



THE HONG KONG
POLYTECHNIC UNIVERSITY

香港理工大學

Pao Yue-kong Library

包玉剛圖書館

Copyright Undertaking

This thesis is protected by copyright, with all rights reserved.

By reading and using the thesis, the reader understands and agrees to the following terms:

1. The reader will abide by the rules and legal ordinances governing copyright regarding the use of the thesis.
2. The reader will use the thesis for the purpose of research or private study only and not for distribution or further reproduction or any other purpose.
3. The reader agrees to indemnify and hold the University harmless from and against any loss, damage, cost, liability or expenses arising from copyright infringement or unauthorized usage.

If you have reasons to believe that any materials in this thesis are deemed not suitable to be distributed in this form, or a copyright owner having difficulty with the material being included in our database, please contact lbsys@polyu.edu.hk providing details. The Library will look into your claim and consider taking remedial action upon receipt of the written requests.

KINETICS OF RADIOCESIUM SORPTION IN SOILS

SUBMITTED BY

CHU PUI YI

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF PHILOSOPHY IN PHYSICS

AT

THE DEPARTMENT OF APPLIED PHYSICS

THE HONG KONG POLYTECHNIC UNIVERSITY

AUGUST 2003



**Pao Yue-kong Library
PolyU · Hong Kong**

CERTIFICATE OF ORIGINALITY

I HEREBY DECLARE THAT THIS THESIS IS MY OWN WORK AND THAT, TO THE BEST OF MY KNOWLEDGE AND BELIEF, IT REPRODUCES NO MATERIAL PREVIOUSLY PUBLISHED OR WRITTEN NOR MATERIAL WHICH HAS BEEN ACCEPTED FOR THE AWARD OF ANY OTHER DEGREE OR DIPLOMA, EXCEPT WHERE DUE ACKNOWLEDGEMENT HAS BEEN MADE IN THE TEXT.

SIGNATURE:

NAME: CHU PUI YI



ABSTRACT

Abstract of thesis entitled 'Kinetics of Radiocesium Sorption in Soils'.

Submitted by Chu Pui Yi

for the degree of Master of Philosophy in Physics

at The Hong Kong Polytechnic University in August 2003.

The general purpose of this study is to investigate the kinetics and sorption behaviour of radiocesium (^{137}Cs) in soils in Hong Kong reservoirs. This is important as the sorption of radiocesium to soil constituents is one of the major factors which determine the availability of ^{137}Cs to biological systems. Such information provides the long-term mobility of radiocesium in soils which is a useful tool in emergency planning and in countermeasure implementation during any accidental release from the nearby Guangdong and Lingao nuclear power stations.

It is well known that soils can adsorb radiocesium rapidly and strongly. In general, the sorption of radiocesium in soils can be described in terms of three kinds of sorption sites which have different ion-exchange selectivities of cesium.



Abstract

One type of sites is the planar sites from which ^{137}Cs is generally exchangeable and are called the 'regular exchange sites' (RES). The second type of sites is called the 'wedge edge sites' (WES) where ^{137}Cs exchange is sterically limited to cations of similar size and charge. The other sites are interlayer sites from which ^{137}Cs is not readily exchanged and are called the 'frayed edge sites' (FES). Significant methodological development has been proposed to allow a quantitative assessment of both the number and the selectivity pattern of such specific sites in soils (Cremers et al., 1998, 1990). The method is based on the use of the silver thiourea (AgTU) complex to mask the bulk of the RES and the WES. By dispersing soils in a solution containing suitable background level of AgTU, cesium ions are excluded from the bulk of the ion-exchange complex and their action becomes restricted to the FES.

Soil samples in this study were collected from different reservoirs in Hong Kong and characterized for their physical and chemical properties such as clay content, organic matter content, cation exchange capacity, potassium ions availability and soil pH. Two types of experiments were conducted. The first type of experiments was to observe the sorption behaviour of ^{137}Cs on different types of soils as a function of time. 1.0-g soil samples were dispersed in a 200-ml deionized water of initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$ in a 1.25- ℓ high density Polyethylene (HDPE) container. The Cs^{137} water



activity was monitored with time until equilibrium reached. The experimental data were fitted well with a simple box model by using a simulation software called ModelMaker. Rate constants for different chemical processes of ^{137}Cs sorption in soils were then estimated. Attempts were also made to correlate the rate constants with the characteristic properties of soil samples such as clay content, organic matter content, cation exchange capacity, potassium ions availability and soil pH.

The second type of experiments was to observe the sorption behaviour of ^{137}Cs on the frayed edge sites (FES) in soils as a function of time. Soil samples were dispersed with 0.015M AgTU solution in a 1.25- ℓ HDPE container. The ^{137}Cs water activity was monitored with time until equilibrium reached. Experiments with different masses of soil samples at two different initial ^{137}Cs water concentrations of 160 $\text{kBq } \ell^{-1}$ and 240 $\text{kBq } \ell^{-1}$ were performed. The capacity of the FES was also determined. 16-g of soil samples were dispersed in 0.015M AgTU solution containing varying amounts of cesium and a ^{137}Cs label for 24 h. Sorption isotherm was obtained by plotting the amount of cesium sorbed against various amounts of cesium until a plateau was reached. The capacity of the FES is then the plateau value of the isotherm.

To describe the irreversible ^{137}Cs sorption behaviour on the FES in soils,



Abstract

a two-compartment conceptual model was used. The sorption rate was assumed to depend not only on a rate constant, but also on some other factors, e.g. the difference between the ^{137}Cs water activity concentration in aqueous phase and that in particulate phase, the fractional ^{137}Cs water activity concentration and the number of available sorption sites. Good fitting was obtained between experimental data and theory. The number of the FES for different masses of soils was also postulated and verified by experiments.

Finally, a four-compartment modified model based on the two-compartment conceptual model was proposed using the simulation software of ModelMaker to describe the ^{137}Cs sorption behaviour on the FES in soils. The FES were assumed to be composed of sub-sites where ion exchange and fixation of ^{137}Cs could simultaneously occur. A very good fitting was obtained between experimental data and the model. This model provided a good and reliable tool to investigate the retention of ^{137}Cs in soils.



ACKNOWLEDGEMENTS

I would like to take this opportunity to express my appreciation to my supervisor, Dr. C. K. Man, for his patient, guidance and constant support throughout the two years of my MPhil study.

I would also like to thank Prof. F. G. Shin for his helpful discussion and invaluable suggestions about modelling in my study.

Finally, I would like to give thanks to God, my father and mother, Mr. Gary Chau and my lovely dogs for their support with me in my life.



TABLE OF CONTENTS

ABSTRACT	I
ACKNOWLEDGEMENTS	V
TABLE OF CONTENTS	VI
LIST OF FIGURES	IX
LIST OF TABLES	XII
CHAPTER 1 INTRODUCTION 1	
1.1 BACKGROUND OF HONG KONG	1
1.2 THE GUANGDONG NUCLEAR POWER STATION.....	1
1.3 THE LINGAO NUCLEAR POWER STATION	4
1.4 EFFECTS OF NUCLEAR POWER PLANTS – THE CHERNOBYL ACCIDENT	4
1.5 RADIOLOGICAL IMPACT.....	8
1.6 RATIONALE OF STUDY	9
1.7 OBJECTIVES OF STUDY	11
CHAPTER 2 BEHAVIOUR OF RADIOCESIUM IN SOILS 14	
2.1 DISTRIBUTION COEFFICIENT AND TRANSFER FACTOR.....	14
2.2 FACTORS AFFECTING THE MOBILITY OF RADIOCESIUM IN SOILS.....	15
2.2.1 CATION EXCHANGE CAPACITY	16
2.2.2 CLAY CONTENT	16
2.2.3 ORGANIC MATTER CONTENT	18



2.2.4 POTASSIUM IONS AVAILABILITY	19
2.2.5 SOIL PH.....	20
2.3 SORPTION MECHANISMS OF RADIOCESIUM IN SOILS.....	20
2.4 ISOLATION OF FES – SILVER THIOUREA METHOD	24
CHAPTER 3 MATERIALS AND EXPERIMENTS 27	
3.1 SITES AND SAMPLING.....	27
3.2 SOIL SAMPLES TREATMENT	27
3.3 PARTICLE SIZE ANALYSIS	30
3.3.1 DISPERSION.....	30
3.3.2 SEDIMENTATION	31
3.3.3 SIEVING.....	33
3.4 SOIL CHARACTERIZATION	33
3.5 ¹³⁷ Cs MEASURING SYSTEM.....	35
3.6 PREPARATION OF SILVER THIOUREA (AGTU) SOLUTION	35
3.7 EXPERIMENTAL PROCEDURES.....	37
3.7.1 SORPTION OF ¹³⁷ Cs ON ALL TYPES OF SITES IN SOILS.....	37
3.7.2 SORPTION OF ¹³⁷ Cs ON THE FES IN SOILS	38
3.7.3 DETERMINATION OF THE CAPACITY OF THE FES IN SOILS.....	39
CHAPTER 4 EXPERIMENTAL RESULTS 41	
4.1 PHYSICAL AND CHEMICAL PROPERTIES OF SOILS	41
4.2 SORPTION OF ¹³⁷ Cs ON ALL TYPES OF SITES IN SOILS.....	43
4.3 SORPTION OF ¹³⁷ Cs ON THE FES IN SOILS	49



4.4 DETERMINATION OF THE CAPACITY OF THE FES IN SOILS.....	53
CHAPTER 5 MODELLING SORPTION ON ALL SITES USING MODELMAKER 56	
5.1 MODELMAKER	56
5.2 SIMPLE BOX MODEL	57
5.3 RESULTS AND DISCUSSION	61
5.4 CONCLUSION	69
CHAPTER 6 MODELLING SORPTION ON FES USING A CONCEPTUAL MODEL 70	
6.1 THEORY.....	71
6.2 RESULTS AND DISCUSSION	76
6.3 CONCLUSION	86
CHAPTER 7 MODELLING SORPTION ON FES USING MODELMAKER 87	
7.1 MODIFIED MODEL	87
7.2 RESULTS AND DISCUSSION	92
7.3 CONCLUSION	96
CHAPTER 8 CONCLUSION 99	
REFERENCES 104	
LIST OF PUBLICATION 112	



LIST OF FIGURES

Figure 1.1 Location of Hong Kong. (Source: http://www.info.gov.hk).....	2
Figure 1.2 Location of the three nuclear power plants (Guandong, Qinshan and Lingao) in China. (Source: International Nuclear Safety Center at Argonne National Laboratory).....	3
Figure 1.3 Location of Chernobyl. (Source: http://www.nuclear.org)	5
Figure 1.4 Main environmental pathways of human radiation exposure. (Source: IAEA technical report ISBN 92-0-129191-4 Vienna 1991).....	10
Figure 2.1 Selective sorption in a frayed edge of a weathered mica sheet.	23
Figure 2.2 The three types of ^{137}Cs sorbing sites in soils.....	25
Figure 3.1 Sampling sites of reservoirs in Hong Kong.....	28
Figure 3.2 Hydrometer test.....	32
Figure 3.3 A mechanical shaker with a set of sieves.....	34
Figure 3.4 The NaI(Tl) well-type scintillation detector.....	36
Figure 4.1 Time variations of ^{137}Cs activity in water for soil R1.....	44
Figure 4.3 Time variations of ^{137}Cs activity in water for soil R2.....	44
Figure 4.3 Time variations of ^{137}Cs activity in water for soil R3.....	45
Figure 4.4 Time variations of ^{137}Cs activity in water for soil R4.....	45
Figure 4.5 Time variations of ^{137}Cs activity in water for soil S1.....	46
Figure 4.6 Time variations of ^{137}Cs activity in water for soil S2.....	46



Figure 4.7 Time variations of ^{137}Cs activity in water for soil S3. 47

Figure 4.8 Time variations of ^{137}Cs activity in water for soil S4. 47

Figure 4.9 Time variations of the ^{137}Cs activity in water for different masses of soils at initial ^{137}Cs water activity concentrations of $160 \text{ kBq } \ell^{-1}$ 50

Figure 4.10 Time variations of the ^{137}Cs activity in water for different masses of soils at initial ^{137}Cs water activity concentrations of $240 \text{ kBq } \ell^{-1}$ 51

Figure 4.11 Sorption isotherm for 16.0-g of soil S2. 54

Figure 5.1 Simple box model for ^{137}Cs sorption on all sorbing sites in soils. 58

Figure 5.2 Fitted curve of the simple box model for soil R1. 62

Figure 5.3 Fitted curve of the simple box model for soil R2. 62

Figure 5.4 Fitted curve of the simple box model for soil R3. 63

Figure 5.5 Fitted curve of the simple box model for soil R4. 63

Figure 5.6 Fitted curve of the simple box model for soil S1. 64

Figure 5.7 Fitted curve of the simple box model for soil S2. 64

Figure 5.8 Fitted curve of the simple box model for soil S3. 65

Figure 5.9 Fitted curve of the simple box model for soil S4. 65

Figure 5.10 Modelled curves of the simple box model for Soil S2. Insert shows respective curves at early stage. 68

Figure 6.1 Two-compartment conceptual model for ^{137}Cs sorption on the FES in soils. 70

Figure 6.2 Fitted curves of the two-compartment conceptual model with different combination of exponents u , p and q for 16-g soil sample at initial ^{137}Cs water activity concentration of $160 \text{ kBq } \ell^{-1}$ 77



Figure 6.3 Fitted curves of the two-compartment conceptual model with different combination of exponents u , p and q for 16-g soil sample at initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$ 78

Figure 6.4 Fitted curves of the two-compartment conceptual model with $u=1$, $p=1$ and $q=2$ for different masses of soil sample for initial ^{137}Cs water activity concentration of $160 \text{ kBq } \ell^{-1}$ 80

Figure 6.5 Fitting curves of the two-compartment conceptual model with $u=1$, $p=1$ and $q=2$ for different masses of soil sample at initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$ 81

Figure 6.6 Plot of $\log F$ against $\log m$ 83

Figure 6.7 Sorption isotherm for 13.0-g of soil S2..... 85

Figure 7.1 Model of Absalom et al. (1996) for the sorption of ^{137}Cs on the FES in soils..... 88

Figure 7.3 Fitted curves of the four-compartment modified model for different masses of soil samples at initial ^{137}Cs water activity concentration of $160 \text{ kBq } \ell^{-1}$ 93

Figure 7.4 Fitted curves of the four-compartment modified model for different masses of soil samples at initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$ 94

Figure 7.5 Plot of $\log Fk_1$ against $\log m$ 97



LIST OF TABLES

Table 1.1 Radionuclides released during the Chernobyl accident and their corresponding half-lives	7
Table 1.2 Transfer factors of radionuclides by inhalation and ingestion ...	13
Table 2.1 The International Soil Science Society classification system of soil particles	17
Table 3.1 Details of soil samples	29
Table 4.1 Particle size distribution of soil samples	42
Table 4.2 Characterizations of soil samples	42
Table 4.3 ^{137}Cs activity remaining in water at equilibrium, N_{eq} , and distribution coefficient at equilibrium, K_D , for different soil samples	48
Table 4.4 ^{137}Cs activity remaining in water at equilibrium, N_{eq} , and distribution coefficient at equilibrium, K_D , for different masses of soils at initial ^{137}Cs water activity concentration of $160 \text{ kBq } \ell^{-1}$	52
Table 4.5 ^{137}Cs activity remaining in water at equilibrium, N_{eq} , and distribution coefficient at equilibrium, K_D , for different masses of soils at initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$	52
Table 5.1 Fitted rate constants and R^2 for the simple box model for different soil samples	66
Table 6.1 Fitted values of F and R^2 for the two-compartment conceptual model at the two different initial ^{137}Cs water activity concentrations	82
Table 7.1 Fitted parameters and R^2 for the four-compartment modified model at the two different initial ^{137}Cs water activity concentrations	95



CHAPTER 1

INTRODUCTION

1.1 Background of Hong Kong

Hong Kong is situated at the southeastern tip of China facing the South China Sea (Figure 1.1), with a total area of 1100 square kilometers and over 6 million population. It is consisted of the Hong Kong Island, the Kowloon peninsula, the New Territories and 235 outlying islands. Up to 2003, there are totally three nuclear power plants in China. Two of them, the Guangdong and the Lingao nuclear power stations, are in Guangdong Province in southern China (Figure 1.2).

1.2 The Guangdong Nuclear Power Station

The Guangdong nuclear power station is the first and largest commercial nuclear installation in China. It is located at Da Keng, on the coast of Daya Bay (22:36:0:N, 114:32:0:E), at a distance of 50 km north-east from the city centre of Hong Kong. Two 906 MW (net capacity) pressurized water reactors in the Guangdong station came into commercial operation in February and May 1994,



Figure 1.1 Location of Hong Kong. (Source: <http://www.info.gov.hk>)

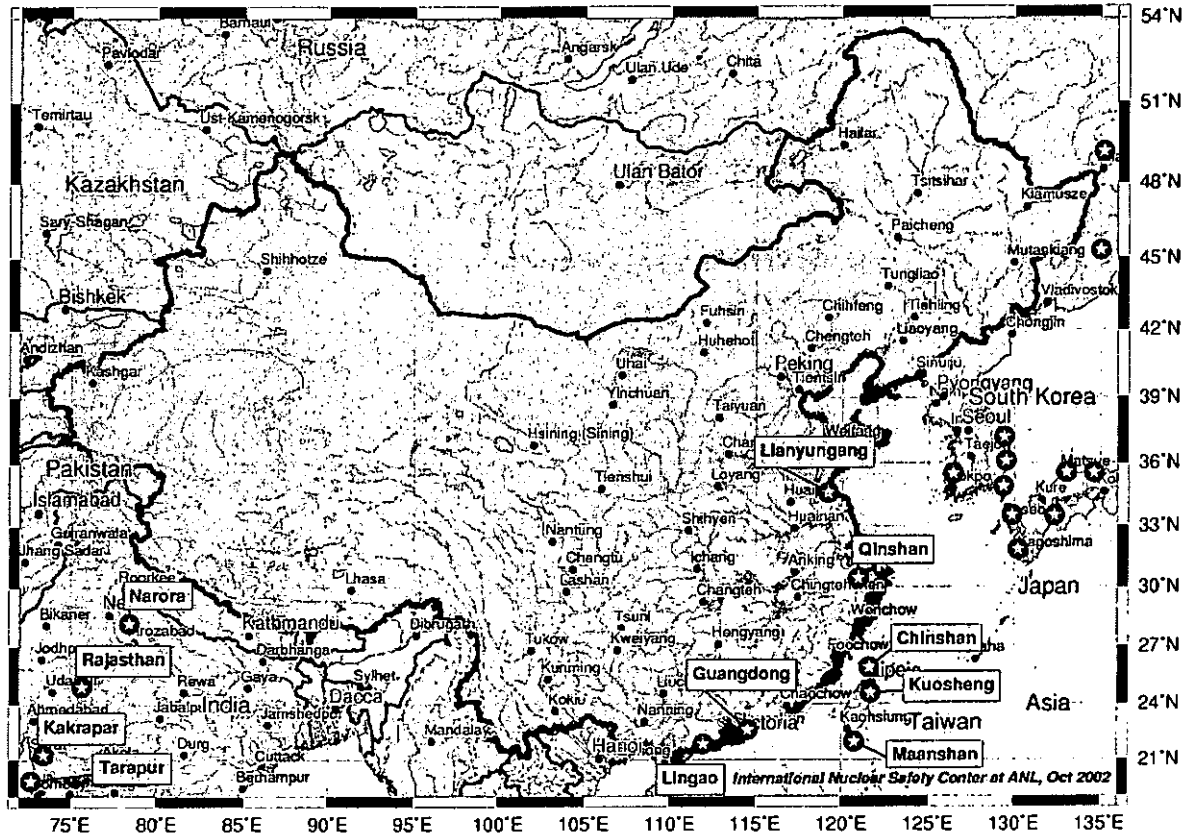


Figure 1.2 Location of the three nuclear power plants (Guandong, Qinshan and Lingao) in China. (Source: International Nuclear Safety Center at Argonne National Laboratory)



respectively. They generate over 10 billion units of electricity per year in which about 70 % is supplied to Hong Kong and the rest is consumed in Guangdong.

1.3 The Lingao Nuclear Power Station

The Lingao nuclear power station, located at 1.2 km (19:55:0:N, 109:38:0:E) east of the Guangdong nuclear power station, is the third nuclear power plant in China. The objective of the plant is to meet the growing power demand of the south-east Guangdong province. There are totally four nuclear reactors in the Lingao plant. Two of them are the 935 MW (net capacity) pressurized water reactors and have entered commercial operation in June 2002 and March 2003, respectively. The other two reactors are under construction, and are expected to be operating in 2006 and 2008.

1.4 Effects of Nuclear Power Plants – The Chernobyl Accident

The April 1986 disaster at the Chernobyl nuclear power plant in the Ukraine was the world's worst nuclear power accident. Figure 1.3 shows the location of Chernobyl. The Chernobyl accident killed more than 30 people immediately, and as a result of the high radiation levels in the surrounding 32 km radius, 13500 people had to be evacuated. If an accident of similar

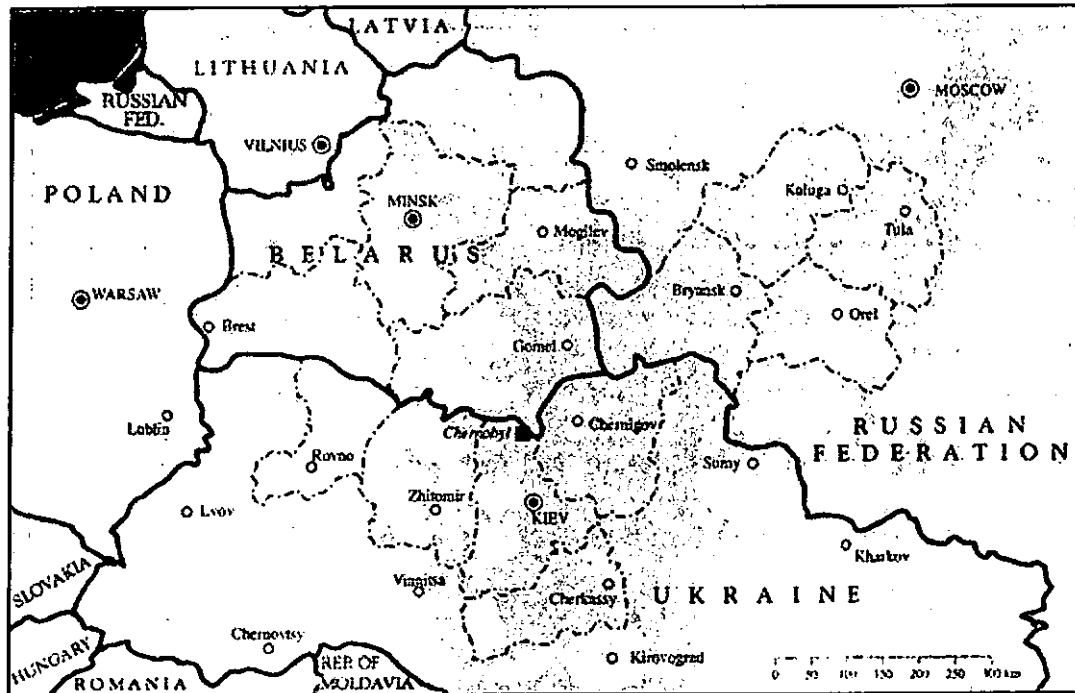


Figure 1.3 Location of Chernobyl. (Source: <http://www.nuclear.org>)



magnitude as the Chernobyl accident were to occur in any one of the reactors near Hong Kong, the lives of the six million plus population will be at stake as evacuating such a large population is next to impossible. If a total evacuation is not feasible, it is important to estimate the consequences to the population due to the release of radioactivity to the atmosphere.

In the Chernobyl accident, a total of about 12×10^{18} Bq of radioactivity were released. The released radionuclides were then transported and dispersed by air plumes to European soils (Persson et al., 1987; Duvernet, 1989; Gudikesen et al., 1989) and European lakes (Smith et al., 1999). Radionuclides deposited onto lakes and reservoirs may be removed through the outflow, by sedimentation of suspended particles (Carlesson, 1978; Robbins et al., 1992) and by direct uptake by the bottom sediments as a result of transport across the sediment/water interface (Santshi et al., 1986; Hesslein, 1987).

Table 1.1 shows the radionuclides released into the environment during the Chernobyl accident and their corresponding half-lives. Most of them (e.g. ^{131}I , ^{103}Ru , ^{106}Ru , etc.), owing to their relatively short half-lives, are hazard to human being only for a limited period following their accidental release. However, radiocesium isotope (^{137}Cs) is one of the radionuclides having the highest impact to humans (Kruyts and Delvaux, 2002; Rigol et al. 2002) because



Table 1.1 Radionuclides released during the Chernobyl accident and their corresponding half-lives

Nuclide	Half-life	Activity during the Chernobyl accident (PBq)
Xe-33	5.3 d	6500
I-131	8.0 d	~1760
Cs-134	2.0 y	~54
Cs-137	30.0 y	~85
Te-132	78.0 h	~1150
Sr-89	52.0 d	~115
Sr-90	28.0 y	~10
Ba-140	12.8 d	~240
Zr-95	1.4 h	196
Mo-99	67.0 h	>168
Ru-103	39.6 d	>168
Ru-106	1.0 y	>73
Ce-141	33.0 d	196
Ce-144	285.0 d	~116
Np-239	2.4 d	~95
Pu-238	86.0 y	0.035
Pu-239	24400.0 y	0.03
Pu-240	6580.0 y	0.042
Pu-241	13.2 y	~6
Cm-242	163.0 d	~0.9



of its long half-life of 30 years and its relatively high abundance. More than 10 years after the Chernobyl accident, the radiocesium contents in plants and animals in numerous areas in Western Europe as well as in the former Soviet Republics, exceeded intervention levels (Jones et al., 1999). In an upland region of Italian Apennines, a relatively high radiocesium concentration, up to 8973 Bq m^{-2} , was found in the superficial mineral soil (Malanca et al., 1996).

1.5 Radiological Impact

If a nuclear accident occurs at a nuclear plant, large quantities of radionuclides may be released into the environment immediately. It can have different effects causing adverse impact on different aspects in both long and short terms.

- Health effect – The number of cancer, especially thyroid cancer, may increase rapidly.
- Psychological effect – Psychological health disorders, such as anxiety, depression, helplessness, despair and other disorders attributable to mental stress, may significantly increase.
- Economic effect – The economy of the affected area declines indirectly.
- Environmental effect – The released radionuclides are widely dispersed and



affect a vast area. The main environmental pathways of human radiation exposure are illustrated in Figure 1.4.

1.6 Rationale of Study

There are now four reactors operating at close proximity to Hong Kong. It is generally recognized that release of radionuclides into the natural environment takes place even during their normal operation, not to mention if an accident occurs. In case a nuclear accident occurs at one of the stations, substantial amount of radioactive substances would be released into the environment. Immediate effect, such as death, may not happen in Hong Kong as the stations are about 50 km far away. However, the biological and its long term impact cannot be neglected because some of the gaseous and volatile radionuclides can be transported by wind to Hong Kong. It is similar to a plume of smoke dispersing into the atmosphere and depositing some of its contents to the ground. The major pathways of radionuclides have been shown in Figure 1.4.

In the pathways shown in Figure 1.4, the most threatening hazard to the Hong Kong population is the contamination of drinking water with radionuclides. Since Hong Kong has no natural lakes or rivers, the major drinking water source

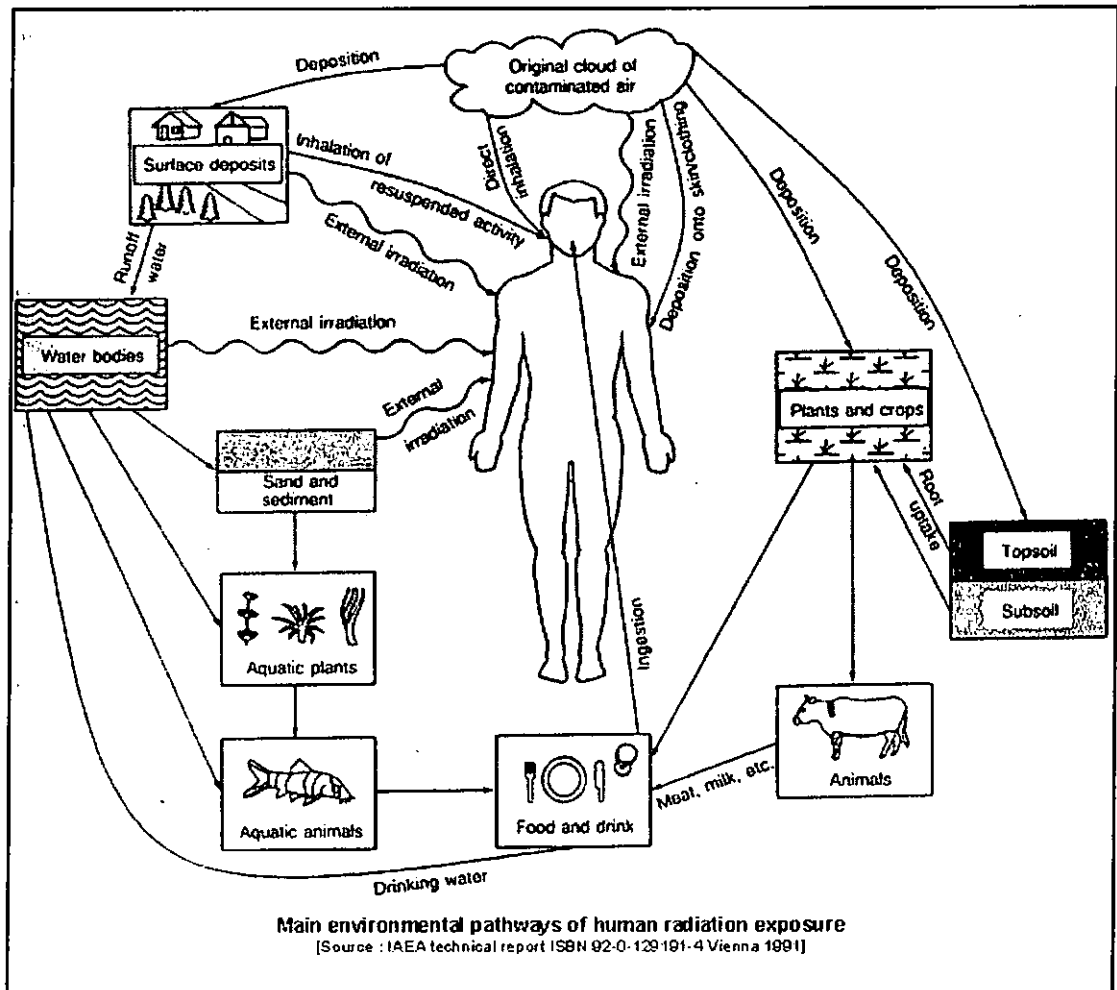


Figure 1.4 Main environmental pathways of human radiation exposure. (Source: IAEA technical report ISBN 92-0-129191-4 Vienna 1991)



is the supply from Guangdong through Dongjiang, the East River. Water extracted from the river at a point 83 km north of Hong Kong is pumped over a series of dams built across the Shima River, one of its tributaries. It is then discharged into the Shenzhen Reservoir before being fed by pipelines to Shenzhen Special Economic Zone and across the border at Muk Wo to the Hong Kong reservoirs. When a major release of radioactivity occurs, the wind may carry the plume to the rivers and reservoirs. This may contaminate the water supplies and increase the radiation dose of the population, as we have no choice but to consume the contaminated water.

1.7 Objectives of Study

^{137}Cs is one of the radionuclides having the highest impact not only because of its relatively long half-life, but also of its large transfer factor by inhalation and ingestion. Table 1.2 shows the transfer factors of radionuclides by inhalation and ingestion. ^{137}Cs is usually present as simple cations with high solubility and mobility in marine environments, the amount of which depends particularly on the sorption of cesium to sediment surfaces (Børretzen and Salubu, 2002). In addition, ^{137}Cs has high biological availability through metabolic similarity to potassium (Evans et al., 1983).



The general purpose of this study is to investigate the sorption behavior and kinetics of ^{137}Cs in soils as it is one of major factors which determine the availability of ^{137}Cs to biological systems. It has been known that ^{137}Cs is strongly sorbed by soils and sediments (Tamura and Jacobs, 1960; Sawhney, 1970, 1972; Smith et al., 1999). This sorption is highly specific, particularly on illitic materials containing a small proportion of sites, frayed edge sites (FES), which have a very strong affinity for cesium (Brouwer, 1983). In this study, soil samples from various reservoirs in Hong Kong were sampled and characterized for their physical and chemical properties. Batch experiments were performed to observe the sorption behavior of ^{137}Cs on different sorbing sites in soils. Different models were then proposed to study the kinetics of radiocesium sorption on the specific sites (FES) and other sorbing sites in soils. Attempts were also made to relate the sorption kinetics with the characteristic properties of soil samples such as clay content, organic matter content, cation exchange capacity, potassium ions availability and soil pH. Results can provide information the mobility of radiocesium in soils which is a useful tool in emergency planning and in countermeasure implementation during any accidental release from the nearby Guangdong and Lingao nuclear power stations.



Table 1.2 Transfer factors of radionuclides by inhalation and ingestion

Nuclide	Transfer factor by inhalation	Transfer factor by ingestion
I-131	1	1
Cs-134	1	1
Cs-137	1	1
Sr-89	0.3	0.3
Sr-90	0.3	0.3
Ba-140	0.1	0.1
Zr-95	0.002	0.002
Mo-99	0.05	0.8
Ru-103	0.05	0.05
Ru-106	0.05	0.05
Ce-141	0.0003	0.0003
Ce-144	0.0003	0.0003
Np-239	0.001	0.001
Pu-238	0.001	0.00001
Pu-239	0.001	0.00001
Pu-240	0.001	0.00001
Pu-241	0.001	0.00001
Cm-242	0.001	0.001



CHAPTER 2

BEHAVIOUR OF RADIOCESIUM IN SOILS

Study of sorption of radiocesium (^{137}Cs) in soils and sediments is important because it determines how much radiocesium remains in water for uptaking by plants and hence into the food chain. The strong and possibly irreversible sorption of radiocesium in soils results in low plant uptake. However, in some ecosystems radiocesium continues to be bioavailable. Sorption therefore plays a determinant role in the mobility and bioavailability of radiocesium in soils (Livens & Loveland, 1988).

2.1 Distribution Coefficient and Transfer Factor

The traditional way to describe the sorption of radiocesium on soils is highly empirical and is based on the measurement of soil-liquid distribution coefficients (K_D) and the soil-plant transfer factor (TF).

Distribution coefficient, K_D , is a useful parameter for describing the



mobility of radionuclides in soils (Sheppard, 1985; Sanchez et al., 2002), defined as the ratio of the activity in the dry sediment (Bq kg^{-1}) to that in water (Bq l^{-1}) (Shenber and Eriksson, 1993; Dumat and Staunton, 1999). The K_D value is a function of sediment-tracer contact time as radiocesium is progressively fixed to sediment particles in (Borretzen and Salbu, 2002). It finally reaches equilibrium and can reflect the extent of radiocesium sorbed by soils.

Transfer factor, TF , is used for the description of transport of radionuclides between the compartments 'soil' and 'plant', defined as the ratio of the activity in plant dry matter (Bq kg^{-1}) to the activity in dry soil (Bq kg^{-1}) (Shenber and Eriksson, 1993; Kruyts and Delvaux, 2002). The TF value is used to investigate the bioavailability of radiocesium in soils. Some researchers (e.g. Strebl et al., 2002) used it to correlate with soil characteristics.

2.2 Factors Affecting the Mobility of Radiocesium in Soils

The mobility of radiocesium in soils is influenced by the nature and properties of soil components. Some factors which affect the mobility of radiocesium in soils are cation exchange capacity, clay content, organic matter content, potassium ions availability and soil pH.



2.2.1 Cation Exchange Capacity

Mineral and organic matter in soils have negatively charged sites which attract positively charged ions. The cation exchange capacity (CEC) of soils is defined as the amount of positively charged ions which the soil can hold and which is expressed in milliequivalents per 100 grams (meq/100g) of soil. The CEC of soils is equal to the CEC of both the mineral and organic fractions. The major source of CEC in the mineral fraction comes from clay. In the organic fraction, the negative charge of organic matter is due mainly to dissociation of H^+ from the $-OH$ of carboxyl and phenolic groups. Thus, the higher are the clay content and organic matter content, the higher is the CEC of the soil.

Cesium sorption on soils correlates strongly with the CEC as the primary master variable for sorption (Grütter et al., 1990). Soils with higher CEC have greater sorption of cesium.

2.2.2 Clay Content

Most soils and sediments are mixture of particles of various sizes. The clay fraction is the smallest particles in soils of less than 0.002 mm in particle diameter. Table 2.1 shows the International Soil Science Society classification



system of soil particles. The clay content of soils is the percentage of clay in the soil samples.

The clay fraction of soils is an important sorbent for radiocesium (Sawhney, 1972; Sanchez et al., 2002). Researchers (Shenber and Eriksson, 1993; Konoplev et al., 2002) had observed that the values of distribution coefficient, K_D , were relatively high for soils with high clay content and relatively low for the soils with low clay content. The sorption of cesium therefore increases with increasing clay content. Sawhney (1972) claimed that increased sorption of Cs^+ by soils of larger clay content was due to increased weathering of mica edges, so the area of the frayed edges was increased for sorption. In addition, Sanchez et al. (1999) found that high transfer factor, TF , of cesium occurred in soil with low clay content.

Table 2.1 The International Soil Science Society classification system of soil particles

Separate	Particle Diameter (mm)
Coarse sand	2.0-0.2
Fine sand	0.2-0.02
Silt	0.02-0.002
Clay	<0.002



2.2.3 Organic Matter Content

Soil organic matter is an accumulation of plant and animal residue in varying stage of decay. These materials are continuously being broken down by microorganisms. Consequently, organic matter becomes one of the soil components and is quoted as the percentage of organic matter (by dry weight).

In many researches, organic matter was found to enhance the mobility of radiocesium in soils (e.g. Comans et al., 1998; Demat et al., 2000). Cremers et al. (1990) found that soils with lower organic matter content could immobilize radiocesium in soils, leading to decrease in availability. It was because organic matter decreased the cesium affinity of clay minerals, thereby reducing their ability to immobilize cesium in soil. Staunton et al. (2002) showed that both destruction and addition of organic matter to mineral clays gave similar results. In addition, Valcke and Cremers (1994) found that soils with high organic matter content had relatively low K_D values and the sorption was readily reversible (Rigol et al., 2002). These predictions were showed by experiments based on a desorption screening with a variety of desorption agents. Valcke and Cremers (1994) found that soils with organic matter in the range of 10 to 40 % had less fixation levels of 30 to 50 %. Soils with high organic mater content, therefore, were often regarded as having large number of the regular exchange sites in soils.



Nature of the regular exchange sites (RES) will be discussed in Section 2.3. Moreover, the radiocesium soil-to-plant transfer factor, TF , was positively correlated with organic matter content of soils (Kruyts and Delvaux, 2002; Sanchez et al., 1999). Radiocesium contamination of soils characterized by high levels of organic matter may present a serious hazard in terms of the soil-to-plant transfer process (Cremers et al., 1990) because radiocesium was more available to biological systems in soils with high organic matter content.

2.2.4 Potassium Ions Availability

Some findings showed that potassium ions (K^+) competed most favorably with cesium ions (Cs^+) in the sediment environment. Potassium ions could come from soils, which were related to the values of soluble ions and exchangeable ions, and from others such as fertilizers. Researches (Shenber and Eriksson, 1993; Konoplev et al, 2002) found that the cesium sorption capacity of soils was reduced when the level of K^+ increased. In addition, sorption of radiocesium to sediments was shown that the value of K_D is inversely proportional to the content of competing ions (e.g. K^+) in the sediment water (Smith et al, 1999; Comans et al., 1989; Valcke and Cremers, 1994). Similar trend had been observed for TF values. Smolders et al. (1997) and Sanchez et al. (1999) found that high TF value of cesium in soils occurred with low potassium availability.



Konoplev et al. (1993) showed that the radiocesium plant uptake was reduced in agricultural soils in potassium fertilization experiments re.

2.2.5 Soil pH

Soil pH is defined as the negative logarithm of the hydrogen ion concentration. The pH scale goes from 0 to 14 with pH 7 as the neutral point. As the amount of hydrogen ions in the soil increases, the soil pH decreases and becoming more acidic. The pH value is related to ion exchange capacity.

For radiocesium sorption in soils, pH values were unaffected by protons down to about pH 3 (Sanchez et al., 2002). However, the interaction of radiocesium with the organic fraction, particularly in highly organic soils, was strongly influenced by pH, since the proton dissociation of the functional groups in humic molecules was pH-dependent. On the other hand, Strebl et al. (2002) found a negative correlation of radiocesium soil-plant transfer with soil pH.

2.3 Sorption Mechanisms of Radiocesium in Soils

Since the early sixties, it was well known that radiocesium was strongly adsorbed to soils (e.g. Schulz et al., 1960; Sawhney, 1972). Many researchers



Chapter 2 Behaviour of Radiocesium in Soils

(e.g. Schulz et al., 1960) had suggested that radiocesium might be even irreversibly adsorbed to soils. In general, the sorption of radiocesium in soils was governed by the partitioning between two major types of cesium sorbing sites, which largely differ in their selectivities for poorly hydrated alkali cations, such as K^+ , NH_4^+ , Rb^+ and Cs^+ (Valcke and Cremers, 1994). They were the regular exchange sites (RES) and the frayed edge sites (FES).

The regular exchange sites (RES) included planar sites on layer silicates (Valcke and Cremers, 1994), which could be found on organic matter and surfaces of clays. The sorption of cations from solution on the RES of soils was usually considered as a simple ion-exchange process with hydrated cations and is reversible. The RES did not specifically sorb Cs^+ ions and the sorbed ions in the RES could be displaced easily by other cations (Rigol et al., 1999).

The frayed edge sites (FES) was located at the edges of interlayer sites of clay minerals and born out from micaceous minerals. The FES sorbed poorly hydrated ions (e.g Cs^+) selectively. There were only small amount of the FES in soils and the FES capacity was estimated to contribute 0.001 to 6 % of the overall cation exchange capacity (CEC) of soils (De Preter et al., 1991; Delvaux et al., 2000, Kruyts and Delvaux, 2002). Because of its irreversible characteristic, it was an important factor to determine the availability of radiocesium to biological



systems. The mechanisms of selective sorption and fixation of radiocesium by the FES is discussed below.

Ions with low hydration energies, such as K^+ , NH_4^+ , Rb^+ and Cs^+ , were the major factor in cation selectivity and fixation (Sawhney, 1972). Since most cations in aqueous solution were hydrated, they were too large to approach interlayers. Ions with low hydration energies could easily lose their hydration shells and penetrate interlayers at frayed edges (Konoplev and Konopleva, 1999). These poorly hydrated cations produced interlayer dehydration and the layers collapsed to fix the cations in interlayer positions. As demonstrated by optical observations in the laboratory, weathering in mica proceeded from the edges inwards (Scott and Smith, 1966; Sawhney and Voigt, 1969). The partially weathered mica in soils consisted of a collapsed of central cores 10 Å and expands frayed edges of 14 Å (Sawhney, 1972; Cremers et al., 1988). The FES selectively sorbed the poorly hydrated cations to produce more stable collapsed structure. K^+ and Cs^+ ions had high selectivities on the FES (Schulz et al., 1960; Sawhney, 1960, 1972), which were ascribed to the ease of collapse of frayed edges. Figure 2.1 illustrates the collapse of frayed edges by a poor hydrated cation. Sawhney (1972) explained that attraction due to the poorly hydrated cation in the interlayer position near the frayed edge and the negative layer charge tended to bring the two ends of the frayed edges together. The cation in the

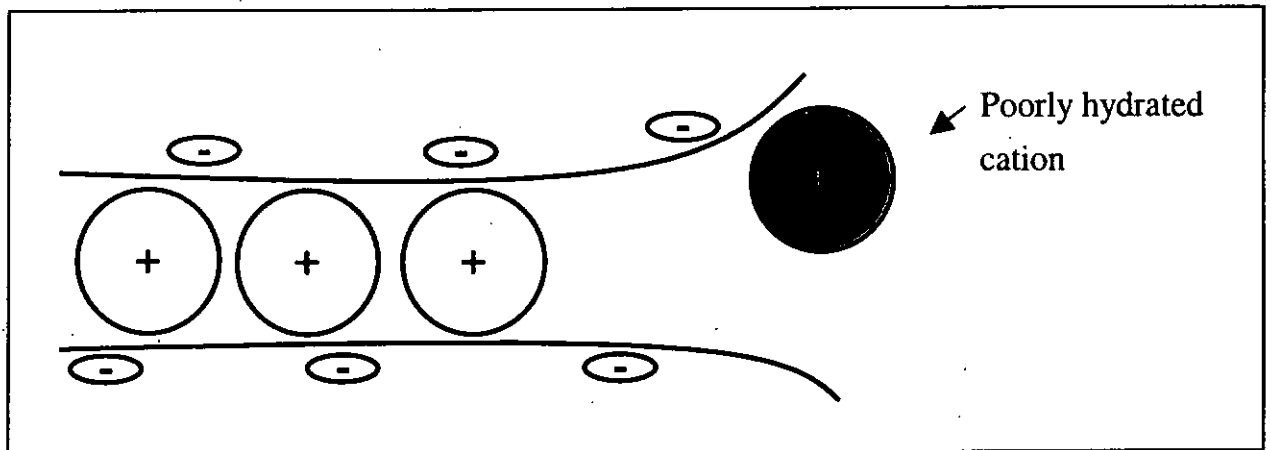


Figure 2.1 Selective sorption in a frayed edge of a weathered mica sheet.



forked edge moved out and be replaced by the poorly hydrated cation. The approaching cation further increased the attraction between the two ends and then collapsed the edge to produce the stable structure. Compared with K^+ , Cs^+ ions, Cs^+ ions were more selective because of their lower hydration energy to hold the layers together strongly (Schulz et al., 1960; Sawhney, 1960, 1972).

Another sorption mechanism was proposed by Evans et al. (1983) who suggested three types of cesium sorbing sites existed in illite clay, as shown in Figure 2.2. The first were the surface and planar sites (i.e. RES) from which radiocesium was generally exchangeable by all cations. The other two sorbing sites were probably located on the clay crystal edges and contributed about 2 % of the overall cation exchange capacity (Brouwer et al., 1983). One was the wedge edge sites (WES) where radiocesium exchange was sterically limited to cations of similar size and charge. The other was the interlayer sites (i.e. FES) from which radiocesium was not readily exchanged and could be regarded as fixed.

2.4 Isolation of FES – Silver Thiourea Method

A procedure was developed which allowed quantitatively measurement of the FES capacity in soils (Cremers et al., 1988, 1990). The method was based on the use of the silver thiourea ($AgTU$) complex to mask the bulk of the ion

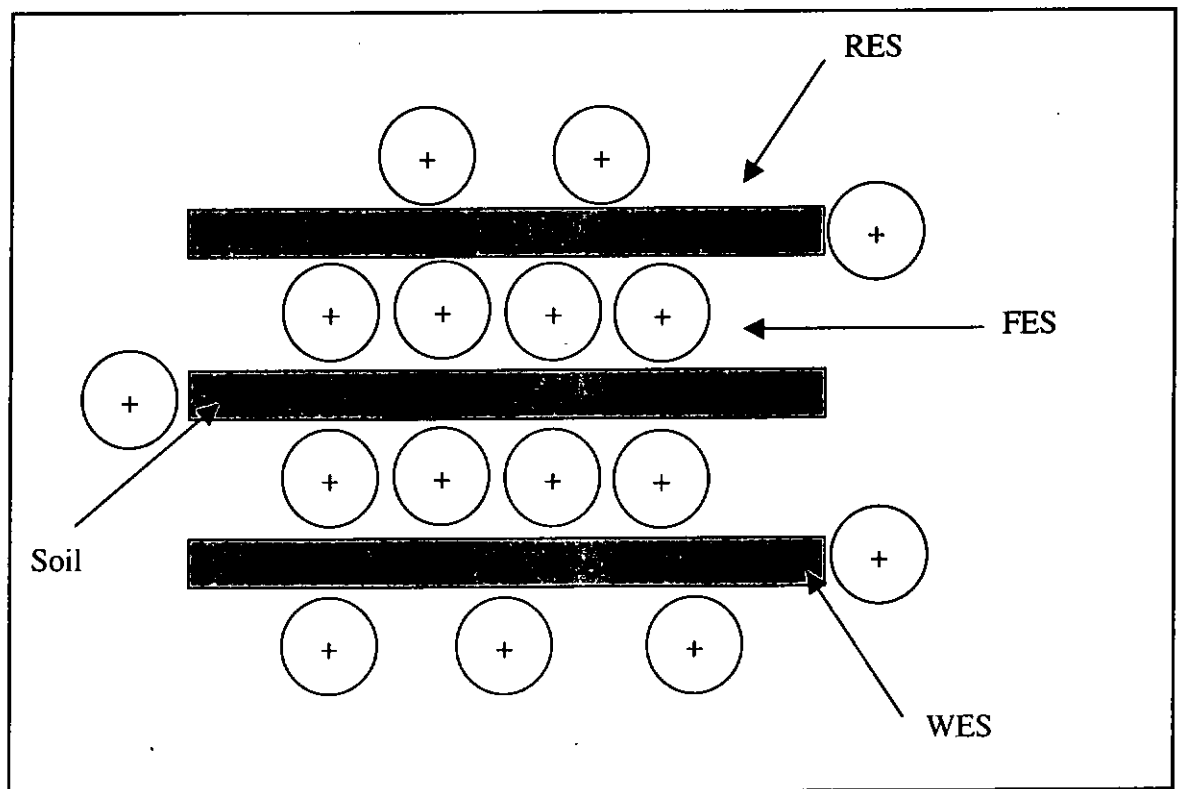


Figure 2.2 The three types of ^{137}Cs sorbing sites in soils.



exchange complex of the clay, specifically the planar ion-exchange sites (i.e. RES) (Pleysier and Cremers, 1973; Cremers et al, 1988). By dispersing soils in a solution containing suitable background level (usually 0.015 M) of AgTU, cesium ions were then excluded from the bulk of the FES and their action became restricted to the small number of specific sites (i.e. FES). Zachara et al. (2002), however, found this method to be problematic in practice. They found that the technique was difficult to perform due to the unstable chemical nature of AgTU. AgTU thus did not block all planar sites and the FES concentration was overestimated. This method was adopted in this study because it was easier to be handled.



CHAPTER 3

MATERIALS AND EXPERIMENTS

3.1 Sites and Sampling

Four soils samples were collected from each of the four different reservoirs in Hong Kong (see Figure 3.1). They were Plover Cove Reservoir, High Island Reservoir, Tai Tam Tuk Reservoir and Tai Lam Chung Reservoir. Details of reservoirs, such as location, storage capacity and sampling information are listed in Table 3.1. High Island Reservoir has the largest capacity and Plover Cove Reservoir has the largest covered area in Hong Kong. Soil samples collected by another local researcher (Man and Cheung, 2002) were also used. They were collected from locations in the vicinity of the Shek Lei Pui Reservoir and other locations in Hong Kong. Details of all soil samples are showed in Table 3.1.

3.2 Soil Samples Treatment

Soil samples collected were dried in an oven maintained at about 50 °C overnight. They were then subjected to homogenization by crushing with pestle.

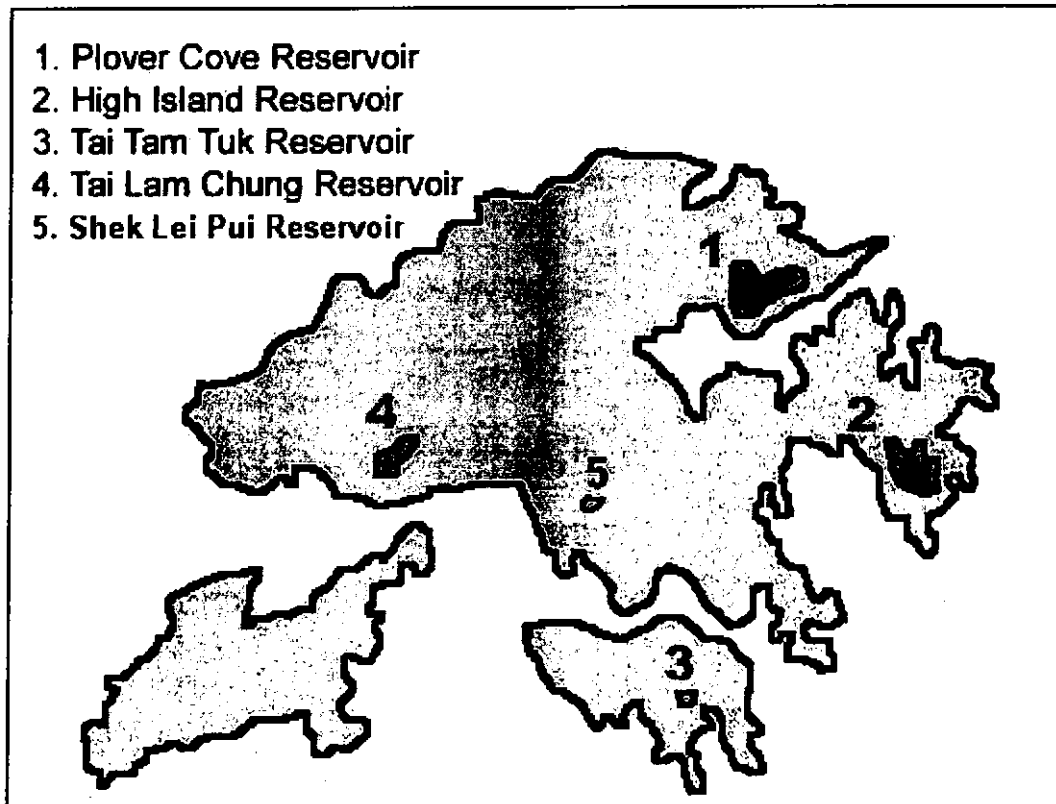


Figure 3.1 Sampling sites of reservoirs in Hong Kong.



Table 3.1 Details of soil samples

Soil	Loaction	District	Storage Capacity (10^6 m^3)	Sampling Date	Sampling Depth (cm)
R1	Plover Cover Reservoir	Tai Po, N. T. ¹	170	11 Aug 2002	0 - 10
R2	High Island Reservoir	Sai Kung, N. T. ¹	280	11 Aug 2002	0 - 10
R3	Tai Tam Tuk Reservoir	Southern, H. K. ²	6.2	16 Aug 2002	0 - 10
R4	Tai Lam Ching Reservoir	Tuen Mun, N. T. ¹	20	16 Aug 2002	0 - 10
S1 ³	Shek Lei Pui Reservoir	Kowloon	2.9	03 Sep 1998	0 - 5
S2 ³	Garden	Yeun Long, N. T. ¹	-	09 Sep 1999	0 - 5
S3 ³	Shek Lei Pui Reservoir	Kowloon	2.9	11 Sep 1999	0 - 5
S4 ³	Garden	Hung Hom, Kowloon	-	11 Sep 1999	0 - 5

1 : N. T. - New Territories

2 : H. K. - Hong Kong Island

3 : S1-S4 (Source: Man & Cheung, 2002)



Sub-samples were analyzed for their physical and chemical properties.

3.3 Particle Size Analysis

The particle size analysis was carried out in accordance with BS 1377: Part 2:1990. Combined sieving and sedimentation procedures enabled a continuous particle size distribution curve of a soil to be plotted from the size of the coarsest particles down to the clay size. Soil samples for analysis were oven dried (i.e. over 100 °C) for 24 h to give a minimum mass, then subjected to homogenization by crushing with pestle. Before sedimentation and sieving procedures, dispersion of soil samples was performed.

3.3.1 Dispersion

For each soil sample, 70 g oven-dried soil sample was dispersed with 100 ml of a dispersing agent in a conical flask for overnight. Sodium hexametaphosphate, a solution of sodium carbonate and hexametaphosphate, was used as the dispersing agent. The soil mixtures were left for the sedimentation analysis. This procedure could prevent the clay particles foam flocculating into larger particles.



3.3.2 Sedimentation

The purpose of sedimentation was to determine the size distribution of the fine particles of a soil sample. The hydrometer test was used for sedimentation which was very effective in determining the amount of silt- and clay-sized particles in a soil sample. The principle of the hydrometer test was that the soil particles settled in a dilute suspension at a terminal velocity which was a function of the particle size.

After dispersion, the soil mixtures in the conical flasks were shaken in a mechanical shaking device for at least 10 min. Each soil mixture was then transferred to a 1-l measuring cylinder and made up to 990 ml with deionized water. A rubber stopper was inserted into the cylinder and was shaken end by end for 10 min. The cylinder with the soil suspension was then placed upright and the timer started. A hydrometer was immersed in the soil suspension simultaneously and allowed to float, as shown in Figure 3.2. The reading on the hydrometer was taken after periods of 0.5 min, 1 min, 2 min, 4 min, 8 min, 15 min, 30 min, 1 h, 2h, 6h and 24h. The sedimentation was repeated for each soil sample. The particle size and its mass proportion were related to the hydrometer reading and the elapsed time.

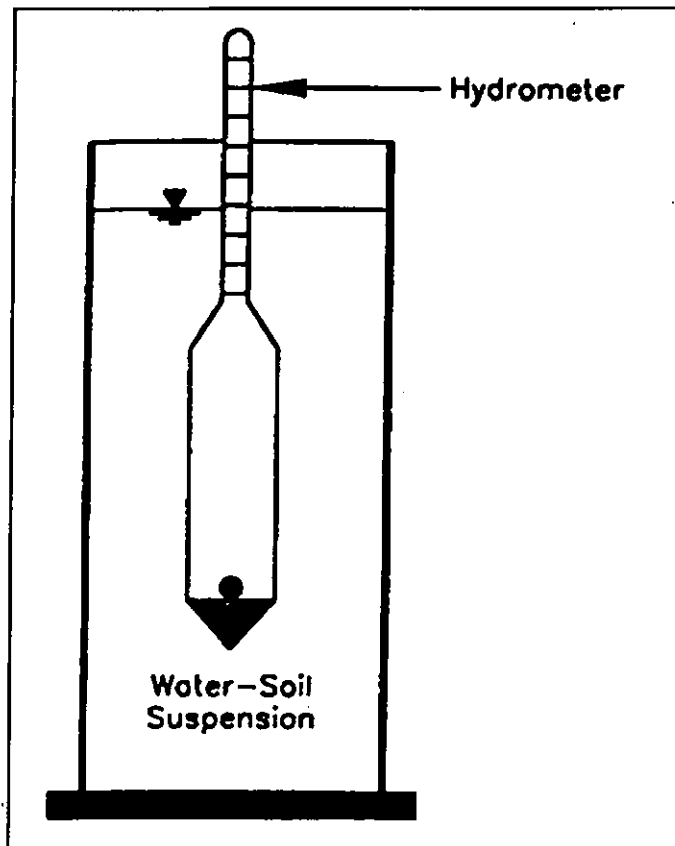


Figure 3.2 Hydrometer test.



3.3.3 Sieving

The dry sieving method was used to quantitatively determine the particle size distribution in a cohesionless soil down to the fine-sand size. Each soil mixture in the cylinder after the hydrometer test was sieved through a 63 μm test sieve. Soils retained from the 63 μm test sieve were transferred to an evaporating dish and dried in an oven maintained at 105 $^{\circ}\text{C}$ to 110 $^{\circ}\text{C}$ overnight. Different mesh-size test sieves, from 63 μm to 2 mm, were assembled with the largest mesh-size at the top and a receiving pan at the bottom. After cooling, the soil sample was placed to the top of the sieve. The set of sieves were shaken by a mechanical shaker for 10 min as shown in Figure 3.3. The procedure was repeated for each soil sample. The masses with different sizes of the soil samples were obtained. Combining the data from sedimentation and sieving, a complete and continuous particle size distribution curve of a soil sample was obtained.

3.4 Soil Characterization

Soil characteristics including cation exchange capacity (CEC), organic matter content, and soluble potassium ions and soil pH were determined in dried and crushed soil samples. The cation exchange capacity (CEC) was determined

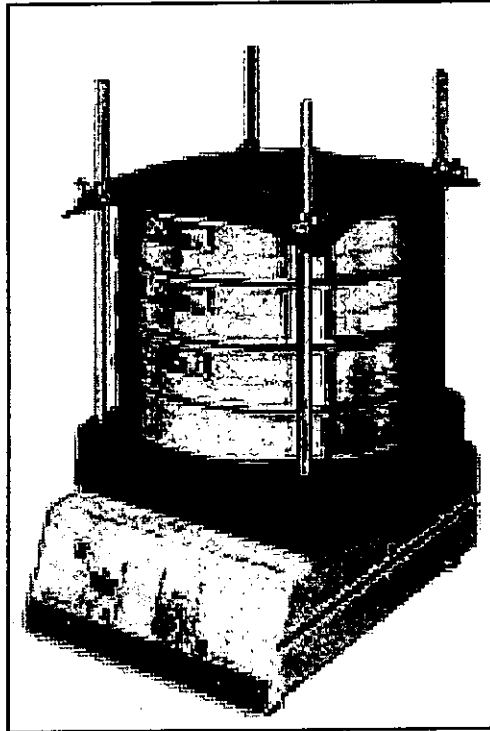


Figure 3.3 A mechanical shaker with a set of sieves.



by the ammonium acetate (pH 7) method which was a standard method used in the classification of soils. The organic matter content was obtained by ignition loss. The soluble potassium ions concentration was determined by using Atomic Absorption Spectroscopy (AAS). The soil pH was measured in a 1:20 suspension of soil and water.

3.5 ^{137}Cs Measuring System

A 3-inch NaI(Tl) well-type scintillation detector was used to assay the ^{137}Cs contents as shown in Figure 3.4. The detector was housed inside a lead shield of 5 cm thick and 20 cm diameter and connected to an EG&G ORTEC NOMAD Portable Spectroscopy System, Model 92X-P. The efficiency of the well of the NaI(Tl) detector was obtained by measuring 10 ml solution of known ^{137}Cs activity in a Polypropylene (PP) test tube and its value was 17 %. Samples were counted for about 5 min and the uncertainties were within $\pm 1\%$.

3.6 Preparation of Silver Thiourea (AgTU) solution

To prepare 0.015 M AgTU solution, 2.55 g silver nitrate (f.w. = 169.87) and 1.14 g thiourea (f.w. = 76.12) were dissolved into 1-ℓ conical flask, and then made to 1 ℓ solution with deionized water. The freshly prepared AgTU solution

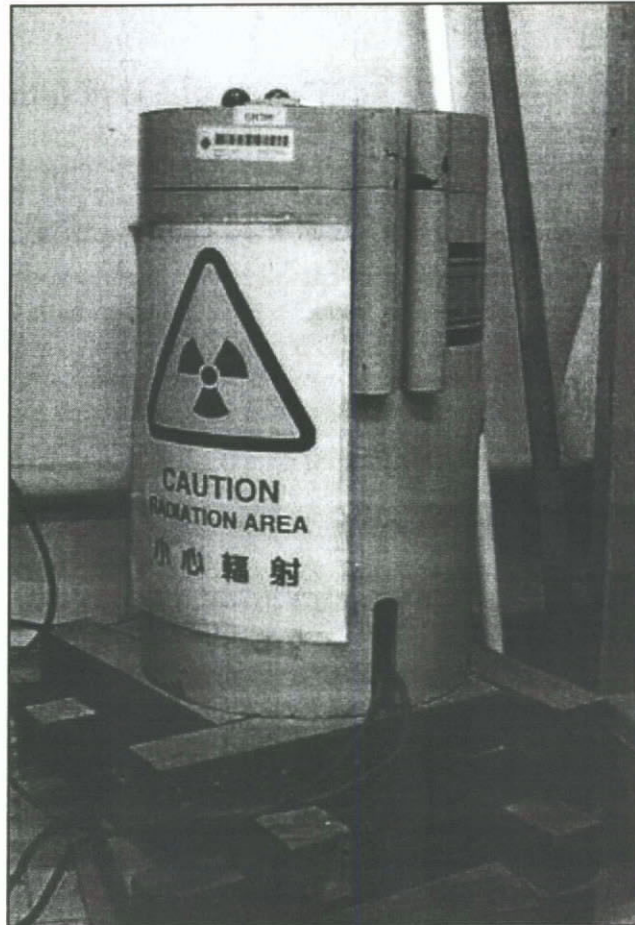


Figure 3.4 The NaI(Tl) well-type scintillation detector.



was used within 48 h after preparation to minimize exposure to light which could induce the reduction of thiourea and the formation of Ag_2S (Pleysier and Cremers, 1973).

3.7 Experimental Procedures

Three sets of experiments were performed to investigate the sorption of ^{137}Cs on different sites in soils.

3.7.1 Sorption of ^{137}Cs on All Types of Sites in Soils

200 ml solution of initial ^{137}Cs water activity concentration of 240 kBq ℓ^{-1} were added to a 1.25- ℓ high density Polyethylene (HDPE) container and allowed to stand for one day. 1.0 g soil samples from different locations in Hong Kong, totally 8 soil samples, were independently added to the solutions. At prescribed intervals, 30 ml mixture were withdrawn and centrifuged at 3000 rpm for 5 min to separate the solution from soils. 10 ml of the supernatant were pipetted and then inserted into a polypropylene (PP) test tube for the measurement of the ^{137}Cs content in the well of the NaI(Tl) system. Solution and soils were then poured back to the container. This procedure was repeated at suitable time points until equilibrium established when the activity of ^{137}Cs in the solution



reached a steady value. The distribution coefficient K_D at equilibrium was calculated and the graphs of the activity of ^{137}Cs remaining in the solution versus time were plotted for different types of soil samples.

It was to be noted that nearly all types of containers sorb ^{137}Cs , the extent depends on the container material. To offset the sorption due to the container, the ^{137}Cs solution was left in the container for a period of about a day to 'saturate' the walls before introducing soils into the solution. It was observed that the concentration of ^{137}Cs fell less than 5 % within the period and was at a steady state at the end of it. Time $t = 0$ was the moment when soils were first introduced into the solution. Only 1.0-g soil samples were used in the experiment as the sorption was too rapid for larger masses to determine with accuracy the time variation of the activity of ^{137}Cs remaining in the solution at the early stage.

3.7.2 Sorption of ^{137}Cs on the FES in Soils

The isolation of the frayed edge sites (FES) from the regular exchange sites (RES) was achieved by the AgTU masking technique (Pleysier and Cremers, 1973; Cremers et al, 1988; Sweeck et al., 1990). Soils were dispersed overnight in a 0.015 M AgTU solution, centrifuged and the supernatants discarded. Soils were then left to dry in air.



200 ml solution of two different initial ^{137}Cs water activity concentrations of $160 \text{ kBq } \ell^{-1}$ and $240 \text{ kBq } \ell^{-1}$, in a background of 0.015 M AgTU , were added to a $1.25\text{-}\ell$ HDPE container and allowed to stand for one day. Soils S2, ranging from 1.0 g to 16.0 g , were added to the solutions. At prescribed intervals, 30 ml mixture were withdrawn and centrifuged at 3000 rpm for 5 minutes to separate the solution from soils. 10 ml of the solution were then inserted into a PP test tube for the measurement of the ^{137}Cs content in the well of the NaI(Tl) system. Solution and soils were then poured back to the container. This procedure was repeated at suitable time points until equilibrium established when the activity of ^{137}Cs in the solution reached a steady value. The distribution coefficient K_D at equilibrium was calculated and the graphs of the activity of ^{137}Cs remaining in the solution verse time were plotted for different masses of the soil sample.

3.7.3 Determination of the Capacity of the FES in Soils

The method of Sweeck et al. (1990) was used to determine the capacity of the FES in soils. 16.0 g of soil S2, the same soil sample as used in Section 3.7.2, was pre-equilibrated with AgTU solution and was dispersed in a 200-ml solution of varying amounts of cesium ions and a ^{137}Cs label of 8 kBq with a background of 0.015 M AgTU solution. Phase separation was made after 24 h .



Chapter 3 Materials and Experiments

Amounts of cesium sorbed were obtained by the difference of the ^{137}Cs levels in the supernatant. This procedure was repeated until the amount of cesium sorbed became constant, indicating that all FES were filled and no more sorption was possible. Sorption isotherm was obtained by plotting the amount of cesium sorbed against various amounts of cesium. The capacity of the FES was simply the maximum amount of cesium sorbed from solution.

16.0-g soil sample were used to determine the capacity of the FES because the difference of the measurable ^{137}Cs levels in the supernatants for smaller mass samples were too small for any certainty in data interpretation.



CHAPTER 4

EXPERIMENTAL RESULTS

4.1 Physical and Chemical Properties of Soils

The particle size distributions and soil characterizations, including soil pH, organic matter content, CEC and soluble potassium ions concentration, are shown in Table 4.1 and Table 4.2, respectively. There are totally 8 various soils sampled at different locations in Hong Kong, described in Section 3.1.

The clay contents of soils ranged from 2 % to 25 %, with soil R1 and soil S2 having the largest and smallest clay content, respectively (Table 4.1). In general, soils in Hong Kong did not have much clay content as compared with those in other countries. From Table 4.2, the pH values of soils ranged from 3.00 to 8.38. All soils, except soil R3 and soil S4, were acidic. The organic matter contents of soils ranged from 0.38 % to 1.84 %, which could not be categorized as organic as its values were less than 20-35 %. Soil S2 and soil R1 had the largest and smallest organic matter contents, respectively. It was interesting to be noted that the soil with large clay content had small organic matter content (e.g. soil R1). In contrast, soil S2 had small clay content but had



Table 4.1 Particle size distribution of soil samples

Soil	Clay (%)	Silt (%)	Sand (%)	Gravel (%)
R1	25	36	37	2.0
R2	16	38	29	17
R3	17	46	24	13
R4	10	29	34	27.0
S1 ¹	22	26	26	26
S2 ¹	2.0	20	49	29
S3 ¹	22	42	28	8
S4 ¹	4	20	54	22

1 : S1-S4 (Source: Man & Cheung, 2002)

Table 4.2 Characterizations of soil samples

Soil	pH (in water)	Organic Matter (%)	CEC (meq/100g dry soil)	Soluble K ⁺ ions (meq kg ⁻¹)
R1	4.50	0.38	5.38	0.22
R2	4.36	0.81	7.92	0.10
R3	7.91	0.75	5.17	0.20
R4	3.94	0.58	4.50	0.15
S1 ¹	3.00	1.83	15.3	0.60
S2 ¹	5.31	1.84	-	-
S3 ¹	4.37	1.75	16.1	0.38
S4 ¹	8.38	1.47	-	-

1 : S1-S4 (Source: Man & Cheung, 2002)



large organic matter content. The CEC and soluble K^+ ions of soils were ranging from 4.5 meq/100g to 16.1 meq/100g and from 0.10 meq kg^{-1} to 0.60 meq kg^{-1} , respectively.

4.2 Sorption of ^{137}Cs on All Types of Sites in Soils

Time variations of the activity of ^{137}Cs in water, $N(t)$, in kBq of different 1.0-g soil samples at initial ^{137}Cs water activity concentration of 240 kBq ℓ^{-1} are separately shown from Figure 4.1 to 4.8, as a combined plot gives indiscriminating curves among soils. It was observed that ^{137}Cs were rapidly sorbed to the soils initially. For all soil samples, more than 80 % of ^{137}Cs were removed from water after one day and their equilibriums reached within not more than one week. All soil samples sorbed ^{137}Cs more than 90 % at equilibrium.

The activity of ^{137}Cs remaining in water at equilibrium, N_{eq} , and the distribution coefficient at equilibrium, K_D , for different soil samples are tabulated in Table 4.3. The values of K_D ranged from 26.7 ($\times 10^3$) ℓkg^{-1} to 139 ($\times 10^3$) ℓkg^{-1} . Soil R1 had the largest value of K_D as it had the largest clay content. This result agreed well with those of Shenber and Eriksson (1993) and Konoplev et al. (2002). Moreover, soil R2 had the smallest soluble K^+ ions and a large K_D , again agreeing well with those of Smith et al. (1999), Comans et al. (1989) and Valcke

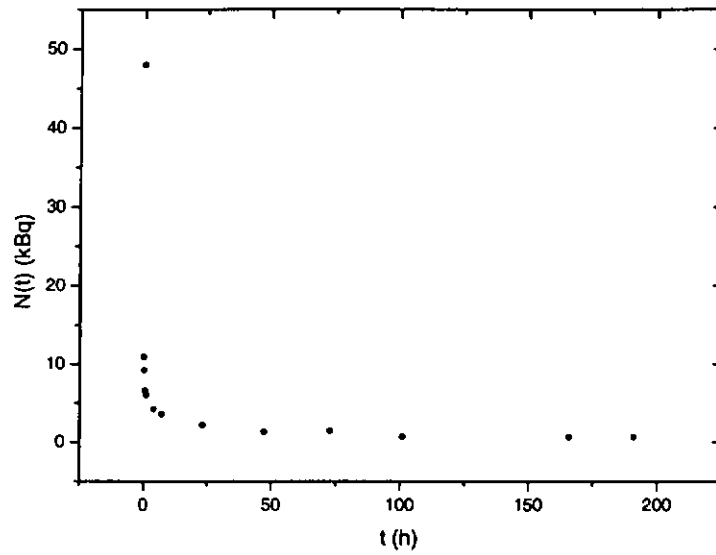


Figure 4.1 Time variations of ^{137}Cs activity in water for soil R1.

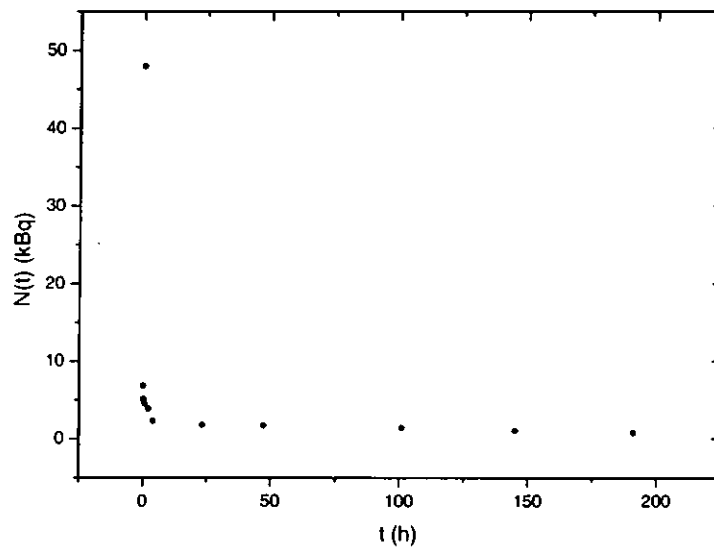


Figure 4.2 Time variations of ^{137}Cs activity in water for soil R2.

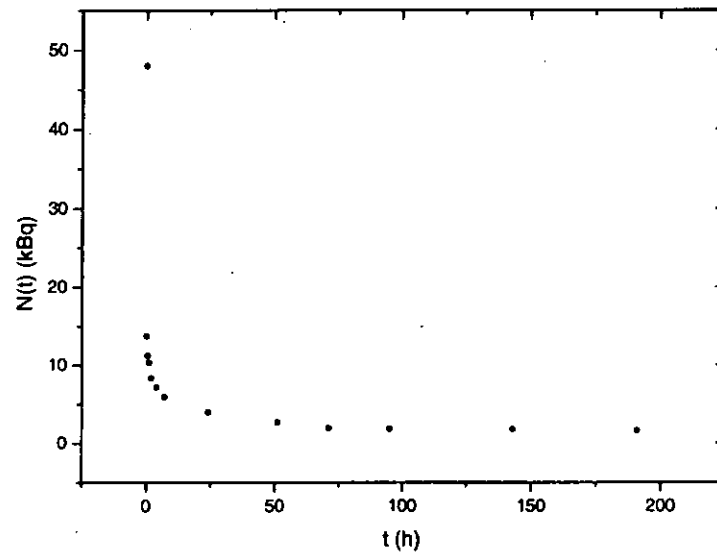


Figure 4.3 Time variations of ^{137}Cs activity in water for soil R3.

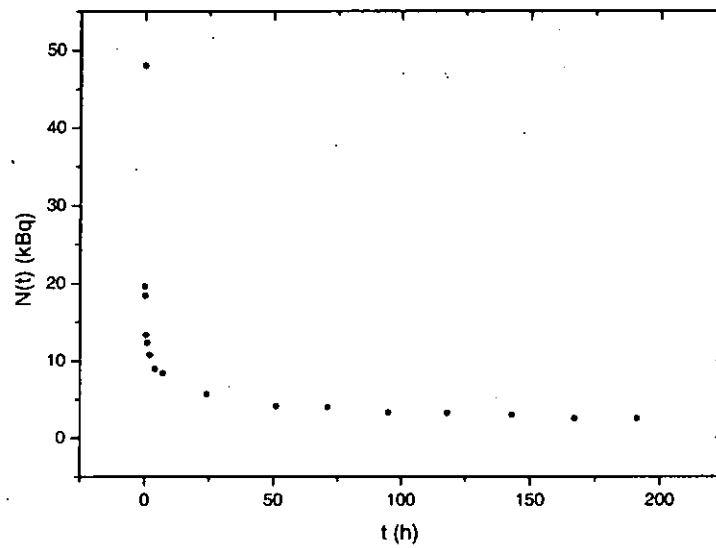


Figure 4.4 Time variations of ^{137}Cs activity in water for soil R4.

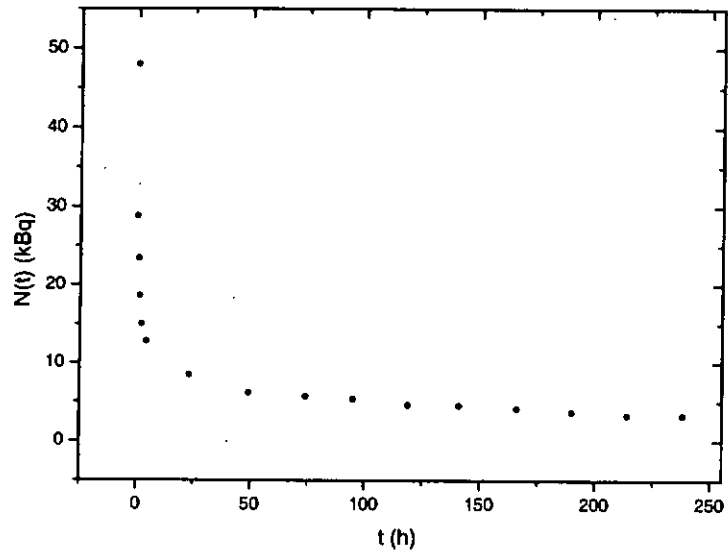


Figure 4.5 Time variations of ^{137}Cs activity in water for soil S1.

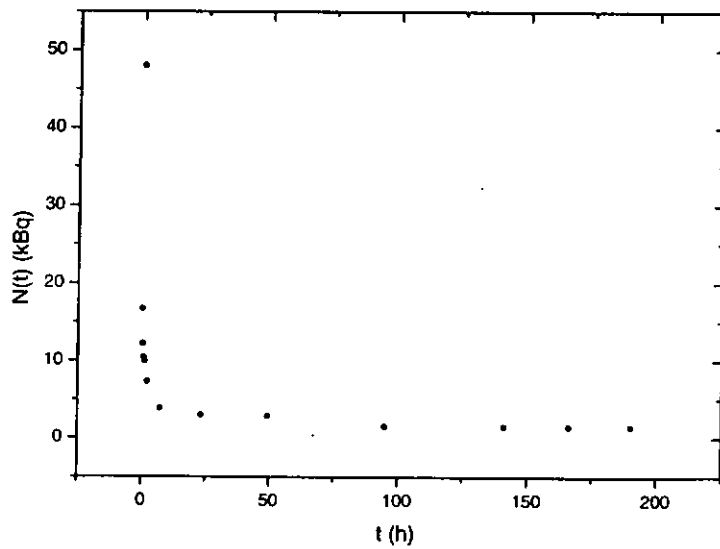


Figure 4.6 Time variations of ^{137}Cs activity in water for soil S2.

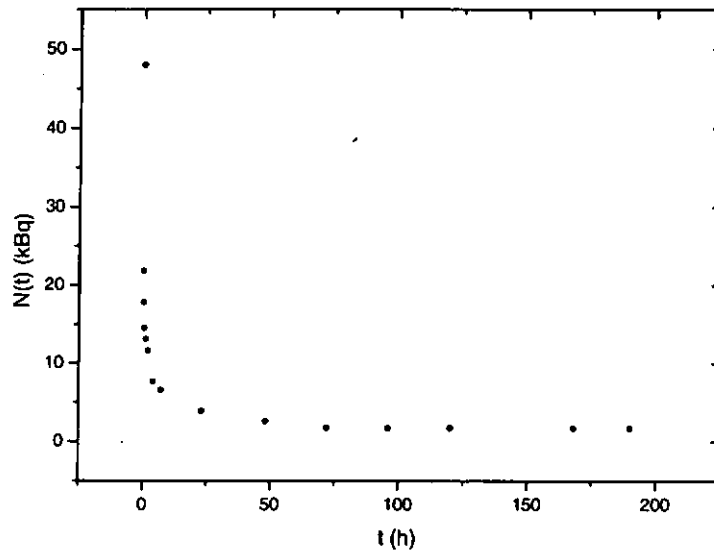


Figure 4.7 Time variations of ^{137}Cs activity in water for soil S3.

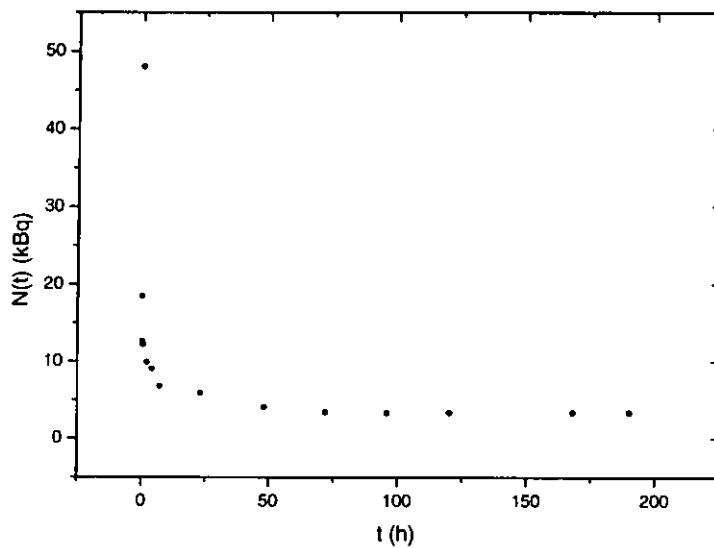


Figure 4.8 Time variations of ^{137}Cs activity in water for soil S4.



Table 4.3 ^{137}Cs activity remaining in water at equilibrium, N_{eq} , and distribution coefficient at equilibrium, K_D , for different soil samples

Soil	N_{eq} (kBq)	K_D (10^3) (l kg^{-1})
R1	0.68	139
R2	0.77	123
R3	1.56	59.5
R4	2.50	36.4
S1	3.28	27.3
S2	1.51	61.6
S3	1.70	54.5
S4	3.35	26.7



and Cremers (1994). In contrast, soil S4 had the smallest value of K_D as it had a small clay content of 4.5 %. Soils S1, with large organic matter and small pH value, had smaller K_D value. This result agreed well with those of Valcke and Cremers (1994) and Strebl et al. (2002).

4.3 Sorption of ^{137}Cs on the FES in Soils

Time variations of the activity of ^{137}Cs in water, $N(t)$, for different masses of soil S2 at initial ^{137}Cs water activity concentrations of $160 \text{ kBq } \ell^{-1}$ and $240 \text{ kBq } \ell^{-1}$ are shown in Figure 4.9 and 4.10, respectively. The rates of decrease in ^{137}Cs water activity were initially very high, higher for larger soil masses, and then slowed down after about 10 h. The larger the mass, the shorter was the time for equilibrium. The equilibrium values were found to decrease with increasing masses.

The ^{137}Cs activity remaining in water at equilibrium, N_{eq} , and the distribution coefficient at equilibrium, K_D , for different masses of soils at initial ^{137}Cs water activity concentrations of $160 \text{ kBq } \ell^{-1}$ and $240 \text{ kBq } \ell^{-1}$ are tabulated in Table 4.4 and 4.5, respectively. The values of N_{eq} were quite different for the same mass at different initial ^{137}Cs water activity concentrations. However, the values of K_D were quite similar for the same mass at different initial ^{137}Cs water

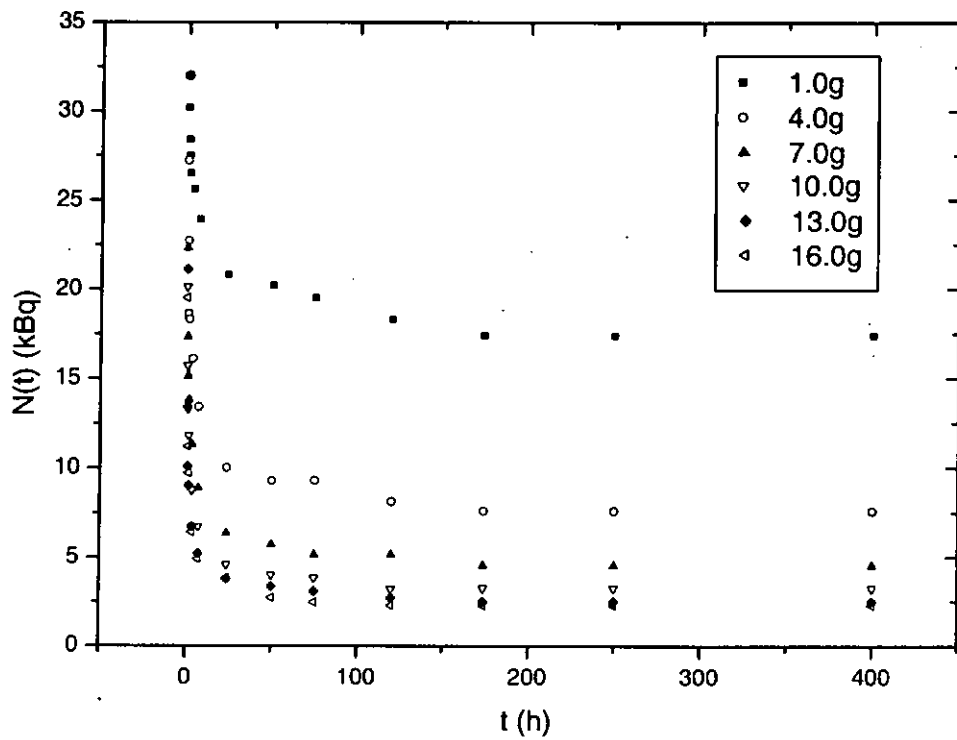


Figure 4.9 Time variations of the ^{137}Cs activity in water for different masses of soils at initial ^{137}Cs water activity concentrations of $160 \text{ kBq } \ell^{-1}$.

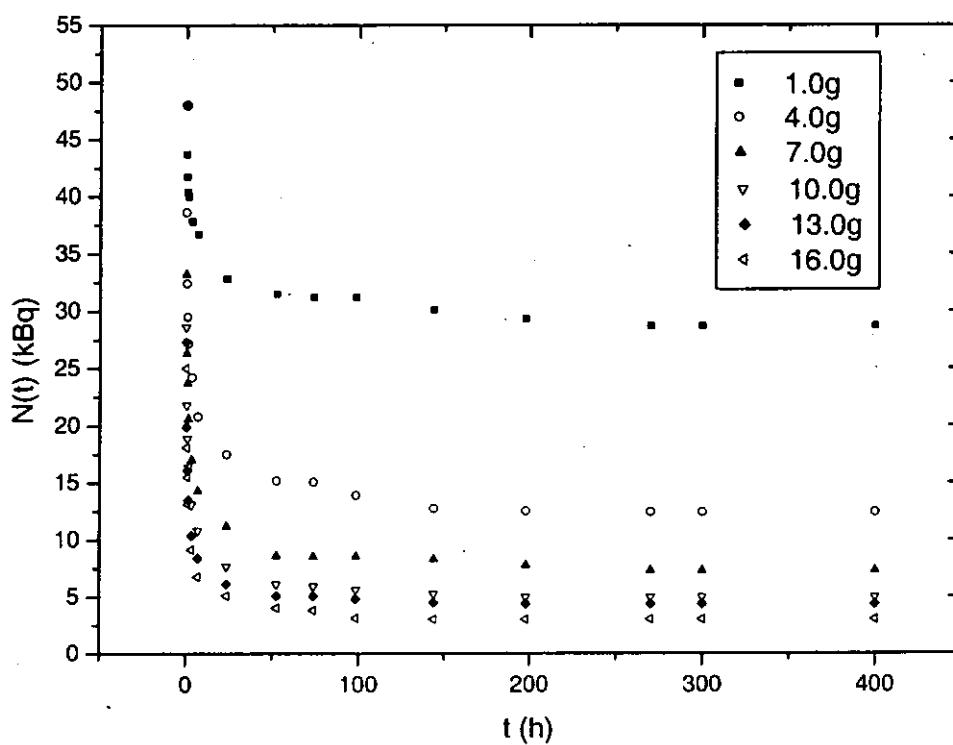


Figure 4.10 Time variations of the ^{137}Cs activity in water for different masses of soils at initial ^{137}Cs water activity concentrations of $240 \text{ kBq } \ell^{-1}$.



Table 4.4 ^{137}Cs activity remaining in water at equilibrium, N_{eq} , and distribution coefficient at equilibrium, K_D , for different masses of soils at initial ^{137}Cs water activity concentration of $160 \text{ kBq } \ell^{-1}$

Mass (g)	N_{eq} (kBq)	K_D ($\ell \text{ kg}^{-1}$)
1.0	17.4	168
4.0	7.59	161
7.0	4.53	173
10.0	3.25	177
13.0	2.50	182
16.0	2.29	162

Table 4.5 ^{137}Cs activity remaining in water at equilibrium, N_{eq} , and distribution coefficient at equilibrium, K_D , for different masses of soils at initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$

Mass (g)	N_{eq} (kBq)	K_D ($\ell \text{ kg}^{-1}$)
1.0	28.7	134
4.0	12.4	144
7.0	7.30	159
10.0	4.95	174
13.0	4.35	154
16.0	3.01	187



activity concentrations. The mean K_D values were $171 \text{ l kg}^{-1} \pm 5\%$ and $159 \text{ l kg}^{-1} \pm 12\%$ for initial ^{137}Cs water activity concentrations of 160 kBq l^{-1} and 240 kBq l^{-1} , respectively. For the same initial ^{137}Cs water activity concentration of 240 kBq l^{-1} , the mean K_D value of 159 l kg^{-1} obtained with the AgTU solution was much smaller than that 61600 l kg^{-1} obtained without the AgTU solution in Section 4.2. This was to be expected because the K_D obtained was for the frayed edge sites (FES) only, with the regular exchange sites (RES) blocked by the complex AgTU. In addition, the sorption rates with AgTU solution were slower than that without the AgTU solution and it took longer time for equilibrium, about 2 to 3 weeks. This was because the sorption of ^{137}Cs in the FES was a relatively slow process (Konoplev et al., 1996) as it needed time for ^{137}Cs to be 'fixed' on the FES in soils.

4.4 Determination of the Capacity of the FES in Soils

The capacity of the FES in soils is usually expressed in milliequivalent (meq) which indicates the number of cations that can be attached in the FES. For cations that are radionuclides such as ^{137}Cs , kBq is used. Taking the half-life of ^{137}Cs as 30 years, 1 kBq is approximately equal to 2.27×10^{-9} meq.

Sorption isotherm for 16.0-g of soil S2 is shown in Figure 4.11. The

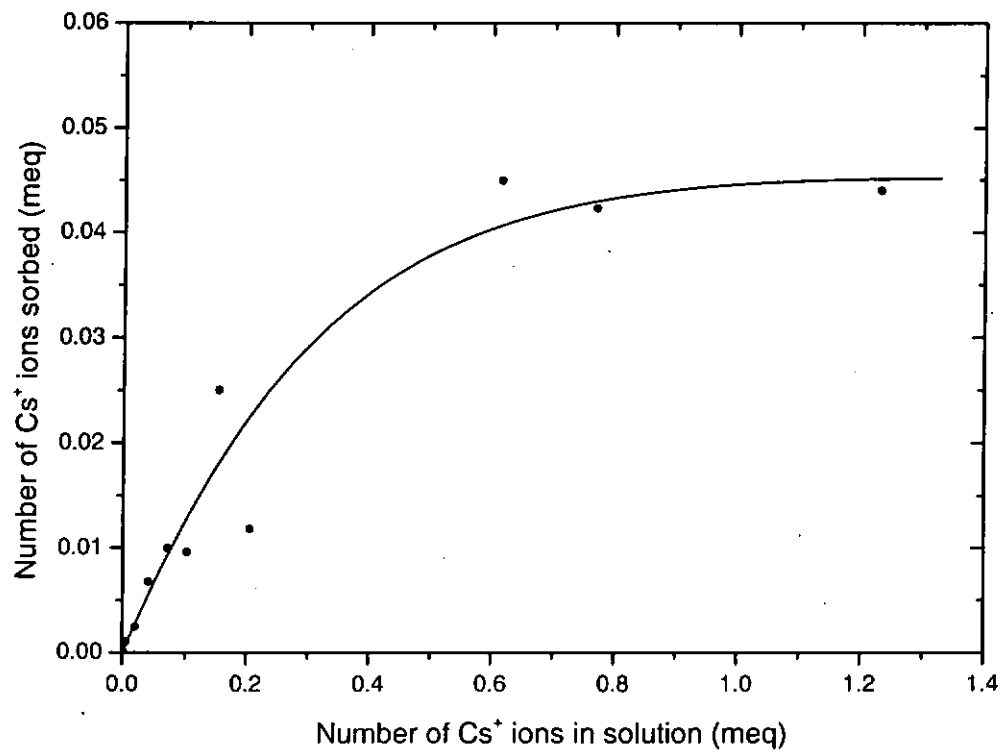


Figure 4.11 Sorption isotherm for 16.0-g of soil S2.



amount of cesium sorbed increased with increasing amounts of cesium, leveling off to a fairly well defined plateau. The capacity of the FES for 16-g soil sample was the plateau value, estimated to be at 0.045 meq (1.98×10^7 kBq), corresponding to 2.8 meq kg⁻¹. From literature, Sweeck et al. (1990) and Kruyts and Delvaux (2002) found that the capacity of the FES for different types of soils ranged from 0.013 to 4.861 meq kg⁻¹. Wauters et al. (1996) also found that the capacity of the FES covered a wide range from 2 to 40 meq kg⁻¹. It could be concluded that the current result agreed well with those in the literature.



CHAPTER 5

MODELLING SORPTION ON ALL SITES USING MODELMAKER

In this chapter, the kinetic behaviour of ^{137}Cs sorption in soils will be described by a simple box model using the simulation software ModelMaker. Rate constants for the different ^{137}Cs sorption processes in soils are estimated and then used for the investigation of ^{137}Cs behaviour in soils. Hopefully, the relative values of the different rate constants can be related to some of the physical and chemical properties of different types of soils.

5.1 ModelMaker

ModelMaker Version 4.0 from Cherwell Scientific Inc. was used in this study. It is an advanced mechanistic modelling program that runs on the Microsoft Windows operating systems. Most researchers admire the ease in which complex mathematical relationships can be developed and solved with ModelMaker, and no programming expertise is required. This reduces the need and time to develop models from scratch and write complex code in a high level



Chapter 5 Modelling Sorption on All Sites using ModelMaker

programming language. However, it can only treat first order differential equations and the program does not recognize poor assumptions or unreliable data input into the system. Nevertheless, ModelMaker is quite a powerful software, especially for models involving only a set of first order differential equations, which can be applied to a wide variety of applications in different aspects, such as chemistry, physics, engineering, biology and even the social sciences (e.g McKellar, 1997; Martin, 1998).

5.2 Simple Box Model

Three types of ^{137}Cs sorbing sites in soils were identified by Evans et al. (1983) and are shown in Figure 2.2. The first type involved the surface and planer sites (i.e. RES) from which ^{137}Cs were generally exchangeable. The second was the wedge sites (i.e. WES) from which ^{137}Cs exchange was limited and the sorption was slower than that on the RES. The third were the interlayer sites (i.e. FES) from which ^{137}Cs was not readily exchangeable and could be regard as fixed.

Børretzen and Salbu (2002) developed simple box models for modelling of ^{134}Cs tracer in a sediment-seawater system in different arrangements of boxes. A parallel four-box model, shown in Figure 5.1, provided the best overall fit and

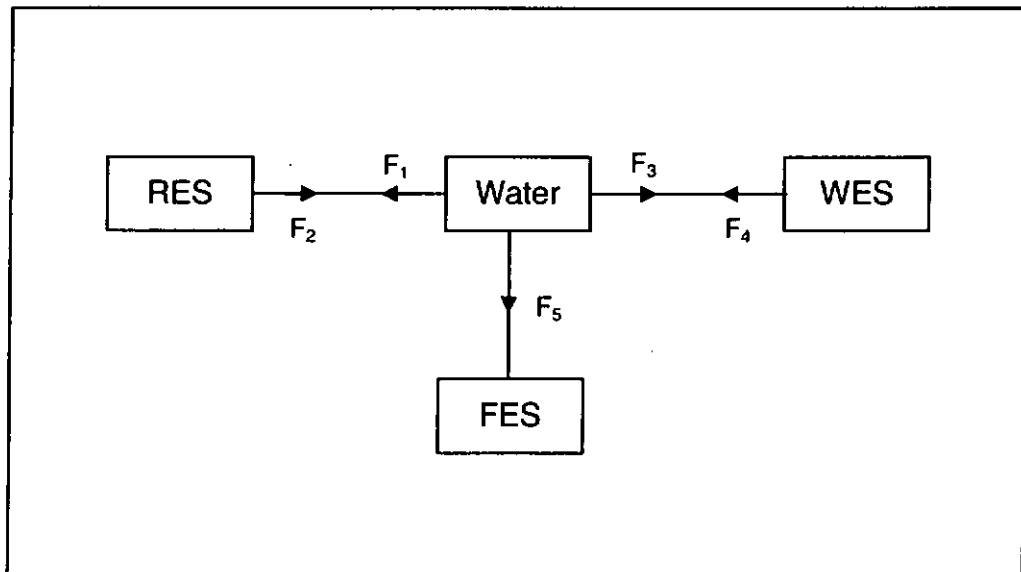


Figure 5.1 Simple box model for ^{137}Cs sorption on all sorbing sites in soils.



Chapter 5 Modelling Sorption on All Sites using ModelMaker

this was adopted to study the kinetic behaviour of ^{137}Cs sorption in all sorbing sites of soils. In Figure 5.1, the four compartmental boxes represent the ^{137}Cs rate of change of ^{137}Cs activity in water, the RES, the WES and the FES; and the arrows labeled from F_1 to F_5 represent the flow of ^{137}Cs into or out of the corresponding compartmental box, with the rate constants identified as from k_1 to k_5 , respectively. The set of differential equations which describes the rate of change of ^{137}Cs activity in each of the compartments is given by

$$\frac{dN_w}{dt} = -F_1 + F_2 - F_3 + F_4 - F_5, \quad (5.1)$$

$$\frac{dN_{RES}}{dt} = F_1 - F_2, \quad (5.2)$$

$$\frac{dN_{WES}}{dt} = F_3 - F_4, \quad (5.3)$$

$$\frac{dN_{FES}}{dt} = F_5, \quad (5.4)$$

where N_w , N_{RES} , N_{WES} and N_{FES} are the activities of ^{137}Cs , in kBq, in water, the RES, the WES and the FES, respectively; and F_1 to F_5 are the flow of ^{137}Cs , in kBq h^{-1} .

The flows of ^{137}Cs , F_1 to F_5 , are expressed as

$$F_1 = k_1 N_w, \quad (5.5)$$



Chapter 5 Modelling Sorption on All Sites using ModelMaker

$$F_2 = k_2 N_{RES}, \quad (5.6)$$

$$F_3 = k_3 N_W, \quad (5.7)$$

$$F_4 = k_4 N_{WES}, \quad (5.8)$$

$$F_5 = k_5 N_W \quad (5.9)$$

where k_1 to k_5 are rate constants in h^{-1} .

To model the kinetics of ^{137}Cs sorption in the water-soil system, the time variations of ^{137}Cs activity in water for 1.0-g of different soil samples at ^{137}Cs initial water activity concentration of $240 \text{ kBq } \ell^{-1}$ (shown in Figure 4.1 to 4.8) were used as experimental data. Once the model was developed and configured in ModelMaker and the initial values for the rate constants and the initial activities of Cs^{137} in each compartment were inputted, the apparent rate constants were estimated by fitting Eqs. (5.1) to (5.4) to the experimental data using the Marquardt optimizing method in ModelMaker. This method was used to minimize the sum of squared deviation between experimental data and model calculations until a best fit was obtained. After the process of optimization, Eqs. (5.1) to (5.4) were updated with the fitted parameters (i.e. k_1 to k_5). The differential equations were then solved numerically by the Runge-Kutta method in ModelMaker to obtain the fitted curves for the model.



5.3 Results and Discussion

Fitted curves for 1.0-g of different soil samples are shown from Figure 5.2 to 5.9. Points are experimental data and the solid lines are fitted curves of the simple box model. Table 5.1 shows the fitted rate constants k_1 to k_5 with the associated R^2 for different soil samples. The R^2 is defined as the ratio of model weighted sum of squares to total weighted sum of squares. The fitting was very good as the least square values R^2 for all soil samples were 0.99. The model was also able to fit the sharp initial decrease of ^{137}Cs in water. For the rate constants of all soil samples, the mean value of k_1 , k_2 , k_3 , k_4 and k_5 were 23.0 h^{-1} , 10.4 h^{-1} , 1.26 h^{-1} , 0.19 h^{-1} and 0.08 h^{-1} , respectively. The mean values of rate constants decreased from k_1 to k_5 , meaning that the sorption process on the FES was the slowest, that on the WES was faster and that on the RES was the fastest. It was to be expected because the sorption on the RES was a simple ion-exchange process and was a fast reaction. In contrast, the sorption on the FES was a slow reaction in which the layers of the FES had to collapse to fix Cs^+ ions in the interlayer positions (Sawheny, 1972). The decrease of rate constants (from k_1 to k_5) could also mean that Cs^+ ions were being reversibly bound on the surfaces initially and then on the edges, released from the edges and then fixed to the interlayers (Børretzen and Salbu, 2002).

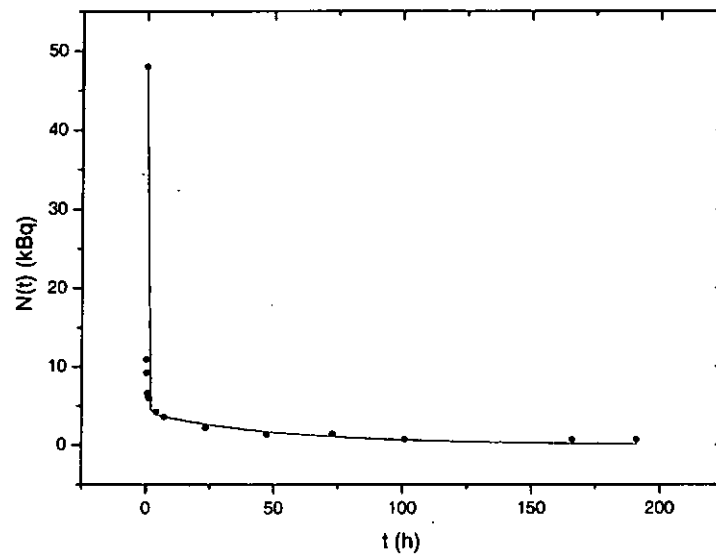


Figure 5.2 Fitted curve of the simple box model for soil R1.

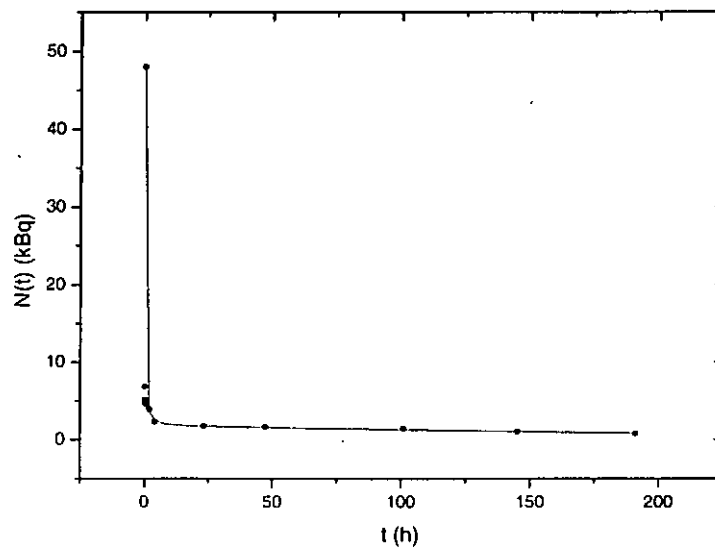


Figure 5.3 Fitted curve of the simple box model for soil R2.



Chapter 5 Modelling Sorption on All Sites using ModelMaker

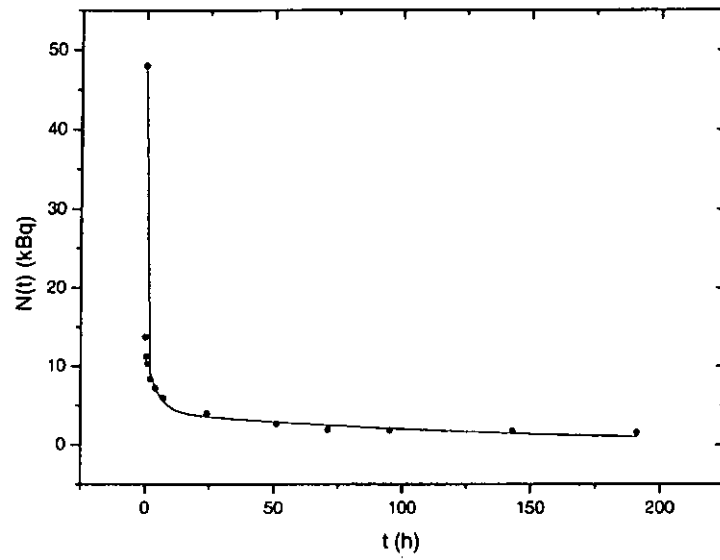


Figure 5.4 Fitted curve of the simple box model for soil R3.

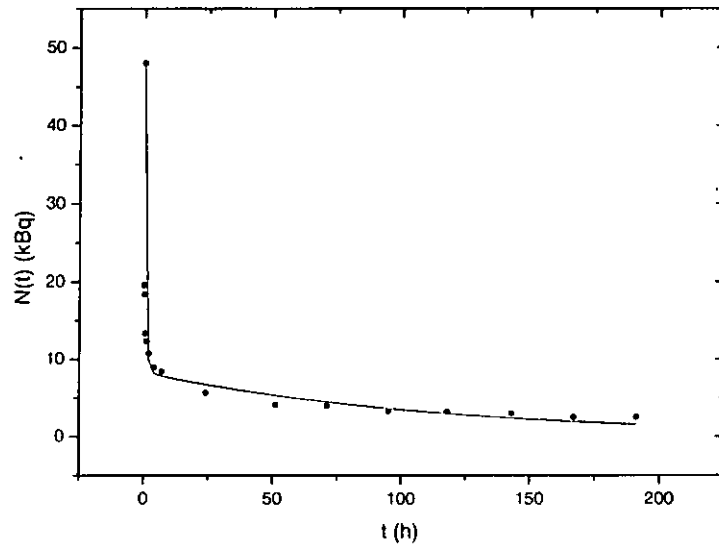


Figure 5.5 Fitted curve of the simple box model for soil R4.

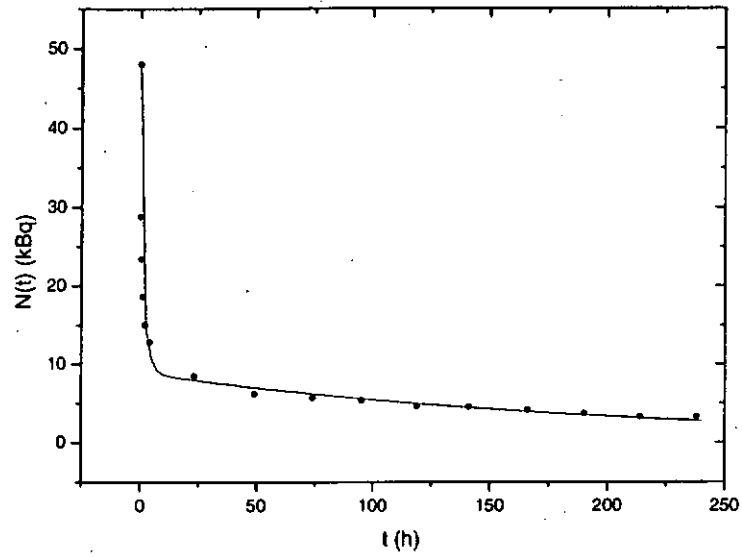


Figure 5.6 Fitted curve of the simple box model for soil S1.

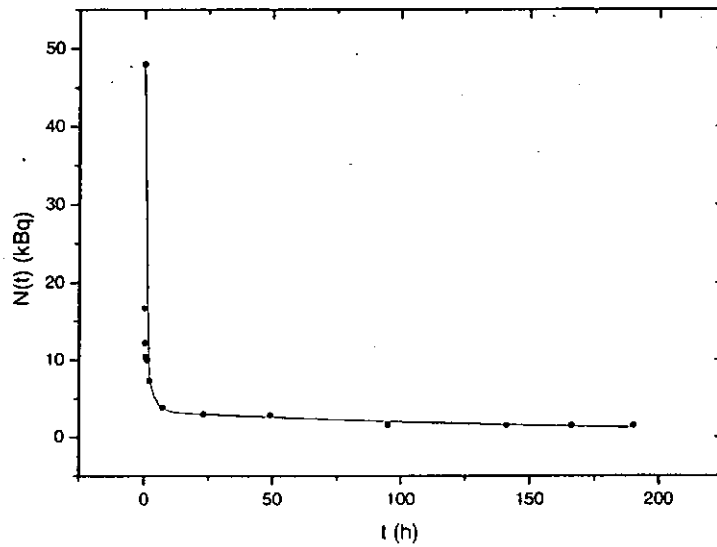


Figure 5.7 Fitted curve of the simple box model for soil S2.

Chapter 5 Modelling Sorption on All Sites using ModelMaker

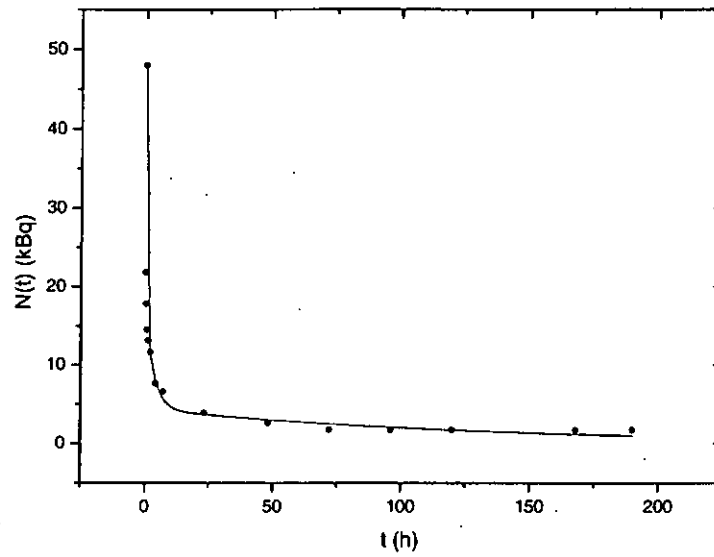


Figure 5.8 Fitted curve of the simple box model for soil S3.

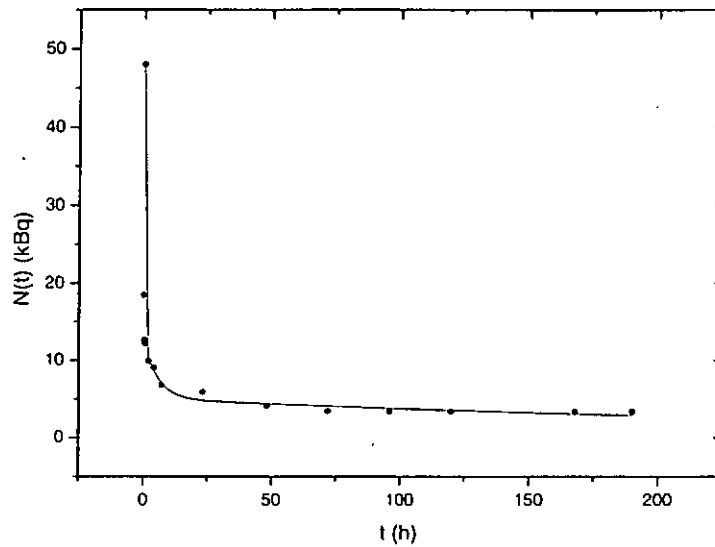


Figure 5.9 Fitted curve of the simple box model for soil S4.



Table 5.1 Fitted rate constants and R^2 for the simple box model for different soil samples

Soil	k_1 (h^{-1})	k_2 (h^{-1})	k_3 (h^{-1})	k_4 (h^{-1})	k_5 (h^{-1})	R^2
R1	35.2 ± 4.08	12.2 ± 1.30	3.59 ± 0.24	0.50 ± 0.04	0.21 ± 0.07	0.99
R2	34.7 ± 5.18	4.94 ± 1.27	2.12 ± 1.10	0.14 ± 0.02	0.10 ± 0.03	0.99
R3	26.7 ± 2.80	9.10 ± 1.31	0.52 ± 0.08	0.08 ± 0.02	0.08 ± 0.01	0.99
R4	27.3 ± 2.41	20.5 ± 2.02	1.32 ± 0.04	0.40 ± 0.01	0.05 ± 0.006	0.99
S1	10.9 ± 2.16	14.3 ± 4.10	0.52 ± 0.07	0.15 ± 0.04	0.03 ± 0.003	0.99
S2	18.5 ± 0.87	7.38 ± 0.56	1.04 ± 0.11	0.11 ± 0.02	0.07 ± 0.01	0.99
S3	14.3 ± 1.38	8.66 ± 1.15	0.55 ± 0.03	0.08 ± 0.03	0.08 ± 0.01	0.99
S4	16.0 ± 0.93	6.07 ± 0.55	0.40 ± 0.07	0.07 ± 0.01	0.03 ± 0.01	0.99

Amongst rate constants of different soil samples, soil R1 had the largest k_1 , k_3 and k_5 which were the rate constants of forward sorptions on the three sorbing sites. One of the reasons might be that soil R1 had the largest clay content. Sheber and Eriksson (1993) and Konoplev et al. (2002) claimed that ^{137}Cs had a strong affinity for clay, especially the frayed edge sites on clay minerals in soils (Cremers et al., 1988). In contrast, soil S1 had small k_3 and the smallest k_1 and k_5 . Since soil S1 had low pH value and the highest soluble K^+ ions, K^+ and H^+ ions competed with Cs^+ ions in the water-soil system. Soil S4



Chapter 5 Modelling Sorption on All Sites using ModelMaker

also had the smallest k_5 as it had the smallest clay content. Many researchers (e.g. Valcke and Cremers, 1994; Rigol et al., 2002) found that soils with high organic matter contents made ^{137}Cs sorption more reversible. For the rate constants of backward sorptions (i.e. k_2 and k_4), it was therefore expected that the rate constants should be proportional to the organic matter content. However, the results were not obvious as the range of organic matter contents of the soil samples tested were too narrow.

The model not only gave the rate constants of the water-sediment system, but also shed some light on the kinetics of the sorption as the ModelMaker was able to calculate the activity of ^{137}Cs on each of the sorbing sites as a function of time. Figure 5.10 shows the modelled curves of the simple box model for soil S2, where points and soil line are the experimental data and the fitted curve, respectively. The modelled curves are the time variations of ^{137}Cs on the RES, the WES and the FES. ^{137}Cs sorbed on the FES increased with time as the sorption was irreversible. In contrast, sorption of ^{137}Cs on the RES and the WES increased for a period of time, and then decreased with time. The reason might be that the Cs^+ ions desorbed from the RES were sorbed by the WES and the FES. Similarly, the Cs^+ ions desorbed from the WES were sorbed by the FES. The results agreed well with those of Oughton et al., 1997 and Børretzen and Salbu, 2002.

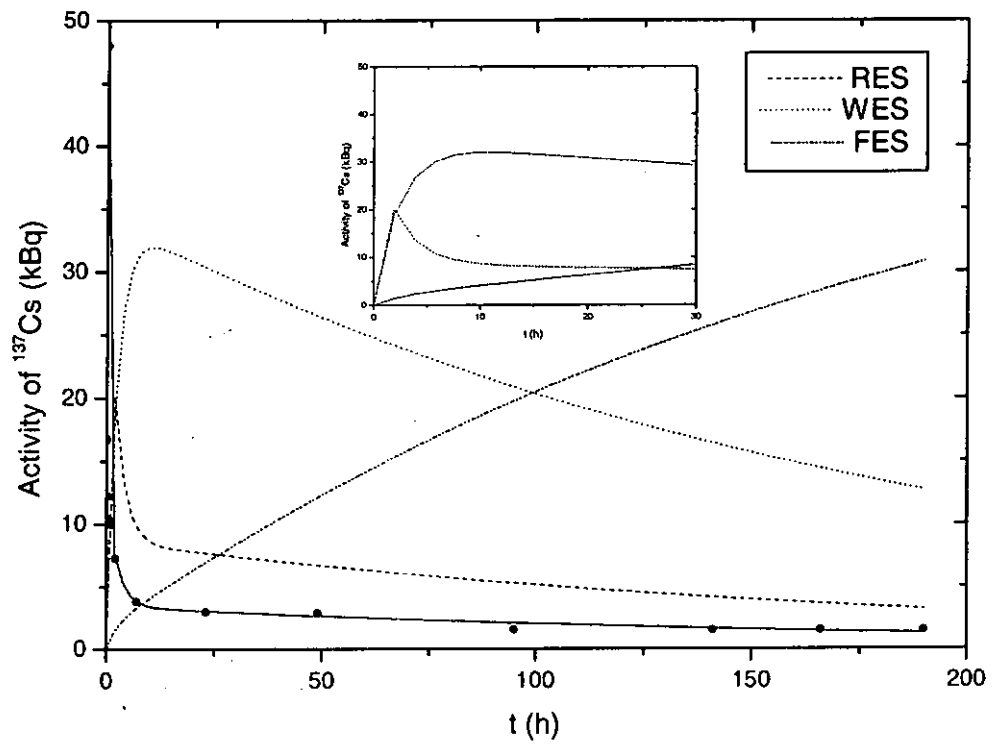


Figure 5.10 Modelled curves of the simple box model for Soil S2. Insert shows respective curves at early stage.



5.4 Conclusion

A simple box model was used to describe the sorption kinetics and the behaviour of ^{137}Cs in soils using the simulation software ModelMaker. The model was quite successful to describe ^{137}Cs sorbed by three types of sites in soils because very good fitting could be obtained for all soil samples. The rate constants for the different ^{137}Cs sorption processes were estimated and were able to reflect the ^{137}Cs sorption mechanism in soils. Soils with larger clay content sorbed ^{137}Cs more readily. It was also found that K^+ and H^+ ions competed strongly with Cs^+ ions in the sorption. In general, considering the simplicity of the model, the rate constant values obtained agreed well with the physical and chemical properties of different types of soils. The model can thus be used as an initial indicator for the retention/exchange processes of ^{137}Cs in soils.



CHAPTER 6

MODELLING SORPTION ON FES USING A CONCEPTUAL MODEL

As the sorption behavior of ^{137}Cs on the frayed edge sites (FES) with finite capacity in soils can be simply treated as an irreversible process, a conceptual model (see Figure 6.1) consisting of an irreversible exchange between two compartments is proposed in this chapter. A parameter called proportionality constant k for a particular type of soils is to be deduced and a mathematical relation between the capacity of the FES and the mass of soil is postulated and verified.

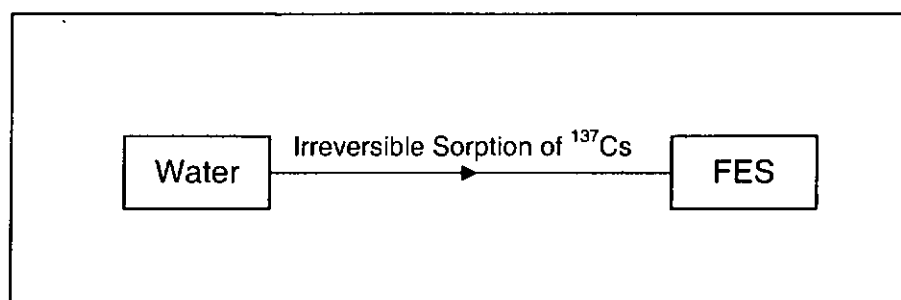


Figure 6.1 Two-compartment conceptual model for ^{137}Cs sorption on the FES in soils.



6.1 Theory

The theory is based on the assumption that the ion-exchange sites (e.g. RES and WES) have been masked by AgTU and no ion-exchange term has to be included in the model. The sorption therefore simply describes the one-way sorption on the FES. The first compartment represents the aqueous phase, while the second compartment represents the FES in soils with finite capacity F . The sorption rate on the FES is assumed to be jointly proportional to the fractional ^{137}Cs water activity concentration, the difference between the ^{137}Cs water activity concentrations in aqueous phase and on the FES, and the number of unoccupied sites (i.e. the difference between the capacity of the FES and the number of sites occupied by ^{137}Cs). The sorption rate on the FES is thus expressed according to the following equation:

$$\frac{dn(t)}{dt} = k \left[\frac{C_w(t)}{C_0} \right]^p \left[C_w(t) - \gamma \frac{n(t)}{m} \right]^q [F - n(t)]^u \quad (6.1)$$

where $n(t)$ = activity of ^{137}Cs in kBq sorbed on the FES in soils at time t in h

k = proportionality constant (>0)

$C_w(t) = N(t)/V = ^{137}\text{Cs}$ water activity concentration in kBq $^{-1}$

$N(t)$ = activity of ^{137}Cs in kBq remaining in aqueous phase at time t



Chapter 6 Modelling Sorption on FES using a Conceptual Model

V = volume in ℓ of aqueous solution

C_0 = initial water activity concentration of ^{137}Cs in kBq^{-1}

m = mass in kg of soil sample in aqueous solution

γ = proportionality constant (>0)

F = capacity of the FES in soils in kBq of mass m

p, q and u are exponents

The first bracket in Eq. (6.1) is referred to as the ‘pressure’ factor representing the number of ^{137}Cs ions per unit volume ‘bombarding’ the soil particles, larger value results in a faster sorption. Normalization with respect to initial ^{137}Cs water activity concentration, C_0 , hopefully leads to a constant k which is independent of initial ^{137}Cs water activity concentration. The use of two different initial ^{137}Cs water activity concentrations in experiments is to check the constancy of k . The second bracket is referred to as the ‘diffusion’ factor which signifies that no sorption occurs when the difference between the ^{137}Cs water activity concentrations in aqueous phase and that in the FES (the latter related to the former by constant γ) is zero. The third bracket is more obvious as sorption will stop when all sites are occupied and there are no more sites available. The exponents p, q and u reflect the degree of contribution of the respective factors in sorption rate to the best fit of theory with experimental data.



Chapter 6 Modelling Sorption on FES using a Conceptual Model

If physical loss, such as sorption of ^{137}Cs to the container and mass loss of water or sediments, are assumed to be negligible, then

$$N_0 = N(t) + n(t) \quad (6.2)$$

where N_0 is the initial activity of ^{137}Cs in kBq in aqueous solution.

Using Eq. (6.2), Eq. (6.1) becomes

$$\frac{dN(t)}{dt} = -k \left[\frac{C_w(t)}{C_0} \right]^p \left[C_w(t) - \gamma \frac{N_0 - N(t)}{m} \right]^q [F - N_0 + N(t)]^u \quad (6.3)$$

At equilibrium (i.e. $t = t_{eq}$) when there is no more decrease in ^{137}Cs water activity concentration, the left-hand-side of Eq. (6.3) is zero. There are two cases for this situation:

$$\text{Case 1: } [F - N_0 + N(t_{eq})] = 0 \quad (6.4)$$

This is the case when all the available FES are filled and there is no more sorption. It will occur when there is enough cesium activity in the aqueous phase.



$$\text{Case 2: } \left[C_w(t_{eq}) - \gamma \frac{N_0 - N(t_{eq})}{m} \right] = 0 \quad (6.5)$$

This is the case when the ^{137}Cs water activity concentrations in aqueous phase and that in the FES are equal. Since $C_w(t_{eq}) = N(t_{eq})/V$, the condition for equilibrium is

$$\frac{N_{eq}}{V} = \gamma \frac{N_0 - N_{eq}}{m} \quad (6.6)$$

where $N_{eq} \equiv N(t_{eq})$.

Rearranging Eq. (6.6),

$$\gamma = \frac{N_{eq}/V}{(N_0 - N_{eq})/m} = \frac{1}{K_D} \quad (6.7)$$

where K_D = the distribution coefficient at equilibrium.

Since the number of ^{137}Cs ions (of the order of 10^{-7} meq ℓ^{-1}) in aqueous phase used in the experiments were much smaller than the FES capacity of the order of 3 meq kg^{-1} (found in Section 4.4). The condition for 'case 1' for



Chapter 6 Modelling Sorption on FES using a Conceptual Model

equilibrium to occur thus would not happen. 'Case 2' becomes the possible condition for equilibrium in this experiment. Due to the extremely small amount of ^{137}Cs used, assumption can be made that $F \gg n(t)$ in the model and Eq. (6.3) can be simplified as

$$\frac{dN(t)}{dt} = -kF^u \left[\frac{C_w(t)}{C_0} \right]^p \left[C_w(t) - \frac{1}{K_D} \frac{V}{m} [C_0 - C_w(t)] \right]^q \quad (6.8)$$

where $C_w(t) = N(t)/V$ and $C_0 = N_0/V$

Time variations of the ^{137}Cs activity in water, $N(t)$, for different masses, m , (from 0.001 to 0.016 kg) of soil S2 at two ^{137}Cs initial water activity concentration, C_0 , of 160 kBq ℓ^{-1} and 240 kBq ℓ^{-1} (shown in Figure 4.9 and 4.10) were used as experimental data. In Eq. (6.8), m , V , N_0 , and K_D were known constants in which the value of K_D could be calculated from experimental data. It is expected that k is a constant for the particular type of soil samples, and F to be a constant for a given mass m . For the 16.0-g soil sample, the value of F was obtained and the only unknowns in Eq. (6.8) were thus k , u , p and q . The way to find the unknowns was to vary k , u , p and q until a best fit was obtained between the theory and experimental data. This operation was performed using the Marquardt optimizing method in ModelMaker and Eq. (6.8) was solved using the



mid-point integration method in ModelMaker. Once the value of k was obtained, this value was assumed to be constant for all masses. Fitting was then performed to find the unknown values of F for other masses.

6.2 Results and Discussion

Using the FES capacity, F , of 0.016-kg soil sample (1.98×10^7 kBq) described in Section 4.4, the values of k were then estimated for different combination of exponents u , p and q using ModelMaker by fitting between Eq. (6.8) and the experimental data of 0.016-kg soil sample. Fitted curves for 0.016-kg soil sample at C_0 of $160 \text{ kBq } \ell^{-1}$ and $240 \text{ kBq } \ell^{-1}$ are shown in Figure 6.2 and 6.3, respectively. The best fit was obtained for $u = 1$, $p = 1$ and $q = 2$ in which the least square values R^2 reached 0.98, indicating that the 'diffusion' factor in Eq. (6.1) contributed the most to the sorption of ^{137}Cs on soils. The values of k obtained for C_0 of $160 \text{ kBq } \ell^{-1}$ and $240 \text{ kBq } \ell^{-1}$ were $4.09 \times 10^{-10} \ell^2 \text{ kBq}^{-2} \text{ h}^{-1}$ and $4.25 \times 10^{-10} \ell^2 \text{ kBq}^{-2} \text{ h}^{-1}$, respectively. The average value of k was $4.17 \times 10^{-10} \ell^2 \text{ kBq}^{-2} \text{ h}^{-1}$ and its percent difference was about 4 %, verifying the constancy of k .

Since k was assumed to be a constant for a particular soil, the average value of k ($4.17 \times 10^{-10} \ell^2 \text{ kBq}^{-2} \text{ h}^{-1}$) was used in Eq. (6.8) to fit the experimental

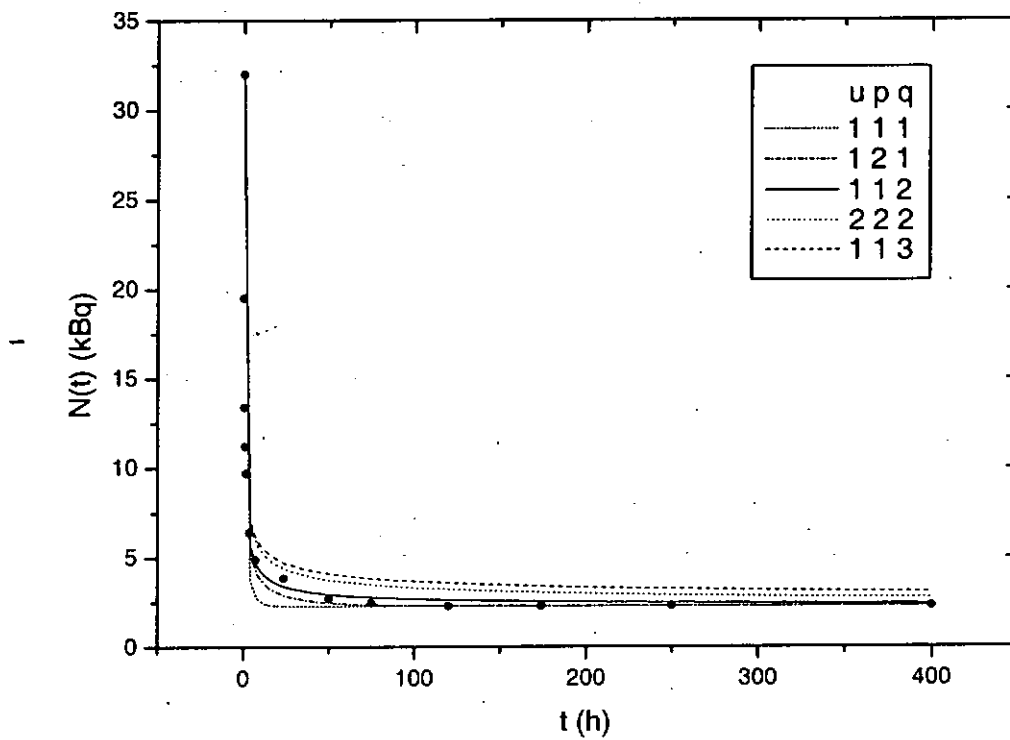


Figure 6.2 Fitted curves of the two-compartment conceptual model with different combination of exponents u , p and q for 16-g soil sample at initial ^{137}Cs water activity concentration of $160 \text{ kBq } \ell^{-1}$.

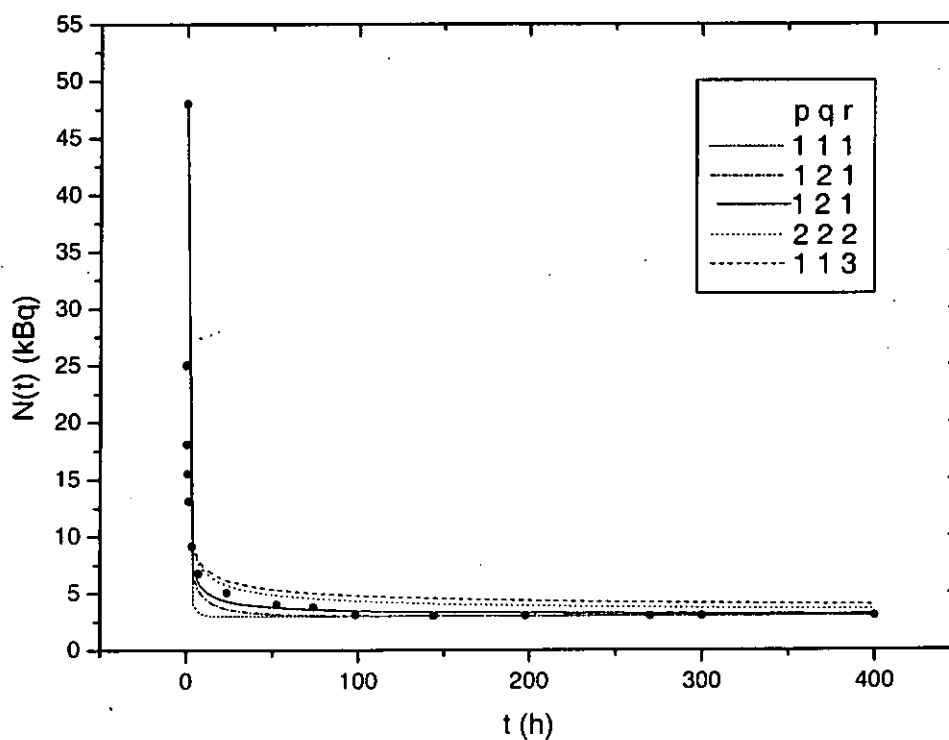


Figure 6.3 Fitted curves of the two-compartment conceptual model with different combination of exponents u , p and q for 16-g soil sample at initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$.



Chapter 6 Modelling Sorption on FES using a Conceptual Model

fitting, F was the fitting parameter. Results of the fitted curves for C_0 of 160 kBq ℓ^{-1} and 240 kBq ℓ^{-1} are shown in Figure 6.4 and 6.5, respectively. Fitted values of F and R^2 for the two different initial water activity concentrations are tabulated in Table 6.1. The fitting was quite good as the least square values R^2 were quite high, ranging from 0.92 to 0.99. The two-compartment conceptual model was thus quite successful in describing the sorption behaviour of ^{137}Cs on soils of different masses at different initial ^{137}Cs water activity concentrations.

It was to be noted that F increased with mass. It was reasonable as F was the number of available frayed edge sites for a given mass. Thus, postulation was made that F was related to mass m of soils according to

$$F = \alpha m^\beta \quad (6.10)$$

where α and β are constants.

If we plot $\log F$ against $\log m$, a straight line should result with the intercept equals to $\log \alpha$ and the slope equals to β . Figure 6.6 shows the plot of $\log F$ against $\log m$ for all data of the two initial ^{137}Cs water activity concentrations. A straight line ($R^2 = 0.99$) resulted with a slope of 1.47 and an intercept of 10.0. Eq. (6.10) was thus a good assumption and independent of

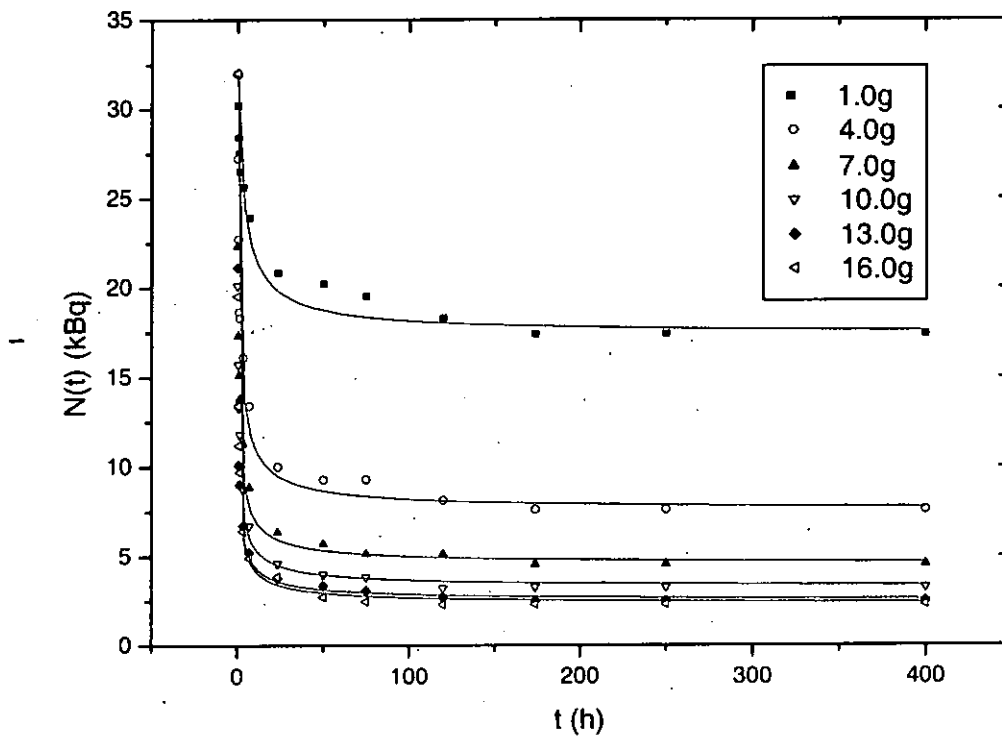


Figure 6.4 Fitted curves of the two-compartment conceptual model with $u=1$, $p=1$ and $q=2$ for different masses of soil sample for initial ^{137}Cs water activity concentration of $160 \text{ kBq } \ell^{-1}$.

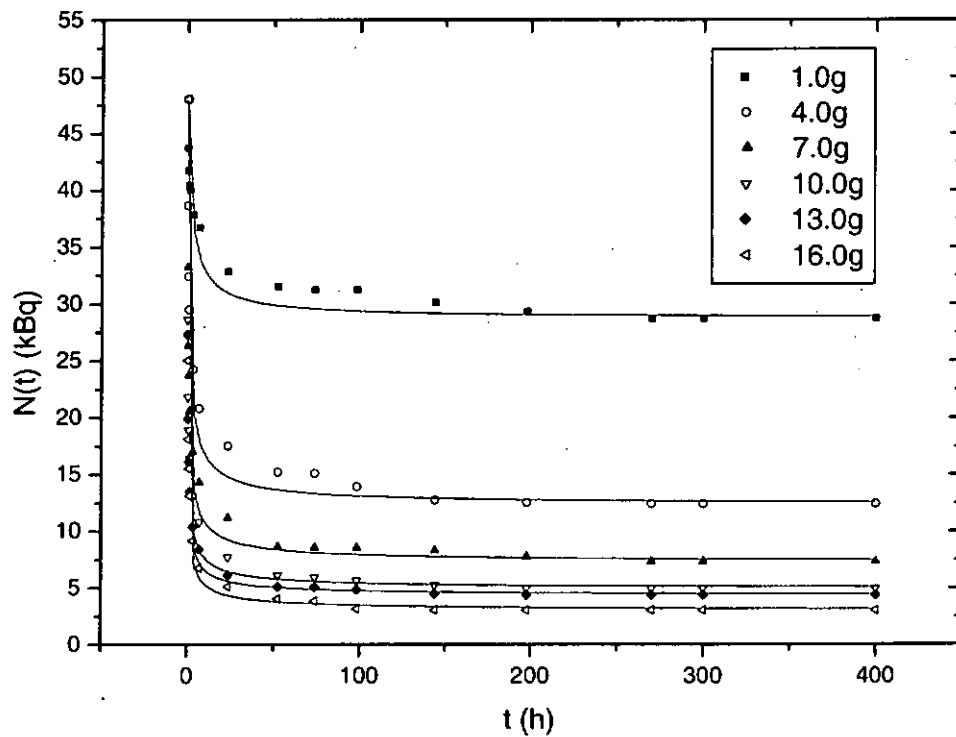


Figure 6.5 Fitting curves of the two-compartment conceptual model with $u=1$, $p=1$ and $q=2$ for different masses of soil sample at initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$.



Table 6.1 Fitted values of F and R^2 for the two-compartment conceptual model at the two different initial ^{137}Cs water activity concentrations

C_0 (kBq l ⁻¹)	m (kg)	F (kBq)	R^2
160	0.001	$4.12 \times 10^5 \pm 6.7 \times 10^4$	0.96
	0.004	$2.97 \times 10^6 \pm 3.3 \times 10^5$	0.98
	0.007	$8.08 \times 10^6 \pm 1.2 \times 10^6$	0.97
	0.010	$1.28 \times 10^7 \pm 2.1 \times 10^6$	0.97
	0.013	$1.88 \times 10^7 \pm 1.2 \times 10^6$	0.99
	0.016	1.98×10^7	0.98
240	0.001	$3.72 \times 10^5 \pm 7.9 \times 10^4$	0.92
	0.004	$2.26 \times 10^6 \pm 3.5 \times 10^5$	0.96
	0.007	$5.64 \times 10^6 \pm 8.8 \times 10^5$	0.96
	0.010	$1.16 \times 10^7 \pm 1.9 \times 10^6$	0.97
	0.013	$1.69 \times 10^7 \pm 2.0 \times 10^6$	0.98
	0.016	1.98×10^7	0.98

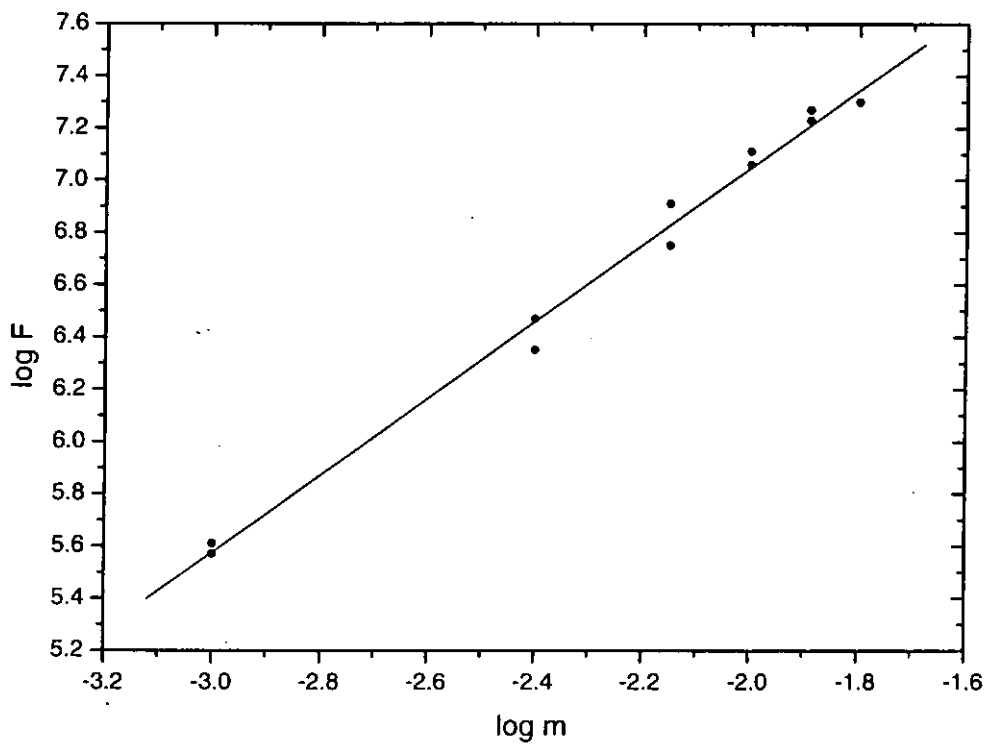


Figure 6.6 Plot of $\log F$ against $\log m$.



Chapter 6 Modelling Sorption on FES using a Conceptual Model

data of different masses using the combination of $u = 1$, $p = 1$ and $q = 2$. In this initial ^{137}Cs water activity concentration. Eq. (6.10) can be formulated approximately as

$$F = 10^{10} m^{1.47} \quad (6.11)$$

where m is in kg, and F is in kBq. Alternatively,

$$F \approx 22.7 m^{1.47} \quad (6.12)$$

where m is in kg, and F is in meq.

To check the validity of Eq. (6.11) or (6.12), the value of F for 13.0-g soil S2 was also measured using the method outlined in Section 3.7.3. The result is shown in Figure 6.7. The experimental value of F of 13.0-g soil sample was obtained from the value of plateau at about 1.4×10^7 kBq (0.032 meq). Using Eqs. (6.11) and (6.12) for $m=0.013$ kg, the value of F should be 1.7×10^7 kBq (0.038 meq). The percentage difference was around 16 % which could be considered as acceptable since the uncertainty associated with smaller mass was relatively large, as explained in Section 3.7.3.

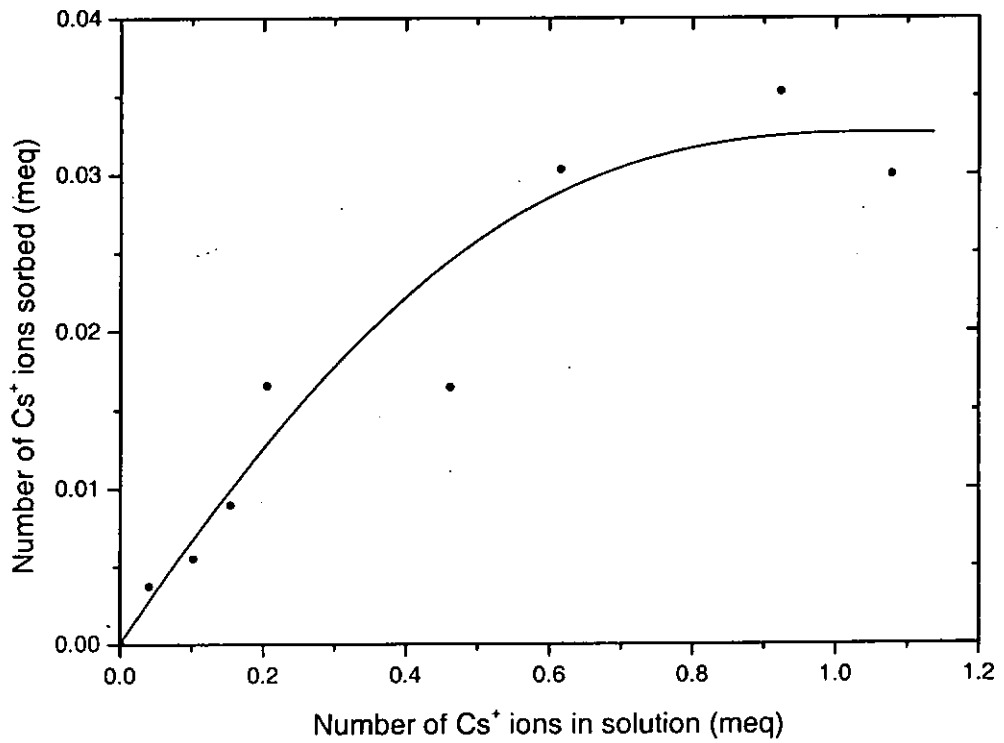


Figure 6.7 Sorption isotherm for 13.0-g of soil S2.



6.3 Conclusion

A simple two-compartment model was used to describe the sorption behaviour of ^{137}Cs on frayed edge sites (FES) of finite capacity in soils for different masses of soils at different initial ^{137}Cs water activity concentrations. The sorption rate was assumed to depend on the fractional ^{137}Cs water activity concentration, the difference between the ^{137}Cs water activity concentration in aqueous phase and that in particulate phase, and the number of available sorption sites. By varying the exponents of the different factors, very good fitting was obtained between the experimental data and the theory. Moreover, the proportionality constant k was found to an accuracy of $\pm 4\%$ for the two initial water activity concentrations with the mean k of $4.17 \times 10^{-10} \ell^2 \text{ kBq}^{-2} \text{ h}^{-1}$. In general, the results were satisfactory for such a simple model.



CHAPTER 7

MODELLING SORPTION ON FES USING MODELMAKER

In Chapter 6, a two-compartment conceptual model was proposed to describe the sorption of ^{137}Cs on the FES in soils. The model was able to give a good fitting to experimental data. A constant parameter, the proportionality constant k , could also be estimated for a particular type of soils. However, it does not have any physical meaning (in units of $\ell^2 \text{ kBq}^{-2} \text{ h}^{-1}$) for the explanation of the sorption process. The model in Chapter 6 involved only two compartments and might be insufficient for the investigation of the sorption mechanism. This chapter aims at developing a modified model using the simulation software ModelMaker to give a better picture for the sorption of ^{137}Cs on the FES in soils. Rate constants for the ^{137}Cs sorption processes on the FES in soils can also be estimated.

7.1 Modified Model

From literature, Absalom et al. (1996) proposed a four-compartment



Chapter 7 Modelling Sorption on FES using ModelMaker

model for ^{137}Cs fixation in soils, as shown in Figure 7.1. The FES was assumed to be consisting of into three regions for the sorption of ^{137}Cs . The three regions were called the expanded interlayer, the wedge zone and the collapsed micaceous core. The collapsed micaceous core was supposed to fix the Cs^+ ions permanently. However, k_4 was found to be non-zero, inconsistent with the original proposition.

Based on the four-compartment model of Absalom et al. (1996), a modified model was proposed using the ModelMaker, as shown in Figure 7.2. The model was an extension of the two-compartment conceptual model used in

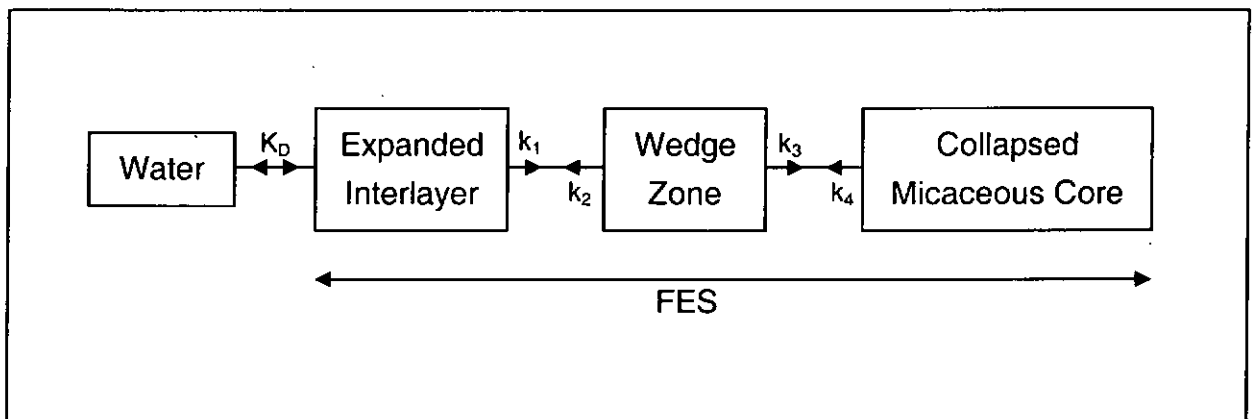


Figure 7.1 Model of Absalom et al. (1996) for the sorption of ^{137}Cs on the FES in soils.



Chapter 6. The first compartment on the left represents the rate of change of ^{137}Cs activity in aqueous phase. The three right compartments represent the rate of change of ^{137}Cs activity at different sub-sites in the FES. FES_1 , FES_2 and FES_3 can be identified as the expanded interlayer, the wedge zone and the collapsed micaceous core, respectively, as in the Absalom's model. The arrows labeled from F_1 to F_5 represent the flows of ^{137}Cs into or out of the corresponding compartmental box in which the rate constants are identified as from k_1 to k_5 . As Wauters et al. (1994) suggested that even ^{137}Cs held strongly at the FES might be considered labile, it was proposed that ^{137}Cs sorption could be reversible from the FES, in contrast to the one-way sorption described in Chapter 6. The ^{137}Cs flows of F_2 and F_4 were added in the modified model to make the sorption of ^{137}Cs in

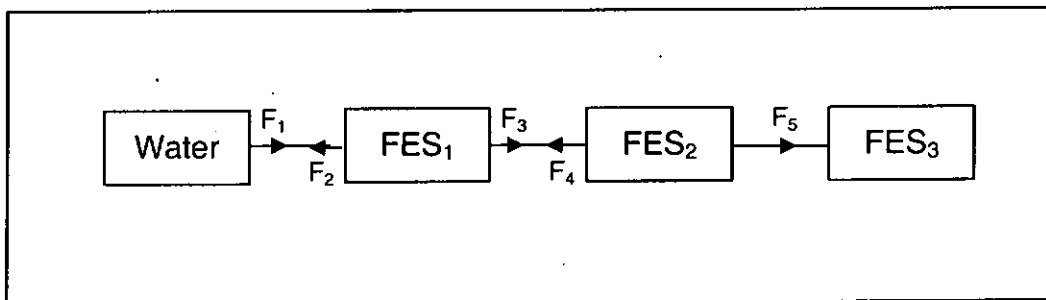


Figure 7.2 Modified four-compartment model for the ^{137}Cs sorption on the FES in soils.



the FES more labile. Nevertheless, ^{137}Cs can eventually be fixed in the FES as indicated by the flow of F_5 , in contrast to the model of Absalom et al. (1996). The set of differential equations which describes the rate of change of ^{137}Cs activity in each of the compartments is given by

$$\frac{dN_w}{dt} = -F_1 + F_2, \quad (7.1)$$

$$\frac{dN_{FES1}}{dt} = F_1 - F_2 - F_3 + F_4, \quad (7.2)$$

$$\frac{dN_{FES2}}{dt} = F_3 - F_4 - F_5, \quad (7.3)$$

$$\frac{dN_{FES3}}{dt} = F_5, \quad (7.4)$$

where t is time in h; N_w , N_{FES1} , N_{FES2} and N_{FES3} are the activities of ^{137}Cs , in kBq, in aqueous phase and the compartments of the FES at time t ; F_1 to F_5 are the flows of ^{137}Cs , in kBq h^{-1} into or out of the corresponding compartmental box.

The flows from F_1 to F_5 are expressed as

$$F_1 = k_1 F \left(\frac{C_w}{C_0} \right) \left(C_w - \frac{1}{K_D} \frac{V}{m} (C_0 - C_w) \right), \quad (7.5)$$

$$F_2 = k_2 N_{FES1}, \quad (7.6)$$



Chapter 7 Modelling Sorption on FES using ModelMaker

$$F_3 = k_3 N_{FES2}, \quad (7.7)$$

$$F_4 = k_4 N_{FES3}, \quad (7.8)$$

$$F_5 = k_5 N_{FES2} \quad (7.9)$$

where F is the capacity of the FES in kBq; V is volume in ℓ of aqueous phase; N_0 is the initial activity of ^{137}Cs , in kBq, in aqueous phase, C_w and C_0 are the ^{137}Cs water activity concentration in kBq^{-1} at time t and initial, respectively; K_D is the distribution coefficient at equilibrium; m is mass in kg of soils in aqueous solution; k_1 is rate constants in $\ell \text{ kBq}^{-1} \text{ h}^{-1}$; k_2 to k_5 are rate constants in h^{-1} .

The definition of F_1 , as indicated by Eq. (7.5), was different from that of Absalom et al. (1996) which was represented by a simple distribution coefficient of K_D . We proposed that the sorption of ^{137}Cs to the FES in soils depended on three factors as discussed in Chapter 6. They were the fractional water activity concentration, the difference between the activity concentration of ^{137}Cs in aqueous phase and that in particulate phase, and the number of available sorption sites.

Time variations of the ^{137}Cs activity in aqueous phase shown in Figure 4.9 and 4.10 were used as experimental data. Once the model was developed and configured in ModelMaker, optimization was performed using the Marquardt



optimizing method until a best fit between experimental data and the model was obtained. After the process of optimization, the product of k_1F and rate constants k_2 to k_5 for the best fit were obtained. Eqs. (7.1) to (7.4) were then updated with the optimizing results and were solved numerically by the Runge-Kutta method in ModelMaker.

7.2 Results and Discussion

Fitted curves for initial ^{137}Cs water activity concentrations of $160 \text{ kBq } \ell^{-1}$ and $240 \text{ kBq } \ell^{-1}$ are shown in Figure 7.3 and 7.4, respectively. Points are experimental data and the solid lines are fitted curves. The fitting seemed to be better for larger masses of soil samples. Table 7.1 shows the fitted parameters with the associated R^2 values. It was observed that the fitting was very good as the least square values R^2 were 0.99, except for the 1.0-g soil samples. The rate constants k_2 to k_5 were expected to be constants for different masses and independent to the initial water concentration. The average values of fitted parameters k_2 , k_3 , k_4 and k_5 were $4.68 \text{ h}^{-1} \pm 13 \%$, $1.07 \text{ h}^{-1} \pm 27 \%$, $0.10 \text{ h}^{-1} \pm 23 \%$ and $0.06 \text{ h}^{-1} \pm 11 \%$, respectively. Considering that the soils were not 100% homogeneous and uniform for all masses, the differences in rate constants obtained were to be expected and can be considered as acceptable. Non-zero values of k_2 and k_4 indicated that reversed sorption did exist in the FES, consistent

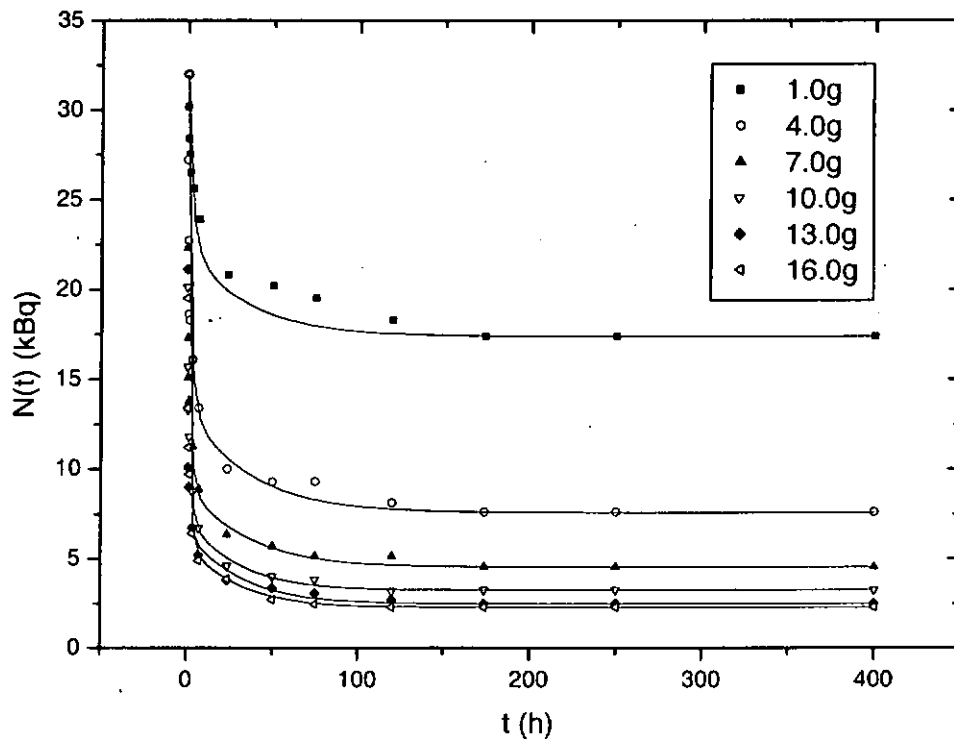


Figure 7.3 Fitted curves of the four-compartment modified model for different masses of soil samples at initial ^{137}Cs water activity concentration of $160 \text{ kBq } \ell^{-1}$.

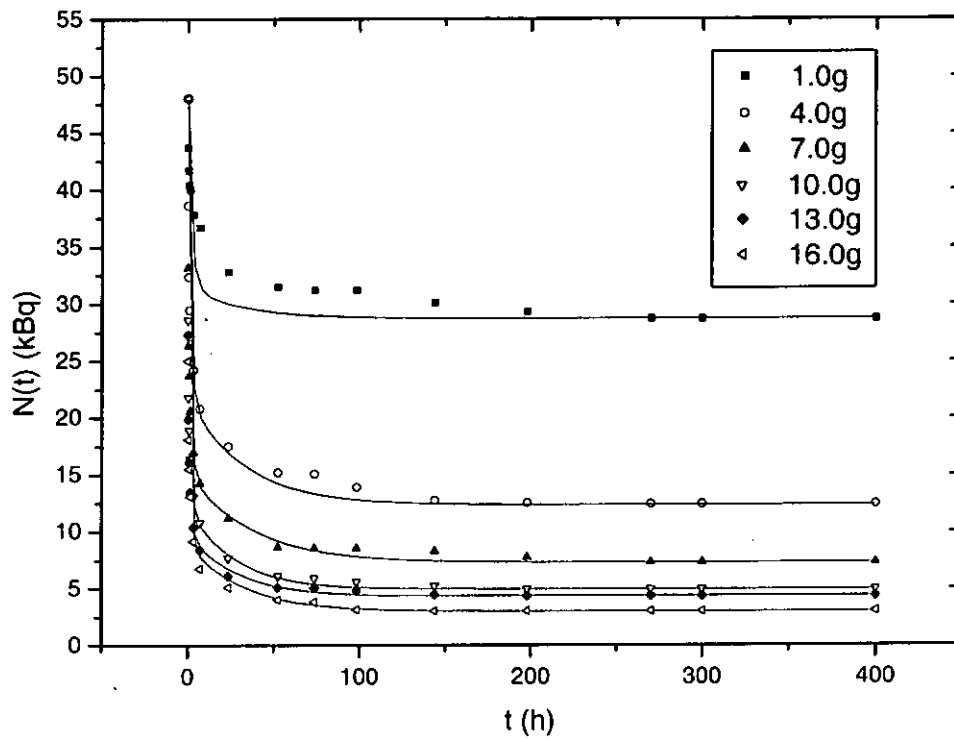


Figure 7.4 Fitted curves of the four-compartment modified model for different masses of soil samples at initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$.

Table 7.1 Fitted parameters and R^2 for the four-compartment modified model at the two different initial ^{137}Cs water activity concentrations

C_0 (kBq l ⁻¹)	m (kg)	k_1F (h ⁻¹)	k_2 (h ⁻¹)	k_3 (h ⁻¹)	k_4 (h ⁻¹)	k_5 (h ⁻¹)	R^2
160	0.001	0.18 ± 0.10	5.06 ± 0.20	0.80 ± 0.20	0.08 ± 0.03	0.05 ± 0.02	0.97
	0.004	0.52 ± 0.14	4.00 ± 1.90	0.90 ± 0.43	0.08 ± 0.06	0.05 ± 0.03	0.99
	0.007	1.41 ± 0.14	4.45 ± 0.95	0.91 ± 0.22	0.08 ± 0.03	0.05 ± 0.02	0.99
	0.010	1.55 ± 0.21	4.00 ± 1.35	1.19 ± 0.42	0.08 ± 0.05	0.06 ± 0.03	0.99
	0.013	1.60 ± 0.19	3.80 ± 1.44	1.80 ± 0.63	0.12 ± 0.06	0.06 ± 0.02	0.99
	0.016	2.07 ± 0.18	4.45 ± 0.96	1.20 ± 0.24	0.06 ± 0.03	0.06 ± 0.02	0.99
240	0.001	0.37 ± 0.10	5.50 ± 1.2	0.80 ± 0.20	0.08 ± 0.03	0.05 ± 0.01	0.86
	0.004	0.8 ± 0.13	5.02 ± 1.55	0.85 ± 0.31	0.13 ± 0.07	0.06 ± 0.02	0.99
	0.007	1.53 ± 0.12	5.57 ± 0.92	1.00 ± 0.18	0.11 ± 0.03	0.05 ± 0.01	0.99
	0.010	2.34 ± 0.12	4.95 ± 0.57	1.03 ± 0.13	0.12 ± 0.03	0.07 ± 0.01	0.99
	0.013	2.65 ± 0.24	5.22 ± 1.09	1.40 ± 0.26	0.10 ± 0.03	0.06 ± 0.02	0.99
	0.016	3.08 ± 0.24	4.12 ± 0.74	1.00 ± 0.19	0.10 ± 0.03	0.06 ± 0.02	0.99



Chapter 7 Modelling Sorption on FES using ModelMaker

with the findings of Wauters et al. (1994) that even ^{137}Cs held strongly at the FES might be considered labile. The findings that k_2 was larger than k_4 indicated that reversed sorption occurred more readily from the FES_1 (the expanded interlayer) than from the FES_2 (the wedge zone). The small value of k_5 showed again that the fixation of ^{137}Cs on the FES in soils was a very slow process. The time scale for the fixation of ^{137}Cs in soils might thus be up to about several months or even years (Konoplev et al., 1996).

Figure 7.5 shows the plot of $\log Fk_f$ against $\log m$ for all data at the two initial ^{137}Cs water activity concentrations. A straight line was obtained with R^2 of 0.95. This could verify the relationship between the mass of soils and the capacity of the FES, as discussed in Chapter 6. However, we could not find the value of F since the value of k_f was unknown.

7.3 Conclusion

A four-compartment modified model was proposed, using ModelMaker, to describe the sorption behaviour of ^{137}Cs on the FES in soils for different masses of soils at different initial water activity concentration. Rate constants with unit of h^{-1} were obtained which were more meaningful and convenient for comparison. Comparing to the model described in Chapter 6, the four-compartment modified

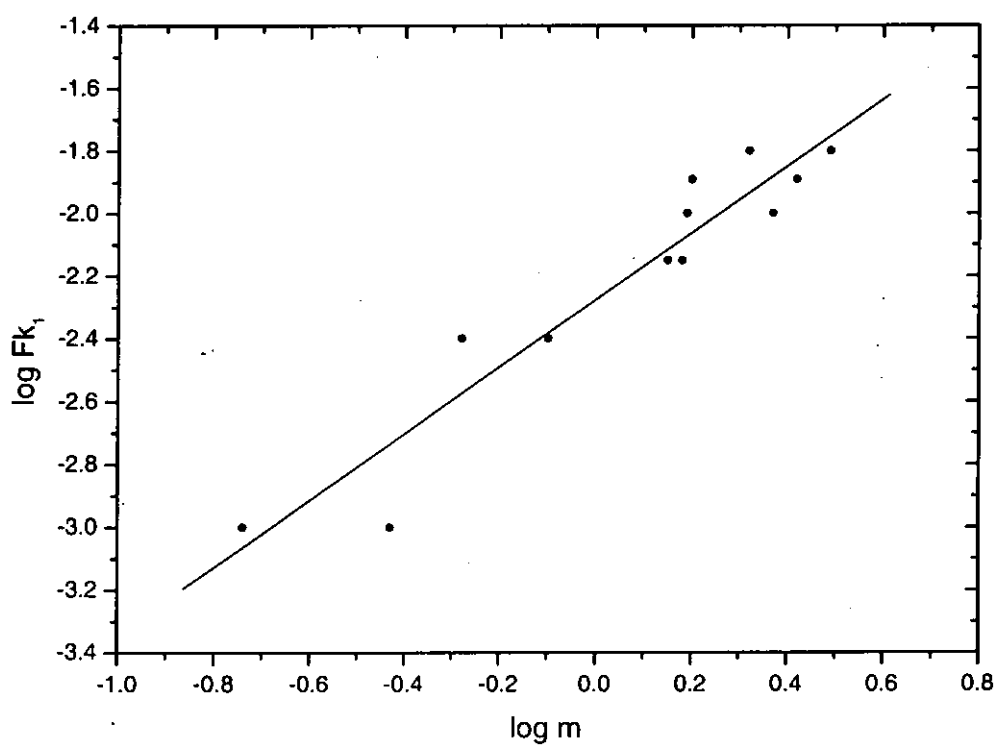


Figure 7.5 Plot of $\log Fk_1$ against $\log m$.



Chapter 7 Modelling Sorption on FES using ModelMaker

model was an improvement to describe the sorption behaviour of ^{137}Cs on the specific sites (FES) in soils as it includes the labile and non-labile characteristics of the FES. A very good fitting obtained between the experimental data and the model indicated the successfulness of the four-compartment modified model.



CHAPTER 8

CONCLUSION

The general purpose of this study is to investigate the sorption behavior and kinetics of radiocesium on soils in Hong Kong reservoirs. This is important as the sorption of radiocesium to soil constituents is one of the major factors which determine the availability of radiocesium to biological systems. It provides information on the mobility of radiocesium in soils which is a useful tool in emergency planning and in countermeasure implementation during any accidental release from the nearby Guangdong and Lingao nuclear power stations.

Many researches showed that ^{137}Cs was strongly sorbed by soils and depended on many factors in which soil properties were one of major factors. In this study, soil samples from various reservoirs and locations in Hong Kong were sampled and characterized for their physical and chemical properties such as clay content, cation exchange capacity (CEC), organic matter content, potassium ions availability and soil pH. The soil samples had clay content ranging from 2.1 % to 25 %, organic matter content ranging from 0.38 % to 1.84 %, soil pH ranging from 3.00 to 8.38, CEC ranging from 4.5 meq/100g to 16.1 meq/100g, and soluble potassium ions concentration ranging from 0.10 meq kg⁻¹ to 0.60 meq kg⁻¹.



In general, soils in Hong Kong tended to be acidic and were relatively low in clay content, organic matter content and CEC.

Two types of batch experiments were separately conducted to observe the sorption behavior of ^{137}Cs on soils. The first type of experiments was to observe the sorption behaviour of ^{137}Cs on all types of sites in soils for different types of soil samples as a function of time. 1.0-g soil samples were dispersed in a 200-ml solution of initial ^{137}Cs water activity concentration of $240 \text{ kBq } \ell^{-1}$ in a 1.25- ℓ high density Polyethylene (HDPE) container. The activity of ^{137}Cs in water was monitored with time until equilibrium reached. In general, the rate of decrease in ^{137}Cs water activity was initially very high, and then slowed down to reach equilibrium. 1.0-g soil samples could sorb ^{137}Cs more than 90 % at equilibrium. Distribution coefficient, K_D , was used to indicate the extent of ^{137}Cs sorption in soils. The values of K_D ranged from $26.7 (\times 10^3) \ell \text{ kg}^{-1}$ to $139 (\times 10^3) \ell \text{ kg}^{-1}$. The results agreed well with the literature that soils with large clay content and small soluble K^+ ions had larger K_D value and soils with large organic matter and small pH value had smaller K_D value.

A simple box model, based on three types of sorbing sites in soils, was proposed to describe the kinetic behaviour of ^{137}Cs sorption on soils using the simulation software ModelMaker. The model was successful because good



fitting could be obtained for all soil samples. Rate constants, from k_1 to k_5 , describing different chemical processes of ^{137}Cs sorption in the model were estimated. The obtained rate constant values agreed well with the physical and chemical properties of soils. The model can thus be used as an initial indicator for the retention/exchange processes in soils.

The second type of experiments was to observe the sorption behaviour of ^{137}Cs on the frayed edge sites (FES) in soils as a function of time. The method was based on the use of the silver thiourea (AgTU) complex to mask the bulk of the regular exchange sites (RES). Soil samples were dispersed with 0.015M AgTU solution in a 1.25- ℓ HDPE container. The activity of ^{137}Cs in the aqueous phase was monitored with time until equilibrium reached. Experiments with different masses of soil samples at two different initial ^{137}Cs water activity concentrations of 160 $\text{kBq } \ell^{-1}$ and 240 $\text{kBq } \ell^{-1}$ were performed. In general, the rates of decrease in ^{137}Cs water activity were initially very high, higher for larger soil masses, and then slowed down to reach equilibrium. The larger the mass, the shorter was the time for equilibrium. The equilibrium values were also found to decrease with increasing masses. The mean K_D values were 171 $\ell \text{ kg}^{-1} \pm 5\%$ and 159 $\ell \text{ kg}^{-1} \pm 12\%$ for initial ^{137}Cs water activity concentrations of 160 and 240 $\text{kBq } \ell^{-1}$, respectively. The values of K_D were thus quite independent of initial ^{137}Cs water activity concentration. The capacity of the FES for 16-g soil



sample was also found to be about 0.045 meq from the sorption isotherm.

As the sorption behavior of ^{137}Cs on the FES in soils with finite capacity in soils can be simply treated as an irreversible process, a conceptual model consisting of an irreversible exchange between two compartments was proposed. The sorption rate was assumed to depend on the ^{137}Cs fractional water activity concentration, the difference between the activity concentration of ^{137}Cs in aqueous phase and that in particulate phase, and the number of available sorption sites. Very good fitting was obtained between experimental data and theory. The proportionality constant k was found to be $4.17 \times 10^{-10} \ell^2 \text{ kBq}^{-2} \pm 4\%$ for the two initial ^{137}Cs water activity concentrations. The mathematical relation between the capacity of the FES and the mass of soils was assumed and the capacity of FES of any mass of soil sample could be estimated. The shortcomings of this model were that the proportionality constant k did not have any physical meaning (in units of $\ell^2 \text{ kBq}^{-2} \text{ h}^{-1}$) for the explanation of the sorption process and the model involved only two compartments which was insufficient for the investigation of the sorption mechanism.

To overcome the shortcomings of the two-compartment conceptual model, a four-compartment modified model was proposed using ModelMaker to describe the sorption behaviour of ^{137}Cs on the FES in soils. The model was



based on the two-compartment conceptual model and the model proposed by Absalom et al. (1996). Very good fitting was obtained between experimental data and the model. Rate constants with more meaningful unit of h^{-1} were obtained. This model was significant because it provided information on factors and mechanism for the sorption of ^{137}Cs on the FES in soils. As the FES is mainly responsible for the retention of radiocesium on soils, the four-compartment modified model can be used to estimate the availability of radiocesium to biological systems which can affect our environment.



REFERENCES

Absalom, J. P., Crout, N. M. J. and Young, S. D. "Modeling radiocesium fixation in upland organic soils of northwest England". *Environmental Science and Technology*, Vol. 30, pp2735-2741 (1996)

Børretzen, P. and Salbu, B. "Fixation of Cs to marine sediments estimated by a stochastic modeling approach". *Journal of Environmental Radioactivity*, Vol. 61, pp1-20 (2002)

Brouwer, E., Baeyens, B., Maes, A. and Cremers, A. "Cesium and rubidium ion equilibria in illite clay". *Journal of Physical Chemistry*, Vol. 87, pp1213-1219 (1983)

Carlesson, S. "A model for the movement and loss of ^{137}Cs in a small watershed". *Health Physics*, Vol. 34, pp33-37 (1978)

Comans, R. N. J., Hilton, J., Voitsekhovitch, O., Laptev, G., Popov, V., Madruga, M. J., Bulgakov, A., Smith, J. T., Movchan, N. and Konoplev, A. "A comparative study of radiocesium mobility measurements in soils and sediments from the catchment of a small upland oligotrophic lake (Devoke water, U. K.)". *Water Research*, Vol. 32, pp2846-2855 (1998)

Comans, R. N. J., Middelburg, J. J., Zonderhuis, J., Woittiez, J. F. W., De Lange, G. J., Das, H. A. and Van Der Weijden, C. H. "Mobilization of radiocaesium in pore water of lake sediments". *Nature*, Vol. 339, pp367-369 (1989)

Cremers, A., Elsen, A., De Preter, P. and Maes, A. "Quantitative analysis of





radiocaesium retention in soils". *Nature*, Vol. 335, pp247-249 (1988)

Cremers, A., Elsen, A., Valcke, E., Wauters, J., Sandalls, F. J. and Gaudern, S. L. "The sensitivity of upland soils to radiocesium contamination". In G. Desment, P. Nassimbeni, and M. Belli (Eds.), *Proceedings of CEC Conference on Transfer of radionuclides in natural and semi-natural environments (Udine)*, Elsevier Applied Science, UK, pp238-248 (1990)

De Preter, P., Van Loon, L., Maes, A. and Cremers, A. "Solid/liquid distribution of radiocesium in boom clay. A quantitative interpretation". *Radiochimica Acta*, Vol. 52/53, pp299-302 (1991)

Delvaux, B., Kruyts, N., and Cremers, A. "Rhizospheric mobilization of radiocesium in soils". *Environmental Science and Technology*, Vol. 34, pp1489-1493 (2000)

Dumat, C., Quiquampoix, H. and Staunton, S. "Adsorption of cesium by synthetic clay – organic matter complexes: effect of the nature of organic polymers". *Environmental Science and Technology*, Vol. 34, pp2985-2989 (2000)

Dumat, C. and Staunton, S. "Reduced adsorption of caesium on clay minerals caused by various humic substances". *Journal of Environmental Radioactivity*, Vol. 46, pp187-200 (1999)

Duvernoy, F. "Prévoir la trajectoire d' un nuage pollué: un pari gagné". *La Recherche*, Vol. 20, pp1406-1408 (1989)

Evans, D. W., Alberts, J. J. and Clark III, R. A. "Reversible ion-exchange fixation of cesium-137 leading to mobilization from reservoir sediments". *Geochimica et Cosmochimica Acta*, Vol. 47, pp1041-1049 (1983)



References

Grütter A., von Gunten, H. R., Kohler, M. and Rössler, E. "Sorption, desorption and exchange of cesium on glaciofluvial deposits". *Radiochimica Acta*, Vol. 50, pp177-184 (1990)

Hesslein, R. H. "Whole-lake radiotracer movement in fertilized lake basins". *Canadian Journal of Fisheries and Aquatic Sciences*, Vol. 44, pp74-82 (1987)

Jones, D. R., Paul, L. and Mitchell, N. G. "Effects of ameliorative measures on the radiocaesium transfer to upland vegetation in the U. K.". *Journal of Environmental Radioactivity*, Vol. 44, pp55-69 (1999)

Konoplev, A., Kaminski, S., Klemt, E., Konopleva, I., Miller, R. and Zibold G. "Comparative study of ^{137}Cs partitioning between solid and liquid phases in Lakes Constance, Lugano and Vorsees". *Journal of Environmental Radioactivity*, Vol. 58, pp1-11 (2002)

Konoplev, A. V., Bulgakov, A. A., Popov, V. E., Hilton, J. and Comans, R. N. J. "Long-term investigation of ^{137}Cs fixation by soils". *Radiation Protection Dosimetry*, Vol. 64, pp15-18 (1996)

Konoplev, A. V. and Konopleva, I. V. "Characteristics of steady-state selective sorption of radiocesium on soils and bottom sediments". *Geochemistry International*, Vol. 37, pp177-183 (1999)

Konoplev, A. V., Viktorova, N. V., Virchenko, E. P., Popov, V. E., Bulgakov, A. A. and Desmet, G. M. "Influence of agricultural countermeasures on the ratio of different chemical forms of radionuclides in soil and soil solution". *The Science of the Total Environment*, Vol. 137, pp147-162 (1993)

Kruyts, N. and Delvaux, B. "Soil organic horizons as a major source for radiocesium biorecycling in forest ecosystems". *Journal of Environmental Radioactivity*, Vol. 58, pp175-190 (2002)



References

- Livens, F. R., and Loveland, P. J. "The influence of soil properties on the environmental mobility of caesium in Cumbria". *Soil Use and Management*, Vol. 4, pp69-75 (1988)
- Malanca, A., Pessina, V. and Dallara, G. "Consequences of the Chernobyl fallout on some Italian underbrush produces: a ten-year study". *Journal of Environmental Science and Health*, Vol. A31(10), pp2583-2593 (1996)
- Man, C. K. and Cheung, Y. P. "Determination and analysis of sorption of ^{137}Cs to soils in Hong Kong reservoir". *Environmental Pollution*, Vol. 117, pp357-364 (2002)
- Martin, S. "A population model for the ectoparasitic mite *Varroa jacobsoni* in honey bee (*Apis mellifera*) colonies". *Ecological Modelling*, Vol. 109, pp267-281 (1998)
- McKellar, R. C. "A heterogeneous population model for the analysis of bacterial growth kinetics". *International Journal of Food Microbiology*, Vol. 36, pp179-189 (1997)
- Oughton, D. H., Børretzen, P., Salbu, B. and Tronstad, E. "Mobilisation of ^{137}Cs and ^{90}Sr from sediments: potential sources to arctic waters". *The Science of the Total Environment*, Vol. 202, pp155-165 (1997)
- Persson, Ch., Rohde, H., De Geer, L. E. "The Chernobyl accident – A meteorological analysis of how radionuclides reached and were deposited in Sweden". *Ambio*, Vol. 16, pp20-31 (1987)
- Pleysier, J. and Cremers, A. "Stability of silver-thiourea complexes in montmorillonite clay". *Journal of Chemical Society Faraday Transactions I*, Vol. 71, pp256-264 (1973)



References

Rigol, A., Vidal, M. and Rauret, G. "Effect of the ionic status and drying on radiocesium adsorption and desorption in organic soils". *Environmental Science and Technology*, Vol. 33, pp3788-3794 (1999)

Rigol, A., Vidal, M. and Rauret, G. "An overview of the effect of organic matter on soil-radiocesium interaction: implications in root uptake". *Journal of Environmental Radioactivity*, Vol. 58, pp191-216 (2002)

Robbins, J. A., Lindner, G., Pfeiffer W., Kleiner, J., Stabel, H. H. and Frenzel, P. "Epilimnetic scavenging of Chernobyl radionuclides in Lake Constance". *Geochimica et Cosmochimica Acta*, Vol. 56, pp2339-2361 (1992)

Sanchez, A. L., Smolders, E., Van den Brande, K., Merckx, R., Wright, S. M. and Naylor, C. "Prediction of in situ solid/liquid distribution of radiocesium in soils". *Journal of Environmental Radioactivity*, Vol. 63, pp35-47 (2002)

Sanchez, A. L., Wright, S. M., Smolders, E., Naylor, C., Stevens, P. A., Kennedy, V. H., Dodd, B. A., Singleton, D. L. and Barnett, C. L. "High plant uptake of radiocesium from organic soils due to Cs mobility and low soil K content". *Environmental Science and Technology*, Vol. 33, pp2752-2757 (1999)

Santschi, P. H., Nyffeler, U. P., Anderson, R. F., Schiff, S. L., O'Hara, P. and Hesslein, R. H. "Response of radioactive trace metals to acid-base titrations in controlled experimental ecosystems: evaluation of transport parameters for application to whole-lake radiotracer experiments". *Canadian Journal of Fisheries and Aquatic Sciences*, Vol. 43, pp60-77 (1986)

Sawhney, B. L. "Sorpton and fixation of microquantities of cesium by clay minerals: effect of saturating cations". *Soil Science Society Proceedings*, Vol. 28, pp183-186 (1964)

Sawhney, B. L. "Potassium and cesium ion selectivity in relation to clay mineral



- structure". *Clays and Clay Minerals*, Vol. 18, pp47-52 (1970)
- Sawhney, B. L. "Selective sorption and fixation of cations by clay minerals: a review". *Clays and Clay Minerals*, Vol. 20, pp93-100 (1972)
- Sawhney, B. L. and Voigt, G. K. "Chemical and biological weathering in vermiculite from Transvaal". *Soil Science Society American Proceedings*, Vol. 33, pp625-629 (1969)
- Schulz, R. K., Roy Overstreet and Barshad, I. "On the soil chemistry of cesium 137". *Soil Science*, Vol. 89, pp16-27 (1960)
- Scoot, A. D. and Smith, S. J. "Susceptibility of interlayer potassium in micas to exchange with sodium". *Clays and Clay Minerals*, Vol. 14, pp69-81 (1966)
- Shenber, M. A. and Eriksson, Å. "Sorption behaviour of caesium in various soils". *Journal of Environmental Radioactivity*, Vol. 19, pp41-51 (1993)
- Shenber, M. I. "Radionuclide partitioning coefficients in soils and plants and their correlation". *Health Physics*, Vol. 49, pp106-111 (1985)
- Smith, J. T., Comans, R. N. J. and Elder, D. G. "Radiocaesium removal from European lakes and reservoirs: key processes determined from 16 Chernobyl-contaminated lakes". *Water Research*, Vol. 33, pp3762-3774 (1999)
- Smith, J. T., Fesenko, S. V., Howard, B. J., Horrill, A. D., Sanzharova, N. I., Alexakhin, R. M., Elder, D. G. and Naylor, C. "Temporal change in fallout ¹³⁷Cs in terrestrial and aquatic systems: a whole ecosystem approach". *Environmental Science and Technology*, Vol. 33, pp49-54 (1999)
- Smolders, E., Sweeck, L., Merckx, R. and Cremers, A. "Cationic interactions in radiocaesium uptake from solution by spinach". *Journal of Environmental*



Radioactivity, Vol. 34, pp161-170 (1997)

Staunton, S., Dumat, C. and Zsolnay, A. "Possible role of organic matter in radiocaesium adsorption in soils". *Journal of Environmental Radioactivity*, Vol. 58, pp163-173 (2002)

Strebl, F., Ringer, W. and Gerzabek, M. H. "Radiocaesium contamination of meadow vegetation – time-dependent variability and influence of soil characteristics at grassland sites in Austria". *Journal of Environmental Radioactivity*, Vol. 58, pp143-161 (2002)

Sweek, L., Wauters, J., Valcke, E. and Cremers, A. "The specific interception potential of soils for radiocaesium". In G. Desment, P. Nassimbeni, and M. Belli (Eds.), *Proceedings of CEC Conference on Transfer of radionuclides in natural and semi-natural environments (Udine)*, Elsevier Applied Science, UK, pp249-258 (1990)

Tamura, T. and Jacobs, D. G. "Structural implications in cesium sorption". *Health Physics*, Vol. 2, pp391-393 (1960)

Valcke, E. and Cremers, A. "Sorption-desorption dynamic of radiocaesium in organic matter soils". *The Science of the Total Environment*, Vol. 157, pp275-283 (1994)

Wauters, J., Madruga, M. J., Vidal, M. and Cremers, A. "Solid phase speciation of radiocaesium in bottom sediments". *The Science of the Total Environment*, Vol. 187, pp121-130 (1996)

Wauters, J., Sweek, L., Valcke, E., Esen, A. and Cremers, A. "Availability of radiocaesium in soils: a new methodology". *The Science of the Total Environment*, Vol. 157, pp239-248 (1994)



References

Zachara, J. M., Smith, S. C., Liu, C., McKinley, P., Jeffrey Serne, R. and Gassman, P. L. "Sorption of Cs⁺ to micaceous subsurface sediments from the Hanford site, USA". *Geochimica et Cosmochimica Acta*, Vol. 66, pp193-211 (2002)



LIST OF PUBLICATION

Man, C. K., and Chu, P. Y. "Experimental and modeling studies of radiocesium sorption on soils in Hong Kong reservoir". Submitted to *Environmental Pollution*.