differ by about 20 % (their uncertainty values, though, overlap) with the recently fitted one overestimating even more the width of the peak.

From figure 7.8, one can see that taking more than one deposition events as initial inputs for the weapons fallout provides better results in the curve fitting outcome (the maximum of the peak is better approached and eventually the overestimation of the peak width decreases). Hence this type of input event is also further used in the new core fitting.

It is important that both algorithms used in this study implemented in R, produced the same results and that they coincided with the ones achieved in the earlier study. This indicates that our results are validated and that the older results are reproducible.

Effective velocities and dispersion constants, even if referring to the same radionuclide, differ between the two fallout sources (by about 85 % for u and 59 % for D). Different migration rates of ¹³⁷Cs were also discussed in Kirchner et. al (2009) mentioning about apparent time dependence of the transport processes (since residence times of weapons and Chernobyl fallout radionuclides differ by 30 years). In our case, the exact reason for the specific differences is not yet known.

• Predicted curves

A graph follows displaying the experimental data of 2014 (Sandkrug) together with two curves accounting for the predicted for 2014 values of Chernobyl and weapons fallout related cesium. These curves were performed by inserting the estimated parameters of Kirchner (1998) to the solution of the convection - dispersion equation.



Figure 7.9: Experimental depth distribution of ¹³⁷Cs (circles with 1 standard deviation error bars) for 2014, Sandkrug. Solid and dashed lines represent the predicted Chernobyl and weapons distributions respectively.

What one can see from this graph, is that the expectations based on the old fitting outcome do not show consistency with the experimental results of 2014. The modell, in this case, failed to predict the evolution of the ¹³⁷Cs profile. This would imply that some of the model assumptions (such as considering steady effective velocity and dispersion constant over space and time) are not suitable or need improvements for describing the real evolution into the soil profile. There would need though more information, such as measuring and fitting the second profile of this region, in order to make correct interpretation.

• Sandkrug - New core fitting

Two parameter fitting (u, D)

Differing u and D were estimated previously for the different fallout sources. However, as a first simple trial here the model was fitted with only two free parameters u and D (not with distinguished $u_{Chernobyl}$, $D_{Chernobyl}$ and $u_{weapons}$, $D_{weapons}$) and the outcome is demonstrated in figure 7.10. The initial deposition densities used are the ones deduced from the 1992 work (as being foretold in subchapter 6.5). Specifically, 4763.12 Bq m⁻² for Chernobyl (1.5.1986) and 4435.7 Bq m⁻² for the weapons fallout (1.1.1964) was considered.



Figure 7.10: Experimental data (circles) are shown with one standard deviation uncertainties and the 2 free parameter model fitted curve for Sandkrug, 2014.

Table 7.3: Two free parameter model fitting results for the 2014 soil core (Sandkrug). G-N and L-M account for the Gauss-Newton and Levenberg-Marquardt algorithms respectively.

Total fitting	u (cm y ⁻¹)	D (cm ² y ⁻¹)	RSS	
¹³⁷ Cs	0.00 ± 0.03	0.97 ± 0.22	19613	(G-N, L-M)

This fitting as can be seen, is not representative of the situation. Moreover, estimated effective velocity was initially given as negative value and only by using constraints the above results were returned.

4 parameter fitting ($u_{Chernobyl}$, $D_{Chernobyl}$ and $u_{weapons}$, $D_{weapons}$) to the 2014 data of Sandkrug

What was done next, was to fit the convective - dispersive model with 4 free parameters accounting for distinguished u and D for Chenrobyl and weapons fallout. Initial deposition densities used are the same with the ones mentioned in the previous case. The resulting fitting is shown in figure 7.11.



Figure 7.11: Experimental data are shown (circles) with one standard deviation uncertainties and the 4 free parameter model fitted curve for Sandkrug, 2014.

Table 7.4: Four free parameter model fitting results for the 2014 soil core (Sandkrug). G-N and L-M account for the Gauss-Newton and Levenberg-Marquardt algorithms respectively.

Total fitting	u (cm y ⁻¹)	$D (cm^2 y^{-1})$	RSS	
¹³⁷ Cs	0.02 ± 0.01	0.33 ± 0.04		Chernobyl (G-N, L-M)
	0.24 ± 0.01	0.39 ± 0.07	3665	weapons (G-N, L-M)

What can be seen here is an improved fitting describing more realistically the measured dataset, something being evident both from looking at the fitted curve and the RSS value. However, improvements need to be taken into account, since it is observed that the model systematically underestimates the data points below 10 cm depth.

Two things were afterwards done to improve and check the fitting:

Case 1: A change was done in the initial weapons related deposition value. The value of 4435.7 Bq m⁻² mentioned above was initially used for a single peak fitting of ¹³⁷Cs activity concentrations related to depths below 12 cm for the 1992 core. This value was taken from Kirchner's work (resulting from averaging the inventory measured only below 12 to 69 cm depth of the old soil core and of the total weapons inventory deduced from cesium separation from 0 to 69 cm). In the case here of total core fitting, the total deduced weapons inventory was used, instead of the abovementioned average. Hence, 4763.12 Bq m⁻² and 5231.20 Bq m⁻² were used for the Chernobyl and weapons fallout respectively. The outcome of this process is demonstrated in figure 7.12. The parameters received from the fitting procedure were used to derive the depth profiles resulting from each source.



Figure 7.12: Experimental data are shown (circles) with one standard deviation uncertainties for Sandkrug 2014. Solid line accounts for the total case 1 fitted curve, dashed and dotted line for Chernobyl and weapons fallout respectively.

Total fitting	u (cm y ⁻¹)	D (cm ² y ⁻¹)	RSS	
¹³⁷ Cs	0.013 ± 0.008	0.34 ± 0.03		Chernobyl (G-N, L-M)
	0.232 ± 0.007	0.51 ± 0.06	1811	weapons (G-N, L-M)

Table 7.5: Case 1 model fitting results for the 2014 soil core (Sandkrug). G-N and L-M account for the Gauss-Newton and Levenberg-Marquardt algorithms respectively.

Case 2: Instead of considering initial deposition densities being the same with the ones referring to the past measurements, Chernobyl and weapons fallout percentages were calculated (60.16% Chernobyl, 39.84 % weapons) from the 1992 separated cesium fractions. These percentages were applied in the recent inventory and the decay corrected densities were then taken as the initial ones for the model. This gave about 5035.29 Bq m⁻² for the Chernobyl and 5569.80 Bq m⁻² for the weapons fallout. The outcome of this process is shown in figure 7.13. The parameters received from the fitting procedure were used to derive the depth profiles resulting from each source.



Figure 7.13: Experimental data are shown with one standard deviation uncertainties for Sandkrug 2014. Soild line accounts for the total case 2 fitted curve, dashed and dotted line for Chernobyl and weapons fallout respectively.

Total fitting	u (cm y ⁻¹)	D (cm ² y ⁻¹)	RSS	
¹³⁷ Cs	0.007 ± 0.009	0.39 ± 0.04		Chernobyl (G-N, L-M)
	0.247 ± 0.08	0.57 ± 0.06	1858	weapons (G-N, L-M)

Table 7.6: Case 2 model fitting results for the 2014 soil core (Sandkrug). G-N and L-M account for the Gauss-Newton and Levenberg-Marquardt algorithms respectively.

What can be seen from figures 7.12 and 7.13 is that the model in both cases presents an improved description of the measured activity concentrations, something that is also apparent by looking at the RSS values which are smaller (table 7.5 and 7.6) in either case than the previous one (table 7.4). These improvements are also visible in the simulated curves from 10 about 25 cm, where both in case 1 and case 2 fittings no systematic underestimation is observed. This also coincides with the bigger values of estimated effective dispersion constants.

Between case 1 and case 2, no big differences are observed for the RSS. Regarding their graphical representation, the first case seems to present a slightly better fitting being more closely to the measured data from 17 to 25 cm depths. The estimated value for the effective velocity has a large uncertainty in case 2, as seen in table 7.6, so according to the model this value cannot be certainly defined to be different from zero.

Finally and since the outcome is sensitive to the input deposition value, the model was fitted again to the data, taking into account 6 free parameters. The 4 different u and D as were used above plus 2 more related to initial deposition density for Chenrobyl and weapons fallout. (The weapons fallout one was fitted exceptionally here as a single event in order not to complex even more the fitting process.)

The resulting values for the initial deposition densities were, $C_{Chernobyl}$ = 4880 ±545 Bq m⁻² and $C_{weapons}$ = 5402 ± 964 Bq m⁻², coinciding well with the ones used as fixed values in the above cases. These values were then used as fixed parameters and applied at our last fitting trial shown in figure 7.14 (considering an analytical deposition history for the global fallout now).

This process was done in order to check the fitting result, check whether the estimated initial depositions are consistent with the calculated ones used above. Since coincidence is observed, taking them afterwards as initial deposition fixed parameters the goal is to see if they provide a better fitting outcome.



Figure 7.14: Experimental data are shown (circles) with one standard deviation uncertainties for Sandkrug 2014. Solid line accounts for the final trial total fitted curve, dashed and dotted line for Chernobyl and weapons fallout respectively.

Table 7.7: Final trial model fitting results for the 2014 soil core (Sandkrug). G-N and L-M account for the Gauss-Newton and Levenberg-Marquardt algorithms respectively.

Total fitting	u (cm y ⁻¹)	$D (cm^2 y^{-1})$	RSS	
¹³⁷ Cs	0.010 ± 0.008	0.36 ± 0.03		Chernobyl (G-N, L-M)
	0.238 ± 0.007	0.53 ± 0.05	1590	weapons (G-N, L-M)

In this case, the comparison between the fitted curve and the experimental data shows a good agreement. Comparing figure 7.14 (final trial) to the two previous graphs (case 1 and 2) no big distinctions can be made.

The estimated parameters (apart from the effective velocity of case 2) have no big discrepancies with the case 1 and 2 examined above. However both simulation and fitted parameters are more consistent between case 1 and the final trial.

By looking at the RSS value, we here see the smallest value observed than in all the previous cases, which denotes a better fitting outcome.

Finally, the 6 free parameter fitting provided meaningful estimated initial deposition densities for the Chernobyl and weapons fallout and by considering those densities as initial ones in the last trial fitting, a slightly better (with respect to RSS) result was obtained. For these reasons the last fitting procedure of 2014 core (figure 7.14) was taken into account for further evaluation.

• Comments on the recent model fitting and comparison with the older one

As can be seen in figure 7.14, according to the CDE model, Chernobyl fallout related ¹³⁷Cs is connected to the peak present in the surface of the soil, while weapons related one is located at around 15 cm depth, overlapping with the previous one. The deeper located peak raises interest if compared to the respective weapons fallout peak in the 1992 core which was already located at around 20 cm depth. This peak location discrepancy between 1992 and 2014 soil profiles, also coincides with a similar difference observed in the ⁴⁰K profiles of Sandkrug (figure 7.6). In this graph, one can see that the ⁴⁰K vertical distributions between the sampling dates have a similar pattern but the 2014 one seems to be shifted to the left.

Parameter estimates of the total fit of the 2014 core (table 7.7) differ from the ones of 1992 (table 7.2), something that was not unexpected if looking back in figure 7.9 and how much the predicted profiles differ from the measured ones. For the effective velocities, inconsistencies of about 80% and 67% related to the Chernobyl and weapons fallout respectively are observed between the 1992 and 2014 results. While effective dispersion constants differ by about 40% and 60% related to Chernobyl and weapons fallout respectively between the two sampling dates. These discrepancies if uncertainties of the estimated parameters are taken into account are not that big for dispersion constants but still remain noteworthy for the migration velocities.

Finally, looking at both figure 7.2 and 7.14, the fitted curve seems to underestimate the activity concentration values observed at deeper depths.

7.3 Comparison of Kaiser's results with the ones obtained at this study

In the following graph, one can see the depth distributions of 137 Cs (in Bq m² cm⁻¹) as calculated in this study and as deduced by the work of Kaiser's thesis in relation to Sandkrug soil profile and depths between 0 and 30 cm.



Figure 7.15: 137 Cs activity concentrations as measured in the two different laboratories for Sandkrug and depths between 0 - 30 cm.

In the case of this study uncertainties of the measurements are much smaller than the ones obtained in Kaisers study, something that would be attributed to the bigger detectors used in our laboratory of 50% relative efficiency, providing higher count rate. On average, there is a difference of about 5 % between the measured values of the two studies. Uncertainties of Kaiser's measurements overlap with the measured values obtained in our case; hence an overall agreement between the measurements of the two different laboratories is noted.

Chapter 8

Conclusions and Outlook

In this master thesis, the first step in the re-examination of ¹³⁷ Cs activity concentrations in two undisturbed sampling locations was done.

Experimental results of ¹³⁷Cs activity concentration from two regions in Northern Germany with different types of soils, revealed different vertical profiles.

In Sandkrug (orthic podsol) Chernobyl related ¹³⁷Cs in 1992 presented mainly diffusive-like movement in soil (Kirchner, 1998). However, a similar observation did not apply for weapons related cesium. In the new core, the majority of inventory was present in the shallower soil layers and clear distinction of two peaks was no longer possible.

In Fischerhude (umbric gleysol), Chernobyl related cesium in 1994 showed larger migration within the soil in comparison to the one in Sandkrug. In the same year, weapons related ¹³⁷Cs (unlike in Sandkrug) showed a uniform distribution inside the soil. In the recent core, Chernobyl related cesium seemed to have migrated downwards, but this observation could not be validated.

In Sandkrug, vertical profiles overall maintained their own characteristic shape between the two sampling dates and the inventories comparison indicated agreement. In Fischerhude, on the other hand, inventories had a relatively big discrepancy and when later comparing the 40 K profiles, disagreement was discovered between the old and new profile. This implied that something is not consistent with respect to soil properties or dynamics or another factor not known yet at this region.

Modelling results regarding Sandkrug, mentioned in Kirchner (1998) were successfully reproduced in this study. The same model was further applied in the current soil core and from the final outcome consistency between the fitted curve and the experimental results was noticed. Predicted profiles resulting from the 1992 parameter estimates did not coincide with the measured distributions. Effective velocity and dispersion constant results deduced from the 2014 fitting were not consistent (especially in the migration rate value) with the ones calculated in the past, something that comes in contrast with the model assumption of constant parameters over space and time and leaves an open question.

Comparison between the measurements done by Kaiser in Sandkrug's core and the ones performed again for the same samples in our study, revealed coincidence between the results originating from the two different laboratories.

Throughout this work several procedures were done. The need for increased measuring time in the already occupied detectors, demanding modelling process, handling of several datasets and interpreting results related to complex environmental processes were some of the difficulties that were faced; hence a considerable amount of time was devoted in an effort to overcome (at least most of) them.

Finally, interesting results and additional information obtained through this work provide a useful tool for further research and analysis since open questions concerning the interpretation of the soil profiles, their time evolution and their modelling representation remain.

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Appendix

A Data

Table A.1: Activity concentration of ¹³⁷Cs for Sandkrug from Kirchner's work in 1992 and from the 2014 study. One standard deviations are shown.

	Sandkrug (1992)			Sandkr	ug (2014)
Depth	¹³⁷ Cs	Uncertainty		¹³⁷ Cs	Uncertainty
(cm)	$(Bq kg^{-1})$	$(\mathbf{Bq} \mathbf{kg}^{-1})$		(Bq kg ⁻¹)	$(\mathbf{Bq} \mathbf{kg}^{-1})$
1	68.060	1.490		30.873	0.834
3	61.030	1.370		26.645	0.597
5	23.790	0.563		21.789	0.495
7	14.660	0.355		15.708	0.467
9	10.520	0.262		9.273	0.314
11	7.150	0.181		8.882	0.345
13	4.581	0.116		7.517	0.213
15	2.945	0.077		7.634	0.180
17	2.670	0.069		6.924	0.180
19	9.638	0.236		5.031	0.138
21	13.359	0.320		3.253	0.122
23	4.173	0.105		2.371	0.147
25	7.887	0.192		1.583	0.060
27	4.737	0.120		1.435	0.053
29	3.664	0.093		1.547	0.078
31	2.638	0.067		1.099	0.039
33	1.897	0.060		0.642	0.028
35	1.404	0.049		0.393	0.026
37	1.054	0.029		0.287	0.015
39	0.938	0.031		0.262	0.028
41	0.875	0.030		0.198	0.037
43	0.573	0.020		0.289	0.013
45	0.890	0.027		0.267	0.039
47	0.380	0.020		0.257	0.024
49	0.273	0.017		0.196	0.016
51	0.209	0.016		0.109	0.025
53	0.224	0.015		0.092	0.011
55	0.197	0.011		0.104	0.009
57	0.249	0.015		0.070	0.009
59	0.424	0.024		0.092	0.009
61				0.104	0.010
63	0.346	0.025		0.078	0.012
65				0.079	0.008
67	0.281	0.025	1	0.049	0.007
69	< 0.110			< 0.047	
71				0.111	0.014

Fischerhude 1994		Fischer	hude 2014	
Depth	¹³⁷ Cs	Uncertainty	¹³⁷ Cs	Uncertainty
(cm)	(Bq kg ⁻¹)	$(\mathbf{Bq} \mathbf{kg}^{-1})^{\mathbf{v}}$	$(\mathbf{Bq} \mathbf{kg}^{-1})$	$(\mathbf{Bq} \mathbf{kg}^{-1})$
1	34.010	1.320	11.238	0.517
3	38.190	1.480	11.548	0.411
5	38.510	1.490	11.150	0.308
7	38.870	1.510	8.682	0.262
9	37.030	1.600	11.492	0.297
11	38.920	1.780	12.654	0.362
13	54.790	2.730	10.318	0.413
15	78.010	3.550	11.058	0.396
17	55.930	2.540	23.891	0.632
19	30.990	1.410	29.777	0.690
21	17.470	0.800	30.981	0.697
23	13.810	0.630	17.218	0.486
25	13.010	0.600	3.750	0.166
27	13.500	0.620	1.354	0.071
29	7.892	0.360	0.467	0.040
31	3.101	0.086	0.168	0.023
33	1.101	0.043	0.165	0.017
35	1.226	0.035	0.152	0.012
37	0.690	0.027	0.160	0.011
39	0.822	0.030	0.201	0.016
41	0.264	0.017	0.178	0.012
43	0.280	0.015	0.154	0.036
45	0.182	0.013	0.114	0.021
47	0.394	0.020	0.109	0.018
49	0.079	0.016	0.161	0.021
51	0.117	0.014	0.081	0.025
53	0.083	0.013	0.211	0.029
55	0.065	0.010	< 0.146	
57	0.061	0.013	< 0.153	
59	0.132	0.014	0.169	0.044
61	0.156	0.012	< 0.258	
63	0.129	0.011	< 0.219	
65	0.089	0.013	< 0.147	
67	0.082	0.013	< 0.276	
69	0.048	0.009	< 0.181	
71			< 0.209	
73			0.155	0.040
75			< 0.414	
77			< 0.316	
79			0.379	0.171
81			< 0.251	

 Table A.2: Activity concentration of ¹³⁷Cs for Fischerhude from Kirchner's work in

 1994 and from the Fischerhude 2014 study. One standard deviations are shown.

	Sandkrug 1992		Fische	rhude 1994
Depth	¹³⁷ Cs	Uncertainty	¹³⁷ Cs	Uncertainty
(cm)	(Bq kg ⁻¹)			
1	4.457	0.119	0.872	0.040
3	3.724	0.112	0.965	0.044
5	1.092	0.053	1.063	0.050
7	0.575	0.037	1.034	0.050
9	0.344	0.032	0.912	0.049
11	0.259	0.028	1.118	0.058
13			1.675	0.087
15			2.64	0.128
17			1.747	0.086
19			0.804	0.042
21			0.231	0.019
23			0.087	0.017
25			< 0.080	
27			0.081	0.015

Table A.3: Activity concentration results of ¹³⁴Cs regarding Sandkrug 1992 fromKirchner (1998) and regarding Fiscerhude 1994 from Kirchner (unpublished data).

Table A.4: Activity concentration results of ¹³⁷Cs regarding Sandkrug 2014, compared between Kaiser's work and this study.

Kaiser's work				This study		
Depth	¹³⁷ Cs	Uncertainty		¹³⁷ Cs	Uncertainty	
(cm)	$(Bq m^{-2} cm^{-1})$	$(Bq m^{-2} cm^{-1})$		$(Bq m^{-2} cm^{-1})$	$(Bq m^{-2} cm^{-1})$	
1	430.87	45.35		432.22	11.68	
3	384.05	37.91		373.03	8.35	
5	331.47	34.97		305.04	6.93	
7	249.97	24.03		219.91	6.54	
9	162.80	15.78		129.82	4.39	
11	134.52	13.11		124.35	4.83	
13	115.39	12.07		105.24	2.98	
15	114.05	10.83		106.88	2.52	
17	91.02	7.49		96.93	2.53	
19	78.35	8.31		70.43	1.93	
21	51.29	5.49		45.55	1.71	
23	32.04	3.03		33.19	2.06	
25	25.91	2.44		22.16	0.84	
27	21.17	2.42		20.09	0.74	
29	17.44	1.79		21.65	1.10	

	Fischerhude 1994		Fischer	Fischerhude 2014		
Depth	⁴⁰ K	Uncertainty	⁴⁰ K	Uncertainty		
(cm)	(Bq kg ⁻¹)	$(Bq kg^{-1})$	(Bq kg ⁻¹)	$(\mathbf{Bq} \mathbf{kg}^{-1})$		
1	226.58	11.30	130.95	6.75		
3	214.76	10.71	142.41	6.70		
5	217.26	10.86	146.04	6.36		
7	212.91	10.65	136.73	5.80		
9	209.44	10.47	146.96	6.44		
11	194.44	9.72	155.07	6.92		
13	186.51	9.31	114.64	5.21		
15	191.77	9.60	114.86	5.48		
17	188.99	9.45	116.35	5.15		
19	185.86	9.27	93.16	3.96		
21	191.74	9.57	88.67	3.52		
23	185.96	9.30	91.11	4.34		
25	189.42	9.47	149.45	5.90		
27	195.04	9.74	188.63	8.12		
29	198.69	9.89	171.21	7.17		
31	245.35	6.17	160.36	6.85		
33	214.53	10.71	185.54	5.97		
35	229.51	5.72	205.78	8.59		
37	233.48	5.87	227.80	7.19		
39	223.33	5.62	305.22	12.73		
41	240.33	6.04	144.85	6.20		
43	272.70	6.81	143.96	5.26		
45	272.90	6.81	116.80	4.29		
47	277.43	6.95	79.08	2.99		
49	290.00	7.34	64.32	2.12		
51	285.26	7.14	45.29	2.00		
53	270.90	6.78	23.51	1.27		
55	272.96	6.80	27.79	1.18		
57	280.48	7.02	22.70	1.43		
59	276.87	6.94	31.63	1.97		
61	283.97	7.08	32.10	1.91		
63	282.39	7.05	26.77	2.51		
65	296.53	7.42	40.33	2.12		
67	294.57	7.37	40.95	2.24		
69	295.26	7.35	49.75	1.91		
71			49.46	2.19		
73			50.66	1.96		
75			39.28	2.66		
77			45.03	2.41		
79			39.21	4.14		
81			32.23	2.12		

Table A.5: Activity concentration of ⁴⁰K for Fischerhude from Kirchner's work in 1994 and from the Fischerhude 2014 study. One standard deviations are shown.
	Sandkrug (1992)		1	Sandkrug (2014)			
Depth	¹³⁷ Cs	Uncertainty		¹³⁷ Cs Uncertainty			
(cm)	(Bq kg ⁻¹)	$(\mathbf{Bq} \mathbf{kg}^{-1})$		(Bq kg ⁻¹)	$(\mathbf{Bq} \mathbf{kg}^{-1})$		
1	123.63	3.18		138.01	5.70		
3	133.05	3.43		95.04	3.69		
5	137.00	3.56		122.30	3.99		
7	143.99	3.65		111.70	4.58		
9	149.35	3.81		106.89	4.89		
11	140.28	3.55		127.51	6.19		
13	146.05	3.61		114.77	5.07		
15	131.96	3.26		100.44	3.34		
17	126.11	3.05		87.10	2.98		
19	<60.18			77.22	2.63		
21	124.77	3.01		66.79	3.09		
23	126.20	3.11		74.01	3.18		
25	89.81	2.19		64.60	2.67		
27	61.58	1.54		66.12	2.74		
29	56.37	1.43		71.96	2.30		
31	51.50	1.28		67.27	2.30		
33	49.39	1.37		75.55	3.26		
35	52.70	1.44		84.14	3.68		
37	66.83	1.63		89.57	2.85		
39	76.55	1.93		101.84	4.37		
41	80.57	2.01		99.83	4.06		
43	94.06	2.29		108.76	4.36		
45	88.82	2.21		121.06	3.98		
47	100.89	2.54		123.22	3.99		
49	106.43	2.62		128.01	5.15		
51	116.83	2.88		129.28	4.03		
53	118.43	2.95		142.35	5.98		
55	121.14	2.97		144.80	4.59		
57	<43.94			140.95	5.64		
59				152.25	6.36		
61				147.64	5.90		
63	129.73	3.28	1	156.16	6.70		
65			1	155.32	6.48		
67	168.40	4.22	1	143.50	5.73		
69				157.92	6.30		
71				136.32	4.90		

Table A.6: Activity concentration of ⁴⁰K for Sandkrug from Kirchner's work in 1992 and from the Sandkrug 2014 study. One standard deviations are shown.

B Separation of ¹³⁷Cs fractions

Sandkrug (1992)					
Depth	Chernobyl	Uncertainty		weapons	Uncertainty
(cm)	¹³⁷ Cs (Bq kg ⁻¹)	(Bq kg ⁻¹)		¹³⁷ Cs (Bq kg ⁻¹)	(Bq kg ⁻¹)
1	64.752	1.988		3.308	2.484
3	54.103	1.822		6.927	2.280
5	15.865	0.807		7.925	0.984
7	8.354	0.552		6.306	0.657
9	4.998	0.471		5.522	0.539
11	3.763	0.411		3.387	0.449
13				4.581	0.116
15				2.945	0.077
17				2.670	0.069
19				9.638	0.236
21				13.359	0.320
23				4.173	0.105
25				7.887	0.192
27				4.737	0.120
29				3.664	0.093
31				2.638	0.067
33				1.897	0.060
35				1.404	0.049
37				1.054	0.029
39				0.938	0.031
41				0.875	0.030
43				0.573	0.020
45				0.890	0.027
47				0.380	0.020
49				0.273	0.017
51				0.209	0.016
53				0.224	0.015
55				0.197	0.011
57				0.249	0.015
59				0.424	0.024
63				0.346	0.025
67				0.281	0.025

Table B.1: Chernobyl and weapons related ¹³⁷Cs regarding Sandkrug 1992 results obtained by Kirchner's work and also reproduced in this study.

Fischerhude 1994					
Depth	Chernobyl	Uncertainty		weapons	Uncertainty
(cm)	¹³⁷ Cs (Bq kg ⁻¹)	(Bq kg ⁻¹)		¹³⁷ Cs (Bq kg ⁻¹)	(Bq kg ⁻¹)
1	22.960	1.109		11.050	1.724
3	25.408	1.221		12.782	1.919
5	27.989	1.383		10.521	2.033
7	27.225	1.380		11.645	2.045
9	24.013	1.340		13.017	2.087
11	29.437	1.591		9.483	2.387
13	44.103	2.386		10.687	3.626
15	69.511	3.531		8.499	5.007
17	45.999	2.369		9.931	3.4731
19	21.169	1.151		9.821	1.820
21	6.082	0.509		11.388	0.948
23	2.299	0.444		11.511	0.771
25					
27	2.133	0.383		11.367	0.729
29				7.892	0.360
31				3.101	0.086
33				1.101	0.043
35				1.226	0.035
37				0.690	0.027
39				0.822	0.030
41				0.264	0.017
43				0.280	0.015
45				0.182	0.013
47				0.394	0.020
49				0.079	0.016
51				0.117	0.014
53				0.083	0.013
55				0.065	0.010
57				0.061	0.013
59				0.132	0.014
61				0.156	0.012
63				0.129	0.011
65				0.089	0.013
67				0.082	0.013
69				0.048	0.009

Table B.2: Chernobyl and weapons related ¹³⁷Cs regarding Fischerhude 1994 results obtained by Kirchner's work and also reproduced in this study.

C Model input

Table C.1: Initial deposition densities for Sandkrug as taken from Kirchner's work in 1992.

Source	Reference date	Initial deposition density
Weapons fallout	01.01.1964	4435.7
Chernobyl	01.05.1986	4763.12

Table C.2: Initial deposition densities for	Sandkrug by	using the	whole	weapons	related
cesium inventory.					

Source	Reference date	Initial deposition density
Weapons fallout	01.01.1964	5231.20
Chernobyl	01.05.1986	4763.12

Table C.3: Initial deposition densities for Sandkrug by applying to the new core inventory the 60.16 % (for Chernobyl) and 39.84 % (for weapons fallout) percentages which were calculated from Kirchner's work in 1992.

Source	Reference date	Initial deposition density
Weapons fallout	01.01.1964	5569.80
Chernobyl	01.05.1986	5035.29

D R script

#1992 SANDKRUG

library(ggplot2) library(pracma)

Define data

yCh=c(1,3,5,7,9,11)

yCherr=c(1,1,1,1,1,1)

xCh=c(874.8,730.7,214.26,112.81,67.5,51.2) # Activity data taken from Kirchner's work xCherr=c(85.65,72.22,22.7,12.87,8.94,7.34)

xwf=c(44.61,61.39,39.76,36.05,130.11,188.36,58.84,111.21,66.79,51.66,40.89,29.4,21.76,16.34,14.54,13.65,8.94,13.88,5.93,4.26,3.39,3.63,3.19,4.03,6.87,5.61,4.55)

ywf=c(11,13,15,17,19,21,23,25,27,29,31,33,35,37,39,41,43,45,47,49,51,53,55,57,59,63,67)

xwferr=c(7.73,1.55,1.04,0.93,3.19,4.51,1.48,2.71,1.69,1.31,1.04,0.93,0.76,0.45,0.48,0.47,0.31,0.42,0. 31,0.27,0.26,0.24,0.18,0.24,0.39,0.41,0.41)

Define data frame

df<-data.frame(yCh,xCh,xCh+xCherr,xCh-xCherr)

df<-data.frame(ywf,xwf,ywferr,xwferr)

Define constants

1=0.022974716 # Cs-137 decay constant

t1=6.505 #time since Chernobyl accident 1.5.1986

```
t2=28.835 #time since weapons fallout 1.1.1964
#analytical history for weapons fallout
t58=12723/365.25
t59=12177/365.25
t61=11446/365.25
t63=10716/365.25
t64=10350/365.25
t65=9985/365.25
t67=9255/365.25
t71=7794/365.25
t76=5967/365.25
t81=4141/365.25
#Define initial deposition densities
#Chernobyl
C1=4763.12
#weapons
C2=4435.7 # single fallout event
Ctot92=2286.82
C58=0.095*Ctot92*exp(0.022974716*t58)
C59=0.095*Ctot92*exp(0.022974716*t59)
C61=0.1384*Ctot92*exp(0.022974716*t61)
C63=0.2586*Ctot92*exp(0.022974716*t63)
C64=0.1189*Ctot92*exp(0.022974716*t64)
C65=0.1082*Ctot92*exp(0.022974716*t65)
C67=0.0713*Ctot92*exp(0.022974716*t67)
C71=0.0624*Ctot92*exp(0.022974716*t71)
C76=0.0408*Ctot92*exp(0.022974716*t76)
C81=0.0113*Ctot92*exp(0.022974716*t81)
# Define fit function
#Chernobyl
F<-function(yCh,u,D){C1*exp(-1*t1)*(((exp(-(yCh-u*t1)^2/(4*D*t1)))/(sqrt(pi*D*t1)))-(sqrt(pi*D*t1)))}
((u/(2*D))*exp((u*yCh)/D)*erfc((yCh+(u*t1))/(2*sqrt(D*t1)))))
#weapons single fallout input event
F<-function(ywf,u,D){C2*exp(-1*t2)*(((exp(-(ywf-u*t2)^2/(4*D*t2)))/(sqrt(pi*D*t2)))-(sqrt(pi*D*t2)))}
((u/(2*D))*exp((u*ywf)/D)*erfc((ywf+(u*t2))/(2*sqrt(D*t2)))))
#weapons deposition history
Fnew=function(ywf,u,D){C58*exp(-1*t58)*(((exp(-(ywf-u*t58)^2/(4*D*t58)))/(sqrt(pi*D*t58)))-
((u/(2*D))*exp((u*ywf)/D)*erfc((ywf+(u*t58))/(2*sqrt(D*t58)))))+C59*exp(-1*t59)*(((exp(-(ywf-1*t59)))))+C59*exp(-1*t59)))))
u*t59)^2/(4*D*t59)))/(sqrt(pi*D*t59)))-
((u/(2*D))*exp((u*ywf)/D)*erfc((ywf+(u*t59))/(2*sqrt(D*t59)))))+C61*exp(-1*t61)*(((exp(-(ywf-1)))))+C61*exp(-1*t61)))))
u*t61)^2/(4*D*t61)))/(sqrt(pi*D*t61)))-
((u/(2*D))*exp((u*ywf)/D)*erfc((ywf+(u*t61))/(2*sqrt(D*t61)))))+C63*exp(-1*t63)*(((exp(-(ywf-1)))))+C63*exp(-1*t63)))))
u*t63)^2/(4*D*t63)))/(sqrt(pi*D*t63)))-
((u/(2*D))*exp((u*ywf)/D)*erfc((ywf+(u*t63))/(2*sqrt(D*t63)))))+C64*exp(-1*t64)*(((exp(-(ywf-1*t64))))))+C64*exp(-1*t64)))))
u*t64)^2/(4*D*t64)))/(sqrt(pi*D*t64)))-
((u/(2*D))*exp((u*ywf)/D)*erfc((ywf+(u*t64))/(2*sqrt(D*t64)))))+C65*exp(-1*t65)*(((exp(-(ywf-(u*t64))))))+C65*exp(-1*t65)*(((exp(-(ywf-(u*t64))))))))))
u*t65)^2/(4*D*t65)))/(sqrt(pi*D*t65)))-
```

 $((u/(2*D))*exp((u*ywf)/D)*erfc((ywf+(u*t81))/(2*sqrt(D*t81))))) \}$

#Non linear fitting

Chernobyl fit

```
fitGN <-nls(xCh \sim F(yCh,u,D), data = df, start = list(u = 0.1, D = 0.5), trace = TRUE) \ \#Gaus-Newton \ algorithm fitLM <-nlsLM(xCh \sim F(yCh,u,D), data = df, start = list(u = 0.1, D = 0.5), trace = TRUE) \ \#Levenberg-Marquardt \ algorithm
```

#Weapons fallout fit

fitnls<-nls (xwf~F(ywf,u,D),data=df,start=list(u=0.7,D=0.9),trace=TRUE) # G-N

```
fitnlsLM<-nlsLM(xwf~F(ywf,u,D),data=df,start=list(u=0.7,D=0.9),trace=TRUE) #L-M
```

summary(fitGN)

summary(fitLM)

2014 SANDKRUG

Define data

 $\begin{array}{l} x = c(432.21836,373.02986,305.04222,219.9134,129.821356,124.344836,105.241836,106.877204,96.930624,70.4305126,45.547866,33.194434,22.162854,20.092478,24.1279272,17.142918,10.01106444, 6.13545036,4.4827068,3.71742226,2.81497108,4.101741,3.7952411,3.44832786,2.62353106,1.45414924,1.23795297,1.67671679,1.123331454,1.487616816,1.6781674,1.258587876,1.276734991,0.784071127,1.7876635) \end{array}$

xerr = c(11.6765796, 8.3521368, 6.9326334, 6.5440774, 4.3929564, 4.8287498, 2.9837024, 2.5220076, 2.5245304, 1.9316878, 1.713068, 2.0607314, 0.84180796, 0.74298406, 1.221001236, 0.603513768, 0.435951672, 0.39994734, 0.2355483, 0.401113222, 0.527100734, 0.189704474, 0.553394732, 0.323820782, 0.210801564, 0.337409186, 0.153575926, 0.137203749, 0.140060421, 0.141698306, 0.163182838, 0.188276942, 0.121183493, 0.118252777, 0.226571436)

y=c(1,3,5,7,9,11,13,15,17,19,21,23,25,27,29,31,33,35,37,39,41,43,45,47,49,51,53,55,57,59,61,63,65,6 7,71)

Define data frame

df<-data.frame(x,y,xerr,yerr) **# Define constants** 1=0.022974716 # Cs-137 decay constant t1=28.394 #time since Chernobyl accident (1.5.1986) t2=50.724 # time since weapons fallout (1.1.1964) #analytical history for weapons fallout t58=20718/365.25 t59=20172/365.25 t61=19441/365.25 t63=18711/365.25

```
t64=18345/365.25
t65=17980/365.25
t67=17250/365.25
t71=15789/365.25
t76=13962/365.25
t81=12136/365.25
#Define initial deposition densities
C1=4763.12#Chernobyl
C2=4435.7 # weapons single event
#weapons
Ctot14=1383.08
C58=0.095*Ctot14*exp(0.022974716*t58)
C59=0.095*Ctot14*exp(0.022974716*t59)
C61=0.1384*Ctot14*exp(0.022974716*t61)
C63=0.2586*Ctot14*exp(0.022974716*t63)
C64=0.1189*Ctot14*exp(0.022974716*t64)
C65=0.1082*Ctot14*exp(0.022974716*t65)
C67=0.0713*Ctot14*exp(0.022974716*t67)
C71=0.0624*Ctot14*exp(0.022974716*t71)
C76=0.0408*Ctot14*exp(0.022974716*t76)
C81=0.0113*Ctot14*exp(0.022974716*t81)
# Define fit function
#two free parameters
Fsimple<-function(y,u,D){C1*exp(-1*t1)*(((exp(-(y-u*t1)^2/(4*D*t1)))/(sqrt(pi*D*t1)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t1))/(2*sqrt(D*t1))))+C58*exp(-1*t58)*(((exp(-(y-(u+t1))/(2*sqrt(D*t1)))))+C58*exp(-1*t58)*(((exp(-(y-(u+t1))/(2*sqrt(D*t1))))))))
u*t58)^2/(4*D*t58)))/(sqrt(pi*D*t58)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t58))/(2*sqrt(D*t58)))))+C59*exp(-1*t59)*(((exp(-(y-t)))))+C59*exp(-1*t59))))
u*t59)^2/(4*D*t59)))/(sqrt(pi*D*t59)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t59))/(2*sqrt(D*t59)))))+C61*exp(-l*t61)*(((exp(-(y-(y-t))))))+C61*exp(-l*t61)*(((exp(-(y-t))))))))
u*t61)^2/(4*D*t61)))/(sqrt(pi*D*t61)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t61))/(2*sqrt(D*t61)))))+C63*exp(-1*t63)*(((exp(-(y-ta))))))+C63*exp(-1*t63)*(((exp(-(y-ta)))))))
u*t63)^2/(4*D*t63)))/(sqrt(pi*D*t63)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t63))/(2*sqrt(D*t63)))))+C64*exp(-1*t64)*(((exp(-(y-ta))))))+C64*exp(-1*t64)*(((exp(-(y-ta)))))))
u*t64)^2/(4*D*t64)))/(sqrt(pi*D*t64)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t64))/(2*sqrt(D*t64)))))+C65*exp(-l*t65)*(((exp(-(y-(y-ta))))))+C65*exp(-l*t65)))))
u*t65)^2/(4*D*t65)))/(sqrt(pi*D*t65)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t65))/(2*sqrt(D*t65)))))+C67*exp(-1*t67)*(((exp(-(y-t0)))))+C67*exp(-1*t67)*(((exp(-(y-t0)))))))
u*t67)^2/(4*D*t67)))/(sqrt(pi*D*t67)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t67))/(2*sqrt(D*t67))))+C71*exp(-l*t71)*(((exp(-(y-(y-t)))))+C71*exp(-l*t71))))
u*t71)^2/(4*D*t71)))/(sqrt(pi*D*t71)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t71))/(2*sqrt(D*t71))))+C76*exp(-l*t76)*(((exp(-(y-t)))))+C76*exp(-l*t76)*(((exp(-(y-t))))))+C76*exp(-l*t76)*(((exp(-(y-t)))))))
u*t76)^2/(4*D*t76)))/(sqrt(pi*D*t76)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t76))/(2*sqrt(D*t76)))))+C81*exp(-1*t81)*(((exp(-(y-t1)))))+C81*exp(-1*t81)*(((exp(-(y-t1))))))))
u*t81)^2/(4*D*t81)))/(sqrt(pi*D*t81)))-
((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t81))/(2*sqrt(D*t81)))))
```

4 free parameters

 $\label{eq:F14} F14 <-function(y,u1,u,D1,D) \\ \{C1^*exp(-l^*t1)^*(((exp(-(y-u1^*t1)^2/(4^*D1^*t1)))/(sqrt(pi^*D1^*t1)))) \\ ((u1/(2^*D1))^*exp((u1^*y)/D1)^*erfc((y+(u1^*t1))/(2^*sqrt(D1^*t1))))) \\ + C58^*exp(-l^*t58)^*(((exp(-(y-u1^*t58)))) \\ + C58^*exp(-l^*t58)))/(sqrt(pi^*D^*t58))) \\ + C58^*exp(-l^*t58)^*((exp(-(y-u1^*t1)))) \\ + C58^*exp(-l^*t58)) \\ + C58^*exp(-l^*t58)^*((exp(-(y-u1^*t1)))) \\ + C58^*exp(-l^*t58)) \\ + C58^*exp(-l^*t58)) \\ + C58^*exp(-l^*t58) \\ + C58^*exp(-l^*t58)$

 $((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t58))/(2*sqrt(D*t58)))))+C59*exp(-1*t59)*(((exp(-(y-u*t59)^2/(4*D*t59)))/(sqrt(pi*D*t59))))-(y-t1+2)+C59*exp(-1*t59)))+C59*exp(-1*t59)))+(y-t1+2)+C59*exp(-1*t59))))+(y-t1+2)+C59*exp(-1*t59)))+(y-t1+2)+C59*exp(-1*t59)))+(y-t1+2)+C59*exp(-1*t59)))+(y-t1+2)+C59*exp(-1*t59)))+(y-t1+2)+C59*exp(-1*t59)))+(y-t1+2)+C59*exp(-1*t59)))+(y-t1+2)+C59*exp(-1*t59))))+(y-t1+2)+C59*exp(-1*t59))))+(y-t1+2)+C59*exp(-1*t59))))+(y-t1+2)+C59*exp(-1*t59))))$)

 $((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t61))/(2*sqrt(D*t61)))))+C63*exp(-1*t63)*(((exp(-(y-u*t63)^2/(4*D*t63)))/(sqrt(pi*D*t63))))-(y-t63)*exp(-1*t63))))$

 $((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t71))/(2*sqrt(D*t71)))))+C76*exp(-l*t76)*(((exp(-(y-u*t76)^2/(4*D*t76)))/(sqrt(pi*D*t76))))-((y-t)+C76*exp(-l*t76))))$

((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t81))/(2*sqrt(D*t81)))))

#6 free parameter function

Ftest<-function(y,u1,u,D1,D,Cc,Cw){Cc*exp(-l*t1)*(((exp(-(y-

 $u1*t1)^2/(4*D1*t1)))/(sqrt(pi*D1*t1)))-$

((u1/(2*D1))*exp((u1*y)/D1)*erfc((y+(u1*t1))/(2*sqrt(D1*t1))))+Cw*exp(-1*t2)*(((exp(-(y-x))/(2*a))))+Cw*exp(-1*t2))))

 $u*t2)^{2/(4*D*t2)))/(sqrt(pi*D*t2)))-((u/(2*D))*exp((u*y)/D)*erfc((y+(u*t2))/(2*sqrt(D*t2)))))$

```
#Non linear fitting (this process is repeated for all trials with different initial depositions)
```

 $fitnlssimpleLM <-nlsLM (x \sim Fsimple(y, u, D), data = df, start = list(u = 0.03, D = 0.5), lower = 0.00, lower =$

=c(u=0,D=0),upper=c(u=2,D=8),trace=TRUE) # two free parameter fit

 $fitnls14 <-nls \qquad (x \sim F14(y,u1,u,D1,D), data=df, start=list(u1=0.03, u=0.2, D1=0.4, D=0.5), algorithm = LM', trace=TRUE) \ \# \ G-N$

fitnls14LM<-nlsLM(x~F14(y,u1,u,D1,D),data=df,start=list(u1=0.03,u=0.2,D1=0.4,D=0.5),algorithm = 'LM',trace=TRUE) # L-M

fitnlstest<-

nlsLM(x~Ftest(y,u1,u,D1,D,Cc,Cw),data=df,start=list(u1=0.03,u=0.2,D1=0.4,D=0.5,Cc=5000,Cw=5000),trace=TRUE)

summary(fitnls14)

#plot example

```
plot(y,x,ylim=c(0,500),xlim=c(0,72),ylab=expression("Activity concentration "*" [Bq "*"m"^-2*"cm"^-1*"]"),xlab="Depth [cm]",cex.lab=1.2,cex.axis=1.0,las=1)
```

errorbar(y,x,xerr=yerr,yerr=xerr,"black",add=TRUE)

lines(ycont,xtot)

lines(ycont,xprch,lty="dashed")

lines(ycont,xprwf,lty="dotted")