

Nordisk kernesikkerhedsforskning Norrænar kjarnöryggisrannsóknir Pohjoismainen ydinturvallisuustutkimus Nordisk kjernesikkerhetsforskning Nordisk kärnsäkerhetsforskning Nordic nuclear safety research

> NKS-8 ISBN 87-7893-056-1

Final reports from sub-projects within the Nordic Nuclear Safety Research Project EKO-1

Edited by Sigurður Emil Pálsson Geislavarnir Ríkisins



NKS-8 Previous reference number: NKS/EKO-1(98)TR-1 ISBN 87-7893-056-1

Afd. for Informationsservice, Risø, 1999

The report can be obtained from NKS Secretariat P.O. Box 30 DK – 4000 Roskilde Denmark

Phone +45 4677 4045 Fax +45 4677 4046 http://www.nks.org e-mail: annette.lemmens@catscience.dk

Preface

An NKS report has previously been published summarising the work within the EKO-1 project: "*Marine Radioecology - Final Report of the Nordic Nuclear Safety Research Project EKO-1*", NKS(97)FR4. The report included sections on:

- Model studies
- Laboratory studies
- Quality assurance
- The EKO-1 seminars
- Use of internet technology for the dissemination of information
- Contacts with researchers in the Baltic States within BOK-2

Constraints on the size of this summary report made it impossible to include the papers written by the individual research groups within the project, describing the results of field and laboratory studies. It was therefore decided to publish these papers separately in this present report.

Structure of the NKS/EKO-1 project (1994-1997) on marine radioecology

In the original project plan for the NKS / EKO-1 project it was stated that:

The main aim of this project is to enable better and faster assessments to be made of the effects of releases of radionuclides to the marine environment, taking health and economic factors into account.

The last sentence reflects that policy makers often need to consider sources which are of relatively minor importance as health risks, but which can be of considerable concern for the public (and thus have a major effect on society, e.g. economically).

Assessments are generally based on models describing the main processes influencing the behaviour of the radionuclides. In the marine ecosystem these main processes are:

- 1. water movement and mixing
- 2. sediment-water interaction
- 3. biological transfer (e.g. the uptake of radionuclides by fish)

Of these processes the interaction of sediments with water has been studied relatively less than the other main processes. It was therefore decided to focus the EKO-1 project work on radionuclides in sediments and water, and the interaction between them. Various site specific factors can affect this interaction, e.g. sedimentation rates. The ability of the sediment to bind radionuclides from sea water is also an important factor. This is described by the distribution coefficient (K_d) which gives the ratio of concentration of the radionuclide in sediments to that in water.

The EKO-1 project work was planned as follows:

- 1. Model work Identifying, estimating and validating parameters of main interest
- 2. Research
 - 2a) Field studies:
 - 2a1) Environments typical for various Nordic regions
 - 2a2) Environments with special physical or chemical characteristics
 - 2b) Laboratory studies
- 3. Dissemination of information Seminars, reports, articles

In the project work emphasis was also put on other aspects viewed to be important for the aim of the project:

- Quality assurance
- Use of internet technology for more efficient dissemination of information
- Maintaining a link with the related work done within NKS/EKO-2.3 on freshwater ecosystems
- Following what was being done internationally in a similar field and avoiding duplicate work
- Supporting developments of plans for a Nordic course on radioecology.

Increased Nordic competence and co-operation in marine radioecology

Maybe the most important outcome of the EKO-1 project is the increased Nordic competence and co-operation in marine radioecology, especially concerning the interaction of radionuclides with sediments. Only some of the Nordic countries had previously conducted their own research in this field and there had never been any joint Nordic research or compilation of sedimentation rates and levels of ¹³⁷Cs and ²³⁹⁺²⁴⁰Pu in sediments. The quality of the research done is manifested in the scientific articles that have been published as a result of the project work. Furthermore the EKO-1 project work has formed the basis for one Ph.D. thesis finished in April 1997 and another was finished in 1998. Two M.Sc. theses have also been finished based on the project work.

Results of field and laboratory studies

The field studies were divided into two main categories:

1. Environments with special physical or chemical characteristics (emphasis on processes)

2. Environments typical for various Nordic regions (emphasis on regional characteristics) Each study is identified with a two letter ISO code for the country responsible for the study followed by a serial number (1-3). A detailed description of each study can be found in the following papers of this report.

- Studies of anoxic conditions in Framvaren fjord, Gullmaren fjord and Byfjorden and of mixing between seawater and freshwater at the Kalix river and estuary (SE-1 and SE-2)
- Behaviour of radionuclides in sedimentation processes under varying redox conditions (FI-1)
- Sedimentation rate in the Baltic Sea (FI-2)
- *Run- off and sedimentation processes over the continental shelf along the European Siberian Tundra coast* (SE- 3)
- Radioactivity contamination of the Russian Arctic Seas (FI-3)
- *Radionuclides in marine sediments Distribution and processes* (NO-1)
- *Radionuclides in sediments in Icelandic waters and their use for the determination of sedimentation rates* (IS-1)
- Radionuclides in Sediment Cores From Thule, Greenland (DK-1)

The report on the Norwegian study (NO-1) also includes a section on laboratory studies (these are also described in the summary report).

Summary of results

Environments with special physical or chemical characteristics (process studies)

The process studies focused mainly on the behaviour of plutonium in sediments and its interaction with water. For 20 years there have been speculations about the possible remobilisation of plutonium from sediments, but until now it had not been proven that it takes place. Special attention has been paid to possible releases under anoxic (oxygen deficient) conditions. This is a situation that can occur in near bottom water in the Baltic Sea and also in bays and fjords of Skagerak and Kattegat.

The following studies are described in this section:

- 1. Anoxic conditions, areas of study: Framvaren, Gullmaren and Byfjorden (SE-1)
- 2. Anoxic conditions, area of study: Hästholmsfjärden Bay (FI-2)
- 3. Mixing zone between freshwater and seawater (SE-2)

Anoxic conditions, areas of study: Framvaren, Gullmaren and Byfjorden (SE-1)

The sediments in the anoxic Framvaren fjord acts as a source for actinides to the overlaying water column. The remobilisation process is most likely linked to early diagenetic alteration of the marine organic material in the sediments. This is indicated by the close correlation between Pu, Am and dissolved organic carbon depth profiles in the water column. Speciation studies of the plutonium and americium in the water column shows that both to a large degree are associated to colloidal material in the size range 0.01-0.45 μ m. Less than 2% is retained by a 0.45 μ m filter which is reflected in the low K_D-values obtained of about 20 000, which is at least a factor of 10 lower than in typical coastal waters. It is also proven that the plutonium exist almost entirely in the trivalent state in the anoxic water column.

This study is the first ever to show extensive remobilisation of plutonium and americium from sediments in anoxic marine basins. Similar remobilisation from sediments most likely occur in other anoxic marine waters where early diagenesis results in humic and fulvic acid production.

Although the remobilised actinides in the Framvaren fjord at present don't pose any radiological hazard due to the lack of fish in anoxic waters it is of great concern to identify processes involved in the remobilisation of actinides from anoxic sediments as such sediments likely will be a major source for actinides in the Baltic Sea and other oxygen sensitive basins in the long term perspective. In such basins the remobilised plutonium may reach oxygenated and biological productive waters by convection.

Results from the temporarily oxygen deficient Gullmaren fjord on the Swedish west coast shows that remobilisation from sediments can not be identified during short (a few months) periods of oxygen deficient water. The rapid bioturbation (quantified by tracer studies) in this fjord results in that sedimenting organic material rapidly is buried and distributed within the upper 10-15 cm of sediments. This means that the organic material is diluted with large amounts of inorganic material which may act as traps for the mobilised actinides.

It is likely that anoxic conditions must persist for a long enough time to allow organic rich sediment to accumulate in sufficient amounts before substantial amount of humics are produced that may mobilise the actinides. This time depends on the organic matter flux to the sediments.

Anoxic conditions, area of study: Hästholmsfjärden Bay (FI-2)

Varying redox conditions may affect the occurrence and concentrations of certain radionuclides in the surface layers of sediments and in near-bottom waters by causing remobilization of radionuclides from surface sediments to the overlying water and their settling back into the sediment. In recent decades about 70.000 km² of the sea bottom in the deepest part of the Baltic Sea (about 19% of its total area) have withstood almost continuous anoxic conditions; thus, it is important to know to what extent depletion of oxygen can affect the behaviour of these radionuclides in near-bottom waters. The aim of the project was to

resolve the above question in a coastal basin periodically undergoing anoxic conditions.

Radioecological processes in sediments and in near-bottom water under varying redoxconditions were studied in the deep area of the Hästholmsfjärden Bay in Loviisa (eastern Gulf of Finland) in 1995-1996. The Hästholmsfjärden Bay is a semienclosed basin between the mainland and the archipelago and is connected with the open Gulf of Finland only through narrow, shallow sounds.

In 1995, total depletion of oxygen occurred in the hypolimnion of Hästholmsfjärden Bay during 2 periods in late summer and autumn. In 1996, oxygen conditions were the worst ever observed in the Hästholmsfjärden deep. During early autumn anoxic conditions prevailed for more than 1 month in the near-bottom water. The highest total phosphorus and total nitrogen concentrations in the near-bottom water during these periods were 20- and 4- fold compared with the corresponding values in surface water.

According to the results obtained in this project, remobilization of ¹³⁷Cs and ^{239,240}Pu from sediments to near-bottom water is negligible or non-existent in the Hästholmsfjärden deep. If it does occur, however, it may be so slight that it is not possible to observe with the methods used in this study. Although the anoxic periods are quite short in the Hästholmsfjärden deep, they are of sufficient length for strong remobilization of nutrients. If the initiation of remobilization processes in the case of caesium or plutonium were retarded, then the situation may be different in the deep areas of the Baltic Sea where depletion of oxygen has been almost continuous.

Mixing zone between freshwater and seawater (SE-2)

Laminated sediments and suspended matter collected in the estuary of the Kalix river shows that the input of plutonium to the Baltic Sea from river run-off at present is of rather small importance but may in the long term perspective become one of the more important sources as the residence time of plutonium in the Baltic Sea water column is much shorter than the residence time in the river drainage basins. Drainage basins containing large percentage of mire and wetland will be of particular importance.

Environments typical for various Nordic regions (regional characteristics)

Field studies were carried out in various areas of concern for the Nordic countries. The spanned from Thule on the west coast of Greenland to the Arctic Seas north of Siberia. The Baltic Sea was included and parts of the Atlantic Ocean. In most cases the distribution in sediments of various radionuclides was determined as well as sedimentation rate and distribution coefficient (K_d). The studies helped to determine site specific parameters for the different areas. They also showed that the sedimentation rate could not in some cases be correctly determined by using just one method. In one study there was an extensive comparison of the different methods in the Baltic Sea. None of the methods was judged suitable for routine use and no systemic difference between methods could be seen. More than one method should be used whenever possible. The following study areas are described in this section:

- 1. The Baltic Sea (FI-1)
- 2. Continental shelf along the European-Siberian Tundra Coast (SE-3)
- 3. Russian Arctic Seas (FI-3)
- 4. Various sites from the North Sea to the Arctic (NO-1)
- 5. Icelandic waters (IS-1)
- 6. The Thule area, Greenland (DK-1)

The Baltic Sea (FI-1)

Determination of sedimentation rates plays an important role in material balance and model calculations of seas and other bodies of water. The Baltic Sea offers an exceptionally good opportunity to study processes in sediments and sedimentation rates with radioecological methods, because the concentration peaks of ¹³⁷Cs and ^{239,240}Pu are easily detectable in its sediments. In 1995-1996 sediment profiles were taken at 51 sampling stations situated in the Baltic Proper, Bothnian Bay, Bothnian Sea and Gulf of Finland. The aim was to estimate sedimentation rates in different parts of the Baltic Sea by using alternative methods and to consider reasons for eventual differences in results. The ²¹⁰Pb, ¹³⁷Cs, ^{239,240}Pu and the sediment trap methods were used in estimations.

The results show that the accumulation rates of dry matter may vary between 0.006 and $0.90 \text{ g cm}^{-2}\text{y}^{-1}$ at different sampling stations of the Baltic Sea and the sedimentation rates between 0.2 and 29 mm y⁻¹ depending on the sedimentation itself and the method used in calculation. This is a considerable range in results, considering that all of the sampling stations were located in areas of soft sediment bottoms. In general, the sedimentation rates were highest at the Bothnian Sea sampling stations. In the Gulf of Finland the sedimentation rates were highest in the eastern part, while in the Bothnian Bay and in the Baltic Proper the rates were in general lower than in the 2 areas first mentioned.

The differences among the results obtained with various methods varied unsystematically; thus it was not possible to predict that anyone of the methods would always give higher results than any of the others or *vice versa*. The results show that in the Baltic Sea the use of more than 1 parallel methods in estimation of sedimentation rate is highly recommended. None of the methods is necessarily suitable for routine use in the Baltic Sea. In those cases where the ¹³⁷Cs or ^{239,240}Pu peak is distinct, sharply defined and at sufficient depth, these methods may result in the best estimates. On the other hand, at those stations where the peaks are spread out over a broad range of depths, the methods based on ²¹⁰Pb may give more accurate results.

One of the advantages of the ²¹⁰Pb-based methods is that they give information on sedimentation rate over longer period of time than the ¹³⁷Cs and ^{239,240}Pu methods. In contrast to the ^{239,240}Pu method, ²¹⁰Pb can be analysed gammaspectrometrically; however the gammaspectrometric method for ²¹⁰Pb is very demanding both for the equipment and the staff. At least in the case of our material, the practice used in the CF:CS-model appeared to be most useable ²¹⁰Pb-method for the Baltic Sea sediments.

In comparing the methods the sedimentation rates should be presented as accumulation rates of dry matter $[g \text{ cm}^{-2} \text{ y}^{-1}]$ to avoid the error caused by compaction of the sediment and its impact on the results. The time scale of the estimation should always be considered because of the changes in the Baltic Sea environment affecting the sedimentation rate. The importance of undisturbed and high-quality samples is especially pronounced in the sedimentation rate studies, because the loss of soft surface sediments during sampling may significantly affect the results when using the ¹³⁷Cs and ^{239,240}Pu methods.

The project has markedly increased our knowledge of sedimentation rates in various subregions of the Baltic Sea, and in addition it has provided further data on vertical distribution of ¹³⁷Cs and ^{239,240}Pu, as well as on the total inventory of ¹³⁷Cs in Baltic Sea sediments.

Continental shelf along the European-Siberian Tundra Coast (SE-3)

The contribution of ¹³⁷Cs, ¹³⁴Cs and ⁹⁰Sr from the European sources to the arctic seas have decreased in the first half of the 1990's. This is reflected in the measured activities in the different arctic seas which all show lower concentrations compared to earlier measurements. In the Eurasian shelf seas a continuos decrease towards east is recorded and in the central Arctic Ocean comparisons with earlier measurements show lower activities in 1996. The influence from the Chernobyl accident were about one third of the total activity of ¹³⁷Cs at the Eurasian continental shelf in 1994 and between 10-30 % in the surface water in the central Arctic Ocean in 1996. The distribution pattern of the activity suggests a transport pathway for the European derived activity along the Norwegian coast, passing Barents and Kara Sea to the Laptev Sea. From there the transport is northward and follows the so called transpolar drift across the north pole and onwards to the north Atlantic.

Measurements on ¹³⁷Cs in bottom sediment on the Eurasian continental shelf point at extensive sediment mixing and high deposition, 500-1000 Bq/m². Due to the low sedimentation rates the deposition of ¹³⁷Cs in the central arctic is much lower, 10-100 Bq/m². The obtained results give no indication of any large extra sources for anthropogenic activity besides the well known fallout from atmospheric nuclear bombs test, discharges from European reprocessing plants and the Chernobyl accident releases. However smaller or local contributions from e.g. the dumped nuclear material in the Kara Sea and releases by the Siberian rivers from Russian nuclear facilities are not possible to exclude in this investigation.

Russian Arctic Seas (FI-3)

The levels of the anthropogenic radionuclides in the Russian Arctic Seas are low compared to the potential sources of pollution and originate meanly from the global fallout, Chernobyl fallout and from the western nuclear fuel reprocessing plants. Fresh release of radioactivity was noticed in this study only in the Kola Bay and in two sampling location in the White Sea. The increased ¹³⁷Cs concentrations measured in the estuaries of River Dvina and River Yenisey are caused by the riverine transport from the large catchment area. The sediments of the Russian Arctic Seas are hard. Good and enough long cores for sedimentation rate determination were obtained only in two locations in the White Sea. All the cores from river estuaries were badly mixed.

Various sites from the North Sea to the Arctic (NO-1)

The NO-1 part of EKO-1 involved both laboratory and field studies. The laboratory studies have been described earlier in this report. The following is a summary of the field studies.

At station 26 (Norwegian Sea) the sediments seem to be influenced by radiocesium from the Chernobyl accident. This may be due to direct fallout deposition to the sea surface and followed by a rapid sinking and sedimentation.

At station 16 (North Sea) some influence from Sellafield plutonium is suggested, as the plutonium ratio is significantly higher (0.07-0.09) than would be expected from global fallout (0.03).

Sedimentation rates based on analysis of 210 Pb or 210 Po varied between 0.03 cm/year - 0.25 cm/year. A surprisingly low sedimentation rate was found in the Yenisey Bay (0.05 cm/year). It is possible that the dating method is less suited in this area, due to the long winter ice cover.

In general, the rough estimates on K_d values for ¹³⁷Cs obtained empirically are higher than K_d

values obtained from the laboratory studies. This may be due to the fact that the 2 cm surface sediment in most cases has accumulated over many years, carrying contamination from the early eighties when levels of ¹³⁷Cs in the sea water were higher. The ¹³⁷Cs in the sediment is now fixed, or being remobilized only very slowly. Burial of the contamination by sedimentation may also make it unavailable for exchange with free water masses.

Icelandic waters (IS-1)

The sea bottom around Iceland has a very uneven topology. This is understandable with Iceland being a part of the Mid-Atlantic Ridge. Iceland is also at the junction of different ocean currents. These factors contribute to create rich fishing grounds around Iceland. Over the years there has been considerable oceanographic research in Iceland and there has been some research concerning sediments. But there had been no studies of radionuclides in sediments prior to the start of the EKO-1 project.

Sampling of sediment cores was attempted at 35 stations around Iceland, repeatedly at most of them. The conditions proved however to be very difficult and only 5 good quality sediment cores were obtained. These cores were analysed for ¹³⁷Cs, ²¹⁰Pb and ²²⁶Ra. The sedimentation rates were determined using regression analysis of the unsupported ²¹⁰Pb profile. The obtained fit was very good in all cases (R² ranging from 0.94 to 0.99) which indicates that the results are of good quality. Interpretation of the ¹³⁷Cs profiles was also consistent with the interpretation based on the ²¹⁰Pb data. The shallower depths (106 m – 215 m) gave sedimentation rates of 0.1 - 0.3 g cm⁻² y⁻¹ (3 – 4 mm y⁻¹) while the cores from 256 m and 972 m gave considerably lower rates (0.06 g cm⁻² y⁻¹ and 0.03 g cm⁻² y⁻¹ respectively).

Two of the sediment cores were taken in the same area, but at different times. These are the cores sampled at depths 210 m and 215 m. The difference in the exact position of these two sites is approximately 100 m. The difference in the obtained results illustrates clearly the variability that can be expected within an area.

The project has been important for research in this field in Iceland. Not only has data for the area been obtained, but also valuable experience gained in sampling under these difficult conditions and in the subsequent interpretation of results.

The Thule area, Greenland (DK-1)

Analyses of radionuclide profiles in sediment cores collected in 1991 at Thule in Greenland have provided information on processes that occur in the sediments. The radionuclides include the naturally occurring ²¹⁰Pb, ²³⁹⁺²⁴⁰Pu originating from the aircraft accident in 1968, and ¹³⁷Cs originating from nuclear weapons testing. The processes include mixing of the surface sediments mainly from biological activity and burial of sediments due to particle scavenging. These processes influence the time scale and the extent to which the plutonium contamination is in contact with seawater and thus available for further dispersion. The quantified description of these processes is necessary for numerical modelling of the impact of radioactive contamination of the marine environment. These processes are of particular importance for the transuranic elements due to the relatively high radiotoxicity, the long physical half lives and the sediment-reactive properties of these elements.

The radionuclide profiles have been analysed with a numerical model to identify values of parameters describing the sediment processes. The average parameter values for the Thule area are: 0.3 cm y^{-1} for the sedimentation rate, 5 cm for the mixing depth and 1 cm² y⁻¹ for the mix-

ing rate. It was found that the mixing parameters were not correctly identified from the interpretation of the unsupported ²¹⁰Pb profile alone, but that information from the ²³⁹⁺²⁴⁰Pu profile was necessary. This stresses the need for caution when interpreting ²¹⁰Pb profiles where no other information is available.

Summary of sedimentation rate results

Area	Depth Mass accumulation		Sedimentation
	(m)	rate (g cm ⁻² y ⁻¹)	rate (mm y ⁻¹)
The Baltic Sea (FI-1)		0.006 - 0.90	0.2 - 29
The Kara Sea (NO-1)			0.6
The Barents Sea (NO-1)	290	0.12	1.2
Yenisey Bay (NO-1)			0.5
West of Svalbard (NO-1)	3200		1
Near "Komsomolets" (NO-	1680	0.11	1.2
1)			
Norwegian Sea (NO-1)	270	0.09	0.4
Skagerak (NO-1)	535	0.15	2.7
The North Sea (NO-1)	280	0.04	0.3
NE of Iceland (NO-1)	420	0.11	2.6
NW of Iceland (IS-1)	250-1000	0.03-0.06	0.6-1.1
NW of Iceland (IS-1)	100-220	0.1-0.3	3-4
Thule (DK-1)			3

The following is a summary of some of the sedimentation rate results from the papers of this report. Please go to the papers for more information.

In some cases the values just represent one sediment core, in other cases the values represent values from comprehensive surveys (especially the Baltic Sea survey in FI-1)

List of Contens

Prefacei
Studies of anoxic conditions in Framvaren fjord, Gullmaren fjord and Byfjorden and of mixing between seawater and freshwater at the Kalix river and estuary <i>Per Roos</i>
Behaviour of radionuclides in sedimentation processes under varying redox conditions <i>Erkki Ilus, Tarja K. Ikäheimonen, Jukka Mattila and Seppo Klemola</i> 29
Sedimentation rate in the Baltic Sea Erkki Ilus, Jukka Mattila, Seppo Klemola, Tarja K. Ikäheimonen and Lauri Niemistö38
Run-off and sedimentation processes over the continental shelf along the European- Siberian Tundra coast Dan Josefsson
Radioactivity contamination of the Russian Arctic Seas Kristina Rissanen, Tarja K. Ikäheimonen, Dmitri Matishov and Gennady G. Matishov68
Radionuclides in marine sediments – Distribution and processes Anne Liv Rudjord, Deborah Oughton, Tone D. Bergan and Gordon Christensen81
Radionuclides in sediment in Icelandic waters and their use for the determination of sedimentation rates Sigurður Emil Pálsson, Magnús Danielsen and Elísabet D. Ólafsdóttir
Radionuclides in Sediment Cores From Thule, Greenland

Studies of anoxic conditions in Framvaren fjord, Gullmaren fjord and Byfjorden and of mixing between seawater and freshwater at the Kalix river and estuary

Per Roos

University of Lund, Sverige

Anoxic conditions in Framvaren fjord, Gullmaren fjord and Byfjorden

Framvaren fjord

This fjord has been the most studied among the three included since it constituted the subject for a Ph.D thesis finished in April 1997. Therefore a more detailed description, as compared to the other fjords, of this study site is given below. Compared to the other two fjords, Framvaren shows features found on very few other places in the world which further have resulted in that the main focus has been directed towards Framvaren. The main purpose with the SE-1 project was anoxic basins and potential remobilisation of actinides from the sediments. This process has not been able to detect in the other two fjords and the work there has therefore been very limited.

The main aim of the work in Framvaren has been to explain the mehanisms responsible for the extremely long residence times for some actinides found in the water column (in the order of 100-1000 times longer than for other coastal waters) and to determine the release rate of actinides from the sediments. Both questions are of course of large importance in determining the long-term concentrations of actinides in marine waters subject to a sensitive oxygen balance (e.g. the Baltic Sea or many of the landlocked basins in Norway and western Sweden).

Description of the area

Framvaren fjord is a 9 km long and 1 km wide former meromictic lake situated on the southernmost point of Norway. The fjord is permanently anoxic below about 18 m depth due to a very limited water exchange through a narrow, man made, channel connecting the fjord to the Skagerrak via the Helvik and Lyngdal fjords. Early investigations in the 1930's by Kaare Münster Ström (Ström, 1936), covering a large number of fjords on the south and west coasts of Norway, revealed that Framvaren was one of the most isolated and anoxic fjords on record. Basic data on Framvaren are presented in table 1 below.

At the end of the last glaciation period the fjord was connected to the sea but due to the isostatic uplift following this period, the fjord was cut off from the open sea. The former fjord then turned into a meriomictic lake with sea water in the bottom 80 m, and marine organisms were replaced by fresh water communities in the upper water mass. In 1850 a channel was constructed in order to connect Framvaren with the sea and allow small boats into the fjord. As a result, seawater replaced the freshwater, but it is not clear whether the old seawater was replaced or not. The presence of a relatively large fraction of sulphur, still in the form of sulphate, indicates however that the renewal was complete and that the onset of anoxia started in 1850.

Water column

The hydrogen sulphide concentrations in the bottom water, of the 183 m deep main basin, is today 7-8 mM, or about 25 times the concentation in the Black Sea deep water, classifying

Framvaren fjord deep waters as a super-anoxic water mass. Based on the vertical salinity profile (fig.1) four different water zones may be distinguished. The surface water (0-2 m) with large variations in salinity, the intermediate water (2-18 m) with strong gradients in salinity and oxygen, the deep water (18-80 m), where steep gradients in sulphide and nutrients occur and the bottom water (80-183 m). The probability of water entering Framvaren via the channel, having a salinity high enough to mix with the bottom water, appears to be very low (Stigebrandt and Molvær, 1988). For this to happen, water with a salinity above about 28 ‰ must enter, a value significantly higher than the typical salinities of around 20-22 ‰, encountered in the surface water of Helvik fjord, which constitutes the supply of salt water to Framvaren.



Figure 1.

Depth distribution of salinity (‰) and H_2S [mM·2] in framvaren fjord. Redrawn from Skei (1986).

Apart from the sill separating Framvaren and Helvik fjords, there are three additional shallow sills in the adjacent fjords, which effectively prevents denser Skagerrak water from undiluted reaching Framvaren. As the number of observations on surface water salinity in Helvik fjord are to limited, estimates on the renewal rate of the bottom- and deep water in Framvaren are not presently possible. The major water exchange in Framvaren occurs naturally above the redoxcline and the combined flushing of incoming Helvik surface water (average 10 m³ s⁻¹) and fresh water (average 1 m³ s⁻¹), results in an residence time of the upper 18 m of oxic water (10^8 m³) of about 100 days.

Table 1.	
Some characteristic features of Framvaren fjord.	

Property	Framvaren fjord	
Maximum depth	183 m ^(a)	
Bottom salinity	23.3 ‰ ^(a)	
Renewal time of bottom water	?	
Volume of anoxic water	$0.3 \text{ km}^{3 (a)}$	
Bottom H ₂ S	6-7 mM ^(a)	
Bottom Silica	800 µM ^(a)	
Bottom Phosphate	120 µM ^(a)	
Bottom alkalinity	$20 \text{ meq } l^{-1 (a)}$	
sedimentation rate	$(40-70 \text{ g m}^{-2} \text{ y}^{-1})^{\text{(b-d)}}$	
organic carbon flux to sed.	$22 \text{ g m}^{-2} \text{ y}^{-1}$ (c)	

^(a) (Skei, 1986)	^(e) (Grasshoff, 1975)
^(b) (Skei, 1983)	^(f) (Falkner <i>et.al</i> , 1993)
^(c) (Næs <i>et.al</i> , 1988)	^(g) (Buesseler and Benitz,
	1994)
^(d) (Paper I)	^(h) (Hay <i>et.al</i> , 1990)

Sediments

The gelatinous, varved sediments in Framvaren, is similar to what is found in some other anoxic marine basins, such as the Saanish Inlet in Canada (Gross *et.al*, 1963). The upper black marine sediment is easily distinguishable from the underlying greenish lake sediment, in which fresh water diatom skeletons are found (Skei, 1983). The interface between the two sediment types thus marks the year 1850, when the lake was again connected to the sea. The known length of the marine sediment of 47-49 cm in 1995, may also be used to evaluate losses of top sediments when collecting sediment cores. The very high water content of the sediments (98-99% by mass) means that sediment cores must be collected with extreme caution in order not to loose any material, or disturb the core. Sediment accumulation rates have been determined both via sediment traps and ²¹⁰Pb dating (Skei, 1983; Næs *et.al*, 1988; Roos et.al, 1997), as well as, from marker horizons derived from nuclear bomb test fallout plutonium and Chernobyl radiocesium (Roos et.al, 1997). These results give somewhat different accumulation rates, but are in the range of 40-70 g m⁻² y⁻¹. The flux of organic carbon is in the order of 20 g m⁻² y⁻¹ which is very high when compared to the total flux. Compared with other anoxic marine basins, such as the Black Sea (Ross and Degens, 1974; Hay et.al, 1990), or the Saanish Inlet (Matsumoto and Wong, 1977), the fraction of organic material in the total flux, is roughly ten times higher. This may be explained by the generally low total flux in Framvaren and the relative shallow basin, which permits the organic material to reach the sediments without too much remineralization. In Saanish Inlet and the Black Sea a much higher fraction of the organic material originating from the euphotic zone is mineralised within the water column. In Saanish Inlet this is due to the anoxic zone

constituting only the lower 30 m of a 200 m deep water column and in the Black Sea, due to the depth of around 2000 m, in which material must pass before reaching the sediment. Framvaren fjord is a very suitable natural laboratory for research on marin anoxic waters, since it exhibits extraordinary biogeochemical properties, has a small catchment area with a sparse population (about 100 people) and is generally subject to little non-natural interference. In spite of this comparatively little research has been performed, something that may partly be explained by the difficulties in conducting anything other than small scale expeditions in to the ford, due to the shallow sill preventing the entry of large boats. Consequently heavy equipment is difficult to bring in, and the working area available on the small boats used are very limited. Another reason for finding relatively few published results, from this site, is that continuos research in the fjord did not start until 1979 (Skei, 1986). This may be compared with research in the Black Sea, the world largest anoxic basin, which has been going on since the turn of the century (Grasshof, 1975). Summaries on research conducted up to about 1986 in Framvaren may be found in a special volume of Marine Chemistry (vol. 23:(3-4), 1988), or in a data report published by the Norwegian Institute for Water Research (NIVA) (Skei, 1986). An updated summary on research performed in the fjord is scheduled for publication as a special issue in Marine Chemistry in the near future

Review of plutonium remobilisation from marine sediments

During the GEOSECS program (See *Earth and Planetary Science Letters*, vol. 49, 1980) Bowen reported enhanced concentrations of $^{239+240}$ Pu in near-bottom waters at several stations in the Pacific Ocean. They argued that these enhanced concentrations were due to remobilization from plutonium bearing particles being dissolved at or near the bottom. Nearly the same concentrations, in the bottom waters, were later reported by Nelson *et.al* (1984) and Livingston *et.al* (1987). Livingston *et.al* (1987) argued that as the concentrations had not changed significantly between 1973 (Bowen *et.al*, 1980) and 1980 (Livingston *et.al*, 1987) the plutonium observed originated from maximum fallout period from 1963 to 65. The reason, these enhanced levels have only been observed in the Pacific Ocean, could be due to the very low rate of deep water formation in the central gyres of the Pacific. In the Atlantic Ocean the deep water is continually flushed by water from the polar areas. If assuming these enhanced values were due to the biogenic particles dissolving, with consequent release of the adsorbed trace substances, (including plutonium) it is unfortunate that no analysis of other trace substances were carried out. That would of course greatly helped in determining the cause of the high plutonium concentrations.

Indications of plutonium mobility within the sediments has also been argued from solid phase data (Cochran *et.al*, 1985), which has been based on the observations of plutonium in sediments deeper than the ²¹⁰Pb_{xs} signal. Arguments based on the different results of calculated mixing rate constants from the observed plutonium and ²¹⁰Pb_{xs} depth profiles in sediments have also been forwarded (Stordal *et.al*, 1985). There are however two problems when comparing solid phase ²³⁹⁺²⁴⁰Pu and ²¹⁰Pb_{xs} data, which makes the results insensitive indicators of Pu mobility. The first problem is that in some studies (such as the one performed by Stordal *et.al* (1985)) the ²³⁹⁺²⁴⁰Pu and ²¹⁰Pb_{xs} analysis was not performed on the same cores and therefore between-core variability may cause the observed variations. The second problem lies with the fact that it is difficult to correctly subtract the supported ²¹⁰Pb activity in many cases, whereas it is easy to determine ²³⁹⁺²⁴⁰Pu above a zero background. The errors in the determined ²¹⁰Pb_{xs} may thus be large and in deep sea sediments where supported ²¹⁰Pb activity are much higher than elsewhere, it is difficult to establish how deep down in the sediments ²¹⁰Pb_{xs} signals are observed.

One of the most sensitive methods in determining whether remobilization occurs to any significant degree from sediments is by analysing the interstitial water, the pore water. Due to the low porosity of deep sea sediments the amount of water to collect from a given slice of sediment is very small. Analysing the extremely low levels of plutonium that may be expected in such a sample (in the order of a few μ Bq for a 100 ml sample) is of course a challenge and requires thermal ionisation mass spectrometry (TIMS). The only investigation of deep sea pore water has been performed by Buesseler (1986) on sediments in the Atlantic. Only three earlier studies exist on plutonium in pore water (Heatherington, 1976; Nelson and Lovett, 1981; Sholkovitz and Mann, 1984), all in coastal areas (Irish Sea and Buzzards Bay), and the data presented by Nelson and Lovett (1981) has been questioned by Sholkovitz (1983) as being unreliable, due to exposure to air of the collected pore water samples before filtering. If reducing pore waters containing Fe²⁺ and Mn²⁺ (which they always do to some extent) are exposed to air long enough, both will oxidise and precipitate as oxyhydroxides, coprecipitating the plutonium, which consequently will be lost when filtering.

The proposed mechanism for remobilisation from sediments (marine as well as limnic) has generally been thought to be due to the reduction of Fe (III) and Mn (IV) oxyhydroxides to soluble Fe (II) and Mn (II) during reducing conditions. Trace elements hydrolytically scavenged on to the surface of these particles would then be released and diffuse out of the sediment carried by other colloidal particles. However, the composition of marine particles are much more complex and they are as a rule composed of mixtures of organic and inorganic material. Practically all inorganic particles formed in natural waters rapidly become covered with an organic film, in many cases consisting of humics (humic and fulvic acids). Since both iron and manganese oxyhydroxides, as well as, humic colloids have a high binding capacity for many trace substances, it may therefore be difficult to determine if the scavenging is due to adsorption onto the inorganic, or onto the organic phases. The organic coating may in any case be remobilised, when the oxyhydroxides are solubilized, thus serving as the carrier substance.

The results from the study performed by Buesseler (1986) shows that the shape of the porewater profiles of plutonium closely follows the solid phase data, which means that there is an equilibrium between the two phases. Loss of plutonium to the overlaying water column will thus be compensated by the solid phase plutonium. In all the sediments analysed (from 90 m to 5000 m water depth) the porewater concentrations of plutonium were higher than in the overlaying water by a factor of 5-10. Although the sediments ranged from typical shelf sediments with reducing pore water, to deep sea sediments, with oxic pore water down to several centimetres, there was no significant correlation between pore water plutonium and Fe, Mn or DOC. The flux of plutonium to the overlaying water column, calculated from the pore water profiles, was in the range of 0.5-40 mBq m⁻² y⁻¹, which is approximately 0.1-0.01% of the solid phase inventories per year. This is a rather low flux and would probably not be noticed, as elevated near bottom activity, especially when diluted by the water circulation. Assuming the flux to be constant for at least 10 years would mean a total flux from one of the deeper cores (4460 m, flux calculated to about 7 mBq $m^{-2} y^{-1}$) of 70 mBq. If, during the time period considered, this is distributed over the lower 200 m water column then the results in elevated concentrations would be of about 0.4 μ Bg l⁻¹, or only about 4% of the present concentrations. Fluxes of this magnitude would not support the observed high bottom activities in the Pacific Ocean.

Remobilization of plutonium from weapons testing between 1946 and 1958, at the Marshall Islands. has been studied by Schell *et.al* (1980) and Noshkin (1980). Plutonium in these

sediments, composed mainly by foraminifera shells and coral are readily released. It has been estimated (Noshkin, 1980) that as much as 50% of the total plutonium inventory in these atolls will be released during the coming 250 years, assuming the present release rate to be constant. These carbonate sediments are, however, not representative for sediments elsewhere in the oceans and conclusions of plutonium behaviour in other places should not be drawn from the Marshall Islands data.

If the remobilization of plutonium from certain areas in the pelagic ocean have been accepted without to much discussions, the potential remobilization of plutonium from coastal and shelf sediments has been heavily debated. If remobilization from deep sea sediments has been thought of as being due to mineralization of biological material in an nutrient-poor environment, then remobilization mechanism in coastal sediments has been suggested to be due to the reduction and dissolution of iron- and manganese oxyhydroxides. All of these investigations build their arguments for or against remobilization on the inventories and/or depth distributions, of plutonium in the sediment, in relation to either ²¹⁰Pb dating, or budget calculations, or both (e.g. Livingston and Bowen, 1979; Koide *et.al*, 1975; Koide and Goldberg, 1982; Carpenter *et.al*, 1981; Carpenter and Beasley, 1987). Some of these investigations are critically reviewed in Sholkovitz (1983), where it is concluded that many of the interpretations made in the above papers were erroneous and that evidence for, or against remobilization, cannot be drawn from these data.

The most rigorous dataset on plutonium remobilization from coastal sediments comes from Buzzards Bay, Massachusetts, where a pore water profile of plutonium and several other relevant species (alkalinity, dissolved iron, manganese, DOC, nutrients etc) were presented by Sholkovitz and Mann (1984). The sediments in Buzzards Bay are muddy, oxic down to a few centimetres and with a rather high organic matter content (4-5%) and may thus be considered to represent coastal sediment in a large part of the world. The results from their pore water study shows that plutonium is present in concentrations comparable to, or somewhat lower, than those reported by Buesseler (1986) from the shelf station (90 m). The pore water profile was found to closely follow that of the solid phase profile. The calculated fluxes from the Buzzards Bay sediment were only in the order of $1 \text{ mBq m}^2 \text{ y}^1$, which is only a few percentage of the flux reported by Buesseler. It should be mentioned that in the calculations made in these two investigations, diffusion coefficients for free, uncomplexed, plutonium has been used (a value similar to that for Th⁴⁺ (Li and Gregory, 1974)). If the plutonium is complexed by DOC, which is very likely at the DOC concentrations of 5-50 mg l⁻¹ found in these pore waters, the value of the diffusion constant would be 2-3 orders of magnitude lower and consequently the flux from the sediments would decrease with the same factor.

Although no pore water profile was analysed (successfully) for plutonium in Framvaren fjord, it may be calculated that the average flux from the sediments in order to generate the observed plutonium depth profile in the water column must be in the order of 1000 mBq m⁻² y⁻¹, that is 2-3 orders of magnitude higher than the values reported by Sholkovitz and Mann (1984) and Buesseler (1986) from coastal oxic areas.

Review of plutonium and americium studies in anoxic marine waters

Investigations of plutonium or americium in anoxic aquatic environments have been infrequently performed. Investigations in lakes have been reported by Wahlgren *et.al* (1977), Alberts *et.al* (1977), Alberts and Orlandini (1981), Sholkovitz *et.al* (1982), Buesseler *et.al* (1985) and Sanchez *et.al* (1986), while studies in marine anoxic basins have been reported by Carpenter and Beasley (1981), Sanchez *et.al*(1986, 1991, 1994), Livingston *et.al*, (1988) and

Buesseler & Benitz (1994). The reasons for the limited number of papers is not so surprising, as there are very few locations where anoxic marine waters are to be found. It is, however, somewhat surprising that the number of published papers on actinides in anoxic lakes are so few. There are several lakes in the world with permanent anoxic bottom water, but perhaps more relevant is that many of the lakes in the subarctic zone develop anoxic bottom water during the long ice cover.

The work performed by Carpenter and Beasley (1981) included only sediments and no water, the studied areas were the Saanish Inlet and Dabob Bay in Canada (separated from each other by about 65 km), the Golfo Dulce (Pacific coast of Costa Rica) and the Cariaco Trench (Caribean Sea outside Venezuela). All these basins contain moderate concentrations of H_2S (1-50 μ M) in the bottom water. The main aim of these studies was to compare measured inventories in these basins relative to expected ones from bomb test fallout. The main conclusion was that remobilization does not occur from these anoxic sediments and that the earlier proposed (Livingston and Bowen, 1979) remobilization from the sediments in Cariaco Trench was due to loss of top sediments during sampling.

Investigations by Sanchez covered both the Saanish Inlet (1986), the Black Sea (1991) as well as Framvaren fjord (1994). The Saanich Inlet is a well studied intermittently anoxic fjord with a wealth of background chemical data. Due to the fjord being flushed annually there are limited possibilities of studying the diffusion of remobilized actinides from the sediments. The values for plutonium reported by Sanchez *et.al*, (1986) do not show any particular change in the anoxic water column inventory, over what would be expected. Neither show the data from the Black Sea (Sanchez *et.al*, 1991) any enhanced levels in the anoxic water mass, in fact rather the opposite. It was concluded by Buesseler and Benitz (1994) that approximately 90% of the Black Sea inventory resides in the sediments.

The oxidation state measurements performed in the Black Sea (Sanchez *et.al*, 1991), the first reported in an anoxic marine water column, shows that there is almost no oxidised plutonium below the redoxcline (50-100 m depth), it would therefore be expected to discover plutonium adsorbed to particles. Even though the study by Sanchez *et.al* (1991) was performed on unfiltered samples, Livingston *et.al* (1988) had shown earlier that only about 3% of the plutonium is retained on a 1µm filter. The fraction of filterable material found in Framvaren (0.22 µm or 0.45 µm) was in the order of 1% of the total concentration, even though the suspended load concentrations are roughly one order of magnitude higher in Framvaren than the Black Sea.

The reasons for not finding a similar plutonium depth profile in the Black Sea water column, as in Framvaren, are probably to be found in the type of particles which transport the plutonium to the sediment. In Framvaren fjord little mineralization occurs of the particulate matter as it settles to the bottom, while in the Black Sea some mineralization may occur of the organic material during passage through the 2000 m water column. Most important, however, is that the organic carbon flux to the sediment in Framvaren is nearly ten times as high as in the Black Sea (table 1). The high concentrations of DOC observed in the sediment pore water in Framvaren is a continuous source of DOC to the overlaying water column. As observed from our ultrafiltration data, it is likely that most of the plutonium and americium in the Framvaren water column is associated with the colloidal component, which therefore prevents these actinides from being scavenged onto sedimenting particles from the oxic water mass. Due to the lower fraction of organic carbon flux in the Black sea, plutonium is probably associated to a higher degree with other particles, when descending the water column. A study

of the colloidal fraction of plutonium and americium in the Black Sea would certainly help in clarifying this.

In the Black Sea the porosity of the upper sediment is around 80-85% (Crusius and Anderson, 1991) and the plutonium in the sediment is entirely associated with the upper centimetre of sediment (Buesseler and Benitz, 1994). This means the water volume in the sediment in contact with plutonium containing sediment is only about 8 liters per m^2 , while in Framvaren the corresponding volume is 240 l per m^2 . In fact this, together with high concentration of DOC in the sediment pore water probably explains the much higher flux from the Framvaren sediment although the sediment inventories (Bq m⁻²) are nearly the same.

It would be interesting to perform a closely spaced water sampling near the bottom of the Black Sea in order to detect any remobilization. The reason is even more important when considering that a given sediment layer in the Black Sea, will be closer to the sediment surface for a longer period of time, than in Framvaren and will therefore be influenced by advective movement in the overlaying water. Some indications of remobilization from these sediments on a longer time scale may come from data presented by Huh *et.al* (1994), although they did not consider this aspect. Their data for dissolved ²³²Th in the water column show a significant increase towards the bottom, similar to what we observed, but much more clearly, in Framvaren. The reasons for these elevated concentrations would of course be very interesting to identify and perhaps they could provide further insight into future behaviour of plutonium in the bottom waters in the Black Sea.

Results obtained

Although our first sampling expedition in Framvaren were conducted already in 1989 the main work was done during 1994 (two expeditions) and 1995 (one expedition). It was soon recognised that the concentrations of dissolved Pu, Am and Th isotopes in Framvaren deep water was extremely elevated as compared to both other coastal marine waters and other permanently anoxic marine basins. Figure 2 summarizes the depth profiles of Pu obtained during the four expeditions.

Pu-239+240





As is clearly seen in figure 2 the concentrations increases strongly towards the bottom of the fjord. The bottom water concentrations of 300-400 μ Bq/l are roughly 70 times higher than concentrations normally found in other Nordic marine waters. In fact there are no other marine area known in the world with higher plutonium concentrations originating from global bomb test fallout. In spite of the connection to the North Sea the extremely limited water exchange has transported only a small fraction of reprocessing plutonium in to the fjord as compared to fall-out plutonium. This is clearly seen in figure 3 and 4 below.

Pu-238/Pu-239+240







The influence of reprocessing plutonium may be seen in the upper 30-40 m of the fjord while deep- and bottom waters shows typical fall-out ratios of around 3% or less. The high concentrations of fall-out plutonium present in the deep- and bottom water require substatial input of reprocessing plutonium to occur in order to significantly change the ²³⁸Pu/²³⁹⁺²⁴⁰Pu ratio. This is not likely to occur due both to the presently low plutonium concentrations in the North Sea and the very low probability to inject high density North Sea water over the sills to Framvaren.

It is interestingly to see in fig. 4 that americium seems to be regulated by the same mechanisms in the water column as plutonium. Normally ²⁴¹Am/²³⁹⁺²⁴⁰Pu ratios in coastal waters not affected by reprocessing plants are lower than the typical fallout ratio (in 1995 about 0.36) due to preferrential scavenging of americium. The upper part of the Framvaren water column show influence by reprocessing releases while deeper waters have a ratio representative for bomb test fallout.

Am-241/Pu-239+240



Am-241/Pu-239+240

Figure 4. ²⁴¹Am/²³⁹⁺²⁴⁰Pu ratios found in Framvaren water column 1989-95.

The source of plutonium to the water column in Framvaren is the sediments. Although direct measurements of the flux of pore water plutonium into the overlaying water mass has not yet been done the existing observations rather clearly points to the sediments as the source. Existing evidence for this is:

- The shape of the plutonium and americium depth profiles are nearly identical to other constituents known to originate from the sediments (DOC, silica and other nutrients etc.).
 The ²³⁸Pu/²³⁹⁺²⁴⁰Pu and ²⁴¹Am/²³⁹⁺²⁴⁰Pu ratios in deep- and bottom
- The ²³⁸Pu/²³⁹⁺²⁴⁰Pu and ²⁴¹Am/²³⁹⁺²⁴⁰Pu ratios in deep- and bottom water are identical to those found in the sediments.
- The development of the depth profile may be fairly accurately modelled at different times by assuming a pulse release from the sediments in 1963 and using a fixed diffusion coefficient.
- The fact that ²³²Th displays a similar depth profile as Pu and Am with concentrations more than 200 times higher than in other marine waters . This isotope enters the fjord in the crystal lattice of mineral grains which rapidly is transported to the sediments.
- The water column inventory of 232 Th has increased between 1989 and 1995 with a rate of about 2 Bq m⁻² y⁻¹.
- Analysis of ²³²Th in sediment pore water shows high concentrations and is directly proportional to DOC concentrations.

The accumulation rate of sediments in Framvaren has earlier been determined from sediment trap data and one ²¹⁰Pb profile (Skei, 1983; Næs *et.al*, 1988). Sediment trap data reported corresponded to an yearly accumulation rate in the range of 40-114 g m⁻² with an average of 60 g m⁻². The ²¹⁰Pb profile indicated an accumulation rate of 120 g m⁻², twice as much as the

results from sediment traps. The difference was suggested (Næs *et.al*, 1988) to be due to sediment slumping down the steep fjord sides, not recorded by the sediment traps. Large variations in total fluxes during the year was also observed although the average flux at different depths from 40 m down to 160 m was similar as was the organic carbon fluxes (which from C/N ratios around 8-10 was suggested to consist of mainly dead phytoplankton). These observations is of importance as it indicates that the major flux of material to the sediments originates in the upper 20 m of oxygenated water. Hypothetical coagulation and settling of the relatively high concentrations of DOC in the water column is thus of minor importance for the total flux of organic material to the sediments. As it was determined that insignificant mineralization occurs during passage of the water column (Næs et.al, 1988) the cause of high DOC concentrations in the bottom waters is likely due to mineralization occurring in the sediments, followed by diffusion out into the overlying water. This is also obvious from observed depth distributions of silica and alkalinity in the water column (Skei, 1986). The mineralization of organic matter in the sediments is also obvious from an LOI depth profile (fig. 5) where it may be estimated that the annual loss of organic material is in the order of 200 mg m⁻², when assuming an annual sediment accumulation rate of 60 g m⁻².



Loss on ignition



Accumulation rates determined from the ²¹⁰Pb profiles have been calculated assuming a constant flux of material with constant concentration of ²¹⁰Pb, neither of which is true in reality, as has been observed from sediment trap data (Roos *et.al*, 1997). Over longer time scales, as those considered here, the average flux of material and of ²¹⁰Pb to the sediments may be assumed to be constant and average accumulation rates determined by the constant rate of supply model (Appleby and Oldfield, 1978) results in nearly the same accumulation rates as those determined by a constant flux, constant concentration model.





²¹⁰Pb inventories found in the sediments are typical for the expected results in these parts of the world (Appleby and Oldfield, 1992). The ²¹⁰Pb inventories corresponds to annual fluxes of 114, 102 and 198 Bq m⁻² for the cores PN 1801, PN 1230 and PN 288 respectively. PN 288, has roughly a twice as high inventory of all the elements listed than compared with the deeper cores. The explanation to this seems to be the higher total flux of material to this station, which is situated around 4 km south from the other deeper stations. It is possible that sediments here are influenced by the suspended load carried by the incoming Helvik fjord water. This water is denser than the Framvaren surface water and initially follows the bottom topography, where it may resuspend the soft sediments before interleaving in to depths in Framvaren corresponding to the salinity of the mixed water. Resuspended matter may in any

way not constitute any substantial contribution to the 80 m station as the laminations were as clearly visible here as at the other stations.

When examining the data in figure 7 it is obvious that the concentrations of plutonium in the sediments are extremely high, roughly a factor ten higher than in other coastal sediments in the marine environment only exposed to bomb test fallout, but comparable to levels found in top sediments in the Black Sea (Buesseler and Benitz, 1994). The reasons for the high concentrations are of course to be found in the low mass accumulation rate which in turn is due to the minimal inflow from other water bodies (fresh as well as marine). Settling material is for that reason strongly dependant on the biological production rate in the 18 m oxic water mass and the efficiency for scavenging of actinides and many other metals by planctonic material is well known (Fowler *et.al*, 1983). The integrated inventories for plutonium and americium in sediment and water of around 70 and 23 Bq m⁻² are roughly 50 % higher than expected from nuclear weapons test fallout only and may probably be explained by sediment transport from shallower areas in and around the fjord.



Figure 7. Depth distribution of ²³⁹⁺²⁴⁰Pu in Framvaren sediment cores collected in 1994-5.

Since the water column inventory has not changed significantly between 1989 and 1995 it is likely that the remobilised plutonium was released from the sediments during mineralization of easily degradable material and that the fraction remaining is associated to more refractory substances.

It is tempting to view the depth distribution profile in the water column as a result of pure diffusion out from the sediments and applying the expression for a substance diffusing out from a plane surface in to an infinite space (Crank, 1975).

$$C(z,t) := \frac{M}{2 \cdot \sqrt{\pi \cdot D \cdot t}} \cdot \exp\left[-\frac{(z)^2}{4 \cdot D \cdot t}\right]$$

where C(z, t) is the concentration (Bq m⁻³) of the diffusing substance at distance z (m) at time t (s) from the plane. M is the total amount of diffusing substance per surface area (Bq m⁻²), and D the diffusion constant (m² s⁻¹). Fitting the data from 1989 and 1994-95 respectively to this equation yields eddy diffusion coefficients for 1989 and 1995 of 65 and 80 m² y⁻¹ with inventories (M) of 26.2 and 35 Bq m⁻² respectively (R² = 0.98 and 0.99 respectively). It was assumed that all the diffusing substance was formed at the bottom in 1963 (giving diffusion times of 26 and 32 years respectively) and that subsequent accumulating sediment has not contributed to the water column inventory. The model results together with measured data are plotted in figure 8. As can be seen from the figure the model agrees fairly well with measured values even though the model is very simple. A full description of the dynamics of plutonium in the Framvaren water column at various water depths as well as vertical and horizontal eddy diffusion coefficients in the water column at various depths. It would also require knowledge of the flux of plutonium to the sediments from the anoxic water column.



Figure 8.

Comparison between measured plutonium concentrations in 1989 and 1995 and modelled using a single pulse release in 1963.

One of the main questions aimed to clarify during the Framvaren work was the 'speciation' of plutonium (and other actinides) in the water column. In order to determine this we used an ultrafiltration system and chemical methods sensitive to the oxidation state of plutonium. The results are seen in figure 9 and table 2.



10 kD UF Pu and Am

Figure 9.

Pu and Am retention in 10 kD UF experiments on Framvaren water from different depths.

Method	Adsorbed or extracted oxidation state	²³⁹⁺²⁴⁰ Ри [µВ l ¹]	Sum of fractions [µB l ¹]
LaF3 precipitate (10 l); TTA extracted (8 l) Not extracted (water phase)	Pu(III+IV) Pu(IV)	275±11 12±4 271±13	na - 283±15
Adsorbed on AG 1x4 , 8 M HCL. (3 l) Not adsorbed	Pu(IV,V,VI)	14±6 290±17	- 304±20

Table 3.

Results of experiments aimed at determining the oxidation state of plutonium in 0.22 μ m filtered bottom water (140-160 m) from Framvaren fjord. The concentration of ²³⁹⁺²⁴⁰Pu being about 295 μ Bq l⁻¹ in water in 1994.

From the UF and chemical speciation experiments it thus seems as if plutonium and americium to a large degree is associated to fairly large ($10 \text{ kD-}0.2 \mu m$) colloids and that plutonium is present in the Pu (III) valence state.

Several of our findings made in Framvaren during the latest 3-4 years are unique. The remobilisation of plutonium from the sediments in marine anoxic basins have been a special topic worldwide for the last 20 years but have never been possible to prove. In Framvaren we have for the first time been able to prove that remobilisation is occurring and we have also been able to determine and model the release rate which fits well with observed data. Further insight in the mechanisms governing plutonium behaviour in anoxic basins has come from ultrafiltration experiments. While earlier suggestions on the reasons for potential plutonium release from anoxic sediments were built on the process of reduction and subsequent release of iron- and manganese hydroxyoxides, acting as carrier phases for plutonium, the present data from Framvaren clearly shows that organic colloids are the main carrier particles. With chemical methods we have been able to determine that plutonium is present entirely in the trivalent state. This means that the knowledge of the oxidation state of plutonium by no means is indicative for its mobility. In well oxygenated waters reduced plutonium are considered to have a short residence time due to its tendency to hydrolyse and become scavenged by particulate material. An important question is thus why this is not happening in the permanent anoxic Framvaren fjord.

The answer to this question is that colloidal humic substances, originating from the breakdown of organic material, is not consumed by microbial life at the same rate in anoxic waters as in oxygenated waters. The consequence being high concentrations of refractory colloidal matter in anoxic waters which may exist for very long time. These colloids have a well documented high carrying capacity for actinides (actinide-humic/fulvic acid complex), especially tri- and tervalent actinides. The influence of iron or manganese oxyhydroxides thus are completely irrelevant in this case. The build-up of organic colloids in marine water starts as soon as oxygen are depleted and similar situations as in Framvaren may thus form in any marine basin containing sediments with a high fraction of organic matter. The stability of the watermass in Framvaren (the most stable recorded of all fjords in the world) indicate that permanent anoxic conditions must persist for several years with little or no water renewal in order to produce suitable conditions for actinide mobilisation from sediments.

The importance of the organic colloids as carrier phase for actinides are furthermore well shown in our data set for thorium isotopes in water and sediment. The naturally occurring thorium isotopes are excellent tracer isotopes for the particle reactive actinide elements of artificial origin (e.g. Pu and Am). The non-radiogenic ²³²Th is normally only found within the crystal lattice of mineral grains and very low concentrations are therfore found in a 'dissolved' (< 0.45 μ m) state in the world oceans. In Framvaren fjord the concentration of 'dissolved' ²³²Th are roughly 200 times higher than in other coastal areas. The remobilisationrate of ²³²Th from the laminated sediments have been quantified by analysing sediment pore water (by thermal ionisation mass spectrometry) profiles and the concentrations was found to be directly correlated to DOC concentrations. The dissolved (colloidal) organic material thus seems to have the possibility to mobilise even lattice held thorium.

Thorium in the water column is associated to the organic colloids in a way similar to plutonium and americium. The ratios between various thorium isotopes and plutonium or americium is nearly the same between particles, large and small colloids and surface sediments indicating the general non-specific adsorption capacity of these humic colloids with

actinides in the lower oxidation states. It should be mentioned that the actinides are nearly the only particle reactive elements which are remobilised from the Framvaren sediments. Other reactive trace metals are efficiently scavenged as sulphides.

Further unique data comes from our analysis of uranium behaviour. In all anoxic marine basins examined so far reduced uranium have never been observed. In Framvaren uranium seems to exist in two fractions, one reduced form associated to colloids and one oxidised form possibly present in the carbonate form (not verified). The presence of reduced uranium associated to organic colloids is noteworthy as this means that reducing waters by no means nessecary constitute a safe barrier for uranium metal dissolution as long as colloidal matter is present. A fact that also is known from ground water studies.

Framvaren fjord is a unique and excellent natural laboratory for studying the behaviour of various elements under permanent anoxic conditions. The need to better understand processes occurring in such environments are far from only being academic as the processes involved are generally occurring and may become noticed clearly in any aquatic environment where the organic loading becomes sufficiently high.

Gullmaren fjord

The actinide behaviour in this fjord on the Swedish west coast has been far less studied as it was early recognised that the residence time of water was to short to build up sufficiently high colloid concentrations. The Gullmarn fjord has an effective sill depth of 40 m and a maximum depth of about 120 m and is the only true fjord in Sweden. The water column in the Gullmarn fjord may generally be divided into three different water masses. The upper 10 meters consist of water affected by the Baltic surface current and normally has a salinity of 18-30 ‰. Below this water mass resides a layer of shallow Skagerrak water (30-34 ‰) and deeper than about 50 m lays the deep water with a salinity higher than 34 ‰ which originates in the deeper part of Skagerrak where cold and saline water enters from the Norwegian Trench and the North Sea. Normally the bottom water stays trapped in the fjord for 8-12 months, but is renewed in late winter/early spring.

Depth	¹³⁷ Cs [mBq/l]	
1 m	12.1±0.9	
20 m	$14.4{\pm}0.9$	
48 m	$9.8{\pm}0.8$	
90 m	11.6±0.7	

Table 4.

Depth distribution of ¹³⁷Cs in Gullmaren fjord in April 1995.

From measurments of surface sediments on cores collected at various depths the ¹³⁷Cs concentrations range from 40 to 60 Bq/kg.

Depth	Salinity	²³⁸ U [mBq/l]	²³⁴ Th [mBq/l]	Susp.load
	[‰]			[mg/l]
1 m	28.7	32.3	18	0.80
7 m	30.0	33.7	23	NA
20 m	32.1	36.1	28	1.34
48 m	32.9	37.0	28	0.71
90 m	34.3	38.6	34	0.78

Table 5. ²³⁴Th, ²³⁸U, salinity and suspended load concentrations in unfiltered water from the Gullmarn fjord in April 1995.

From the values given in table 5 the residence time of ²³⁴Th in surface waters may be calculated to be in the order of 40 days. It is also obvious that the residence time for particulate reactive substances in deeper layers are relatively short, at least compared with the Framvaren fjord where residence times in the order of thousand days was estimated from ²³⁴Th/²³⁸U disequilibria.

The plutonium concentrations in filtered water are between 5 and 9 μ Bq/l which are normal. The rather intense bioturbation in surface sediments furthermore ensures oxygenated conditions down to about 10 cm depth which means that sedimenting organic material are decomposed more completely than under anoxic conditions which results in less organic colloids. The bioturbation rate in Gullmaren fjord have been determined from a tracer experiment in the Kristineberg mesocosm facility. The results indicate that the bioturbation rate is so large that the upper 10 cm are homogenously mixed in a time period of 1-2 years meaning that a pulse input of contaminated sediments fairly quick would be distributed to large depths although the sedimentation rate is rather low (about 8 mm per year).

Co-58 KRISTINEBERG



Figure 10.

Depth distribution after 191 days of a ⁵⁸Co tracer carefully added to the surface sediments in the mesocosm facility at Kristineberg Marinebiological Station. Smearing effects from the insertion of the tubes in the sediments have been corrected for by removing the outer 1-2 mm of frozen sediments.

Mixing between seawater and freshwater at the Kalix river and estuary

The Kalix River is a relatively large unregulated river (catchment area 23600 km², average water discharge 300 m³/s) situated within the boreal zone, in the northern part of Sweden. The water discharge is almost constant at approximately 50 m³/s during winter baseflow (December-April), when the river is ice-covered. In mid May most of the snowpack melts in the lower part of the catchment and the discharge increases to a maximum around 1500 m³/s.

The Kalix river is draining in to the north part of the Baltic Sea, the Bothnian Bay. This part of the Baltic Sea is especially interesting as the salinity in this region is only between 0-3%. This is thus the region where the limnic waters enters salt water and mix. It is well known from laboratory studies that flocculation and desorption phenomena occurs under such mixing but the salinity required for observing actual effects on dissolved and particulate matter have been unclear. Many reports conclude that few, if any, effects are seen below 5 ‰. Studies in the Kalix River shows that little, if any, coagulation of Fe, Si or humic substances occur within the 3 ‰ zone

During spring discharge in mid May the concentrations of 137 Cs is about 3 times higher than during the rest of the year (3 Bq/m³ as compared to 1 Bq/m³) in spite of an increased water volume discharge by a factor 10-15. Thus the radiocesium is not, in contrary to many other elements, diluted during spring discharge. Approximately 50-60% of the annual radiocesium discharge comes during May-June. The fraction of particle associated (1 µm) radiocesium ranges between 10-25%. The increase in radiocesium during spring discharge may probably be attributed to the increased water flow through otherwise poorly drained areas, such as mires. This has in part been confirmed by the analysis of radiocesium in tributaries draining mire rich areas. The radiocesium concentration in these were 2-3 times higher than in the Kalix River for the same time period. The Chernobyl radiocesium constitutes approximately 80% of the total 137 Cs.

Comparing discharged ¹³⁷Cs with the sedimentary inventory in the estuary is not straightforward as the sediments recieves radiocesium from both the river and the Bothnian Bay waters. The latter at concentrations far higher (30-50 Bq/m³) than the river concentrations. The integrated deposition of bombtest radiocesium in the analysed sediment cores does not show any enrichment as comparedd to tabulated fall-out levels at these latitudes (approximately 3500 Bq/m²).



Cs-137 Kalix Estuary Sediments

Figure 11. ¹³⁷Cs in Kalix estuary sediments.





Figure 12. ²³⁹⁺²⁴⁰Pu in Kalix estuary sediments.

The plutonium concentrations in the river are slightly higher during low water discharge than during spring discharge, 3-3.5 mBq/m³ as compared to 2.4-2.7 mBq/m³. In spite of the the lower concentrations during spring discharge roughly 30% of the annual plutonium output comes in May, 10-20% of this is associated to particles larger than 1 μ m. Assuming 80% of discharged Pu to be in the colloidal form it is interesting to note that an inventory calculation results in that more than 80% is trapped within the estuary despite the salinity endmember being only 3 ‰. No fractionation between Pu and Am has been observed. A plot of the Pu depth distribution in the estuary is given in fig 12. The inventory in this core was 245 Bq/m². Integrated ²¹⁰Pb_{xs} in the same core corresponded to an annual input of 320 Bq/m² which is approximately three times the expected.

References

Alberts, J.J., M.A. Wahlgren, D.M. Nelson and P.J.Jehn (1977). Submicron particle size and charge characteristics of ^{239,240}Pu in natural waters. *Environ. Sci. Technol*, 11: 673-676.

Alberts, J.J. and Orlandini, K.A., (1981). Laboratory and field studies of the relative mobility of $^{239+240}$ Pu and 241 Am from lake sediments under oxic and anoxic conditions. *Geochim. Cosmochim. Acta*, 45: 1931-1940. Appleby, P. G. and F. Oldfield, (1978). The calculation of 210 Pb dates assuming a constant rate of supply of unsupported 210 Pb to the sediments. *Catena*, 5: 1-8.

Appleby, P. G. and F. Oldfield, (1992). Application of Lead-210 to Sedimentation Studies. <u>In</u>: "Uranium-series Disequilibrium", 2:nd edition, 1992. (Ed., Ivanovich, M and R. S. Harmon). Oxford Science Publications.

Bowen, V.T., V.E. Noshkin, H.D. Livingston, and H.L Volchok (1980). Fallout radionuclides in the Pacific Ocean: vertical and horizontal distributions, largely from Geosecs stations. *Earth Planet. Sci. Lett.*, 49: 411-434.

Buesseler K.O., G. Benoit and E. R. Sholkovitz (1985) A Pore Water Study of plutonium in a seasonally anoxic lake. *J. Environ. Radioactivity*, 2:283-292.

Buesseler, K. O. (1986). Plutonium isotopes in the North Atlantic. PhD Thesis, WHOI-86-32. WHOI-MIT joint programme in oceanography, Woods Hole, MA.

Buesseler K.O. and C.R. Benitz (1994) Determination of mass accumulation rates and sediment radionuclide inventories in the deep Black Sea. *Deep-Sea Research*, 41:1605-16015.

Carpenter R.and T.M. Beasley, D. Zahle and B.L.K. Somayajulu (1981) Plutonium and americium in anoxic marine sediments: Evidence against remobilization. *Geochimica et Cosmochimica Acta*, 45: 1917-1930. Carpenter, R. and T.M. Beasley (1981). Plutonium and americium in anoxic marine sediments: evidence against remobilization. *Geochim. Cosmochim. Acta*, 45: 1917-1930.

Cochran, J.K., (1985). Part1cle mixing rates in sediments of the eastern equatorial Pacific: Ev1dence from ²¹⁰Pb, ^{239,240}Pu and ¹³⁷Cs distributions at MANOP sites. *Geochimica et Cosmochima Acta*. 49: 1195-1210. Crank, J., (1975). The Mathematics of Diffusion., 2nd ed. Clarendon Press.

Crusius J. and R.F. Anderson (1991) Immobility of ²¹⁰Pb in Black Sea Sediments. *Acta Geochimica et Cosmochimica*, 55: 327-333.

Falkner K.K, G.P. Klinkhammar, T.S. Bowers, J.F. Todd, B.L. Lewis, W.M. Landing, and J.M. Edmond (1993) The behavior of barium in anoxic marine waters. *Geochimica et cosmochimica Acta*,57: 537-554. Fowler S.W., S.Ballestra, J. La Rosa and R. Fukai (1983) Vertical transport of particulate-associated plutonium and americium in the upper water column of the Northern Pacific. *Deep-Sea Research*, 30 (12A):1221-1233.
Grasshoff K. (1975) The hydrochemistry of landlocked basins and fjords. Chapter 15. <u>In:</u> The Chemical Oceanography, Vol. 3, Academic Press. J.P. Riley and R. Chester (Ed's).

Gross, M.G., S.M. Gucluer, J.S. Creagaer, and W.A. Dawson (1963). Varved marine sediments in a stagnant fjord. *Science*, 141: 918-919.

Hay B.J., S. Honjo, S.Kempe, V. A. Ittekkot, E.T. Degens, T. Konuk and E. Izdar (1990) Interannual variability in particle flux in the southwestern Black Sea. *Deep-Sea Research*, 37 (6): 911-928.

Heatherington, J.A., D.F. Jeffries, and M.B. Lovett (1975) Some investigations into the behaviour of plutonium in the marine environment. <u>In</u> Impacts of Nuclear Releases into the Aquatic Environment. IAEA Symp., (SM-198/29), pp 193-212.

Huh C-A., J.M. Kelley, J.W. Murray and C.-L. Wei (1994) Water column distribution of ²³⁰Th and ²³²Th in the Black Sea. *Deep-Sea Research*, 41(1):101-112.

Koide, M., J.J. Griffin, and E.D Goldberg, (1975). Records of plutonium fallout in marine and terrestrial samples. I. *Geophys. Res.*, 80: 4153-4162. Koide, M. an E.D. Goldberg (1982). Transuranic nuclides in two coastal marine sedimets off Peru. *Earth Planet. Sci. Lett.*, 57: 263-277.

Li, Y.-H. and S. Gregory (1974). Diffusion of ions in seawater and in deep-sea sediments. *Geochim. et Cosmochimica Acta*, 38: 703-714. Livingston, H.D. and V.T Bowen, (1979). Pu and ¹³⁷Cs in coastal sediments. *Earth Planet. Sci. Lett.*, 43: 29-45.

Livingston H.D., D.R. Mann, S.A. Casso, D.L. Schneider, L.D. Surprenant, V.T.Bowen (1987) Particle and solution phase depth distributions of transuranics and ⁵⁵Fe in the North Pacific. *J. Environ. Radioactivity*, 5: 1-24.

Livingston, H.D., K.O. Buesseler, E. Buesseler, E. Izdar and T. Konuk (1988). Characteristics of Chernobyl fallout in the southern Black Sea. <u>In:Radionuclides: a tool for oceanography</u>, J.C. Guary, P. Guegueniat and R.J. Penetreath (Ed.'s), Elsevier, Barking, U.K.: 304-316.

Matsumoto, E. and C.S. Wong (1977). Heavy metal sedimentation in Saanich Inlet measured with ²¹⁰Pb technique. *J.Geophys. Res.*, 82:5477-5482.

Næs, K., J. M. Skei and P. Wassman, (1988). Total particulates and organic fluxes in anoxic Framvaren waters. *Marine Chemistry*, 23: 257-268.

Nelson, D.M. and M.B. Lovett, (1981). Measurement of the oxidation state and concentration of plutonium in interstitial waters of the Irish Sea. <u>In</u>: "Impacts of Radionuclide Releases into the Marine Environment". IAEA Symp., Vienna, 1980.

Nelson, D.M., E.A. Carey and V.T. Bowen (1984). Plutonium oxidation state distributions in the Pacific Ocean during 1980-1981. *Earth Planetary Sci. Letters*, 68: 422-430.

Noshkin, V.E., Transuranium Radionuclides in Components of the Benthic Environment of Enewetak Atoll. <u>In:</u> Transuranic elements in the envionment, W.C. Hanson (Ed.) Technical Information Center/ U.S. Department f Energy.

Roos, P., J. Skei and E. Holm, (1997a). Annual variability of ²¹⁰Pb and ¹³⁷Cs flux in a superanoxic fjord. Manuscript in preparation.

Roos P.,E.Holm, D.Josefsson and M.Eriksson (1997b) Remobilisation of Plutonium and Americium from the sediments in an anoxic fjord:
Framvaren fjord, Southern Norway. Submitted to *Marine Chemistry*.
Ross D.A. and E.T. Degens (1974). Recent sediments of Black Sea. In:
E.T. Degens and D.A.Ross (Editors) The Black Sea- Geology, Chemistry and Biology, Vol. 20, American Association of Petroleum Geologists, Mem.: 183-199.

Sanchez A.L., J.W. Murray, W.R.Schell and L.G. Miller (1986) Fallout plutonium in two oxic-anoxic environments. *Limnol. Oceanogr*, 31(5):1110-1121.

Sanchez A L., J. Gastaud, V. Noshkin and K.O Buesseler (1991) Plutonium oxidation states in the southwestern Black Sea: Evidence regarding the origin of the cold intermediate layer. *Deep-Sea Research*, 38 suppl 2: S845-S853.

Sanchez, A. L., J. Gastaud, E. Holm and P. Roos, (1994). Distribution of plutonium and its oxidation states in Framvaren and Hellvik fjords, Norway. *J. Environ. Radioactivity*, 22:205-217.

Schell, W.R. F.G. Lowman, and R.P. Marshall (1980).Geochemistry of Transuranium Radionuclides at Bikini Atoll. <u>In:</u> Transuranic elements in the envionment, W.C. Hanson (Ed.) Technical Information Center/U.S. Department f Energy.

Sholkovitz, E.R., A. Carey and J. K. Cochran, (1982). The aquatic chemistry of plutonium in seasonally anoxic lake waters. *Nature*, 300: 159-161.

Sholkovitz E.R. (1983) The geochemistry for plutonium in fresh and marine water environments. *Earth-Science Reviews*, 19: 95-161.

Sholkovitz, E.R. and D. R. Mann, (1984). The pore water chemistry of ²³⁹⁺²⁴⁰Pu and ¹³⁷Cs in sediments of Buzzards Bay, Massachusetts. *Geochimica et Cosmochimica Acta*, 48: 1107-1114

Skei, J. (1983). Geochemical and sedimentological considerations of a permanently anoxic fjord-Framvaren, south Norway. *Sedimentary Geology*, 36 131-145.

Skei, J. (1986). The Biogeochemistry of Framvaren. Data report 1931-1985. Norwegian Institute for Water Research (NIVA). ISBN 82-577-1140-3.

Stigebrandt, A. and J. Molvær, (1988). On the water exchange of Framvaren. *Marine Chemistry*, 23: 219-228.

Stordal, M.C., J.W. Johnson, N.L. Guinasso, Jr. and D.R. Schink, (1985). Quantitative evaluation of bioturbation rates in deep ocean sediments. II. Compar1son of rates determ1ned by ²¹⁰Pb and ^{239,240}Pu. *Marine Chemistry*. 17: 99-114.

Strpm, K.M. (1936). Land-locked waters. Hydrography and bottom deposits in badly-ventilated Norwegian fjords with remarks upon sedimentation under anaerobic conditions. *Skr. Nor. Vidensk. Akad.* Oslo,7: 85.

Wahlgren, M.A., Alberts, J.J., Nelson, D.M., Orlandini, K.A. and Kucera, E.T., (1977). Study of the occurrence of multiple oxidation states of plutonium in natural water systems. Argonne Natl. Lab. Annu. Rep., ANL-77-65, part III: 95-98.

Behaviour of radionuclides in sedimentation processes under varying redox conditions

Erkki Ilus, Tarja K. Ikäheimonen, Jukka Mattila and Seppo Klemola STUK-Radiation and Nuclear Safety Authority, Finland

Introduction

The sedimentary behaviour of radionuclides, especially caesium and plutonium, under anoxic conditions at the water/sediment interface has been discussed in many scientific papers. Varying redox conditions may affect the occurrence and concentrations of certain radionuclides in the surface layers of sediments and in near-bottom waters by causing remobilization of radionuclides from surface sediments to the overlying water and their settling back into the sediment.

Inventories made after the Chernobyl accident have shown that about 1.4 PBq of Cs-137 and 18 TBq of Pu-239,240 are bound in Baltic Sea sediments (Ilus et al.,1995). In recent decades about 70.000 km² of the sea bottom in the deepest part of the Baltic Sea (about 19% of its total area) have withstood almost continuous anoxic conditions; thus, it is important to know to what extent depletion of oxygen can affect the behaviour of these radionuclides in near-bottom waters.

The aim of the present project was to resolve the above question in a coastal basin periodically undergoing anoxic conditions. The project was undertaken by the NPP Environmental Laboratory of the Finnish Centre for Radiation and Nuclear Safety (STUK).

Study Area

Radioecological processes in sediments and in near-bottom water under varying redoxconditions were studied in the deep area of the Hästholmsfjärden Bay in Loviisa (eastern Gulf of Finland). The Hästholmsfjärden Bay is a semienclosed basin between the mainland and the archipelago and is connected with the open Gulf of Finland only through narrow, shallow sounds (Fig. 1). The mean depth of the deep area of Hästholmsfjärden is about 15.5 m and the maximum depth 18.1 m; the bottom zone deeper than 15 m covers an area of 175 000 m².

Poor exchange of water in the Hästholmsfjärden Bay coupled with thermal discharges from the Loviisa NPP, situated on the west side of the bay, have resulted in disturbance in the oxygen balance of the basin. These low oxygen concentrations have subsequently resulted in strong remobilization of phosphorus and nitrogen from sediment to water. Total phosphorus concentrations have been as much as 40 times higher in the hypolimnion than in the epilimnion of Hästholmsfjärden Bay, and high concentrations have also been observed in surface water. In addition, slight indications of remobilization of certain radionuclides were found during 1983-1984 when preliminary experiments were performed, although total depletion of oxygen did not occur during that period in the deep area (Ilus et al, 1985).



Figure 1. Hästholmsfjärden, discharge area of the Loviisa NPP and site of the sampling station in the southeast part of the bay. The bathymetric map was published by Launiainen (1977).

Material and Methods

Sampling

The project has proceeded according to schedule. Oxygen, total phosphorus and total nitrogen concentrations, as well as temperature, salinity and pH of the water were monitored in the Hästholmsfjärden deep during May-October in 1995 and 1996. The samples were taken with a Limnos water sampler (volume 2 l) from 0.5 m above the bottom.

In 1995, water samples were taken 5 times for radionuclide analyses with a submerged pumphose system from 0.5 m above the bottom. One part of the water sample was taken directly as raw water, the other part was filtered through 0.45-mm membrane filters (diameter 239 mm). The volumes were 30/100 l (raw/filtered) for gamma nuclide analyses and 100/200 l for plutonium analyses. During the sampling the STUK research boat was moored to a buoy anchored permanently at the site. Sediment samples were taken with a GEMINI Twin Corer immediately after the water samples. Four parallel tubes (2 hauls) were taken and the cores were sliced in 1-cm slices down to a depth of 10 cm. The parallel slices were frozen and freeze-dried before analysis.

In 1996, the aim was to determine the vertical distribution of Cs-137 in the water column at different sampling times, fluctuation of Pu-239,240 activity in near-bottom water and the impact of particles on the observed activities. Samplings were performed 6 times during the season, of which 3 were focused on anoxic periods. Water samples for radionuclide analyses were taken with a the Limnos water sampler from 1 and 0.3 m above the bottom and from the surface water. In addition, some water samples were taken by siphon just above the sediment surface from the coring tubes of the GEMINI corer. The volumes of the samples were generally 3 l for the caesium analyses (1 l in some cases) and 10-70 l for the plutonium analyses. One part of the water samples were taken with 3 alternative corers (Gemini, STUK or Limnos) and the cores were sliced into 1-cm slices down only to a depth of 2 cm.

Analyses

Before measuring by gamma-ray spectrometry the water samples were evaporated to more concentrated volumes. Sediment samples were freeze-dried and homogenized before analyses. Membrane filters were air-dried and pressed into a geometry suitable for gamma-ray measurement. Gamma-ray spectra were measured with high-purity germanium detectors in low-background shields (Rantavaara et al, 1994).

Water samples were analysed for the presence of plutonium by coprecipitating plutonium from the water with hydroxides. Plutonium was then separated by anion exchange and electrodeposited on a stainless-steel disc. Sediment samples and membrane filters were wet-ashed and acid-leached with strong acids before anion exchange. Plutonium activities were measured with an alpha-spectrometer and a multichannel analyser. Pu-242 was used as a tracer (Taipale and Tuomainen 1985).

Results and Discussion

Oxygen conditions and nutrients

In 1995, total depletion of oxygen occurred in the hypolimnion of Hästholmsfjärden Bay during 2 periods in late summer and autumn (August 16-24 and September 13-28). During these periods total phosphorus and total nitrogen concentrations in the near-bottom water increased to their highest levels of 440 mgP m⁻³ and 1355 mgN m⁻³, while the corresponding values in surface water were 37 mgP m⁻³ and 660 mgN m⁻³.

In 1996, oxygen conditions were the worst ever observed in the Hästholmsfjärden deep. During early autumn (August 20-September 24) anoxic conditions prevailed for more than 1 month in the near-bottom water. In addition, a short anoxic period occurred in early August. The highest total phosphorus and total nitrogen concentrations in the near-bottom water during these periods were 860 mgP m⁻³ and 2320 mgN m⁻³. Contrary to all expections, no depletion of oxygen occurred in 1997, although the summer was warmer than normally; therefore, samplings were not performed during autumn 1997.

Cs-137 and Pu-239,240 in near-bottom water and surface sediments

This consideration is based only on the most representative samples taken during the project; however, the remaining samples will most probably not change the conclusions made here.

Cs-137 and Cs-134 were the only artificial gamma-ray nuclides detected in the water samples. No increase of the caesium isotopes or Pu-239,240 could be observed in unfiltered nearbottom water during the anoxic periods in 1995 or in 1996 (Figs. 2 and 3). The variability in concentrations was covered by the measurement errors; thus, it was obvious that remobilization of Cs-137 and Pu-239,240 from sediment to water was negligible, if any. This was confirmed by the fact that no unambiguous difference was noted between the surface and near-bottom concentrations. In some cases the surface water concentrations were even higher than in the near-bottom water, which may be due to the exchange of surface water in the area.

The amounts [Bq m⁻²] of Cs-137 and Pu-239,240 in surface sediments are shown in Figs 4 and 5. It was necessary to plot the amounts against the mass depth, because when concentrations of these nuclides in the 0-1-cm slices of the surface sediments were compared, considerable variations were found. This was due to varying degrees of compaction between the samples taken at different times from the very soft bottom typical of the sampling site. To be able to consider differences between sampling times, amounts of radionuclides at the same mass depths should be compared.

In 1995, no differences related to the anoxic periods were observed in the amounts of Cs-137 or Pu-239,240 in surface sediments (Ikäheimonen et al., 1997). In 1996, however, a slight indication of reduced amounts of Cs-137 could be seen in the surface sediment taken on August 2 and 23 (Fig. 5). On the other hand, these slight differences may also have been due to sources of error included in sediment sampling (cf. Ilus 1996).



Figure 2. Activity concentrations of Cs-137 [Bq m⁻³] and Pu-239,240 [mBq m⁻³] in unfiltered surface and near-bottom water, as well as the concentrations of oxygen [ml l⁻¹] in near-bottom water detected in samples taken at Station LOV3a in 1995.



Figure 3. Activity concentrations of Cs-137 [Bq m⁻³] and Pu-239,240 [mBq m⁻³] in unfiltered surface and near-bottom water, as well as the concentrations of oxygen [ml l⁻¹] in near-bottom water detected in samples taken at Station LOV3a in 1996.



Figure 4. Amounts of Cs-137 and Pu-239,240 [Bq m⁻²] in the uppermost sediment layer in relation to the mass depth [kg m⁻²] at Station LOV3a in 1995. The oxygen concentrations [ml l⁻¹] on various sampling dates are given in parentheses.



Figure 5. Amounts of Cs-137 [Bq m⁻²] in the uppermost sediment layer in relation to the mass depth [kg m⁻²] at Station LOV3a in 1996. The oxygen concentrations [ml l⁻¹] on various sampling dates are given in parentheses. Two parallel samples (a and b) were taken on August 2, 1996.

Conclusions

According to the results obtained in this project, remobilization of Cs-137 and Pu-239,240 from sediments to near-bottom water is negligible or nonexistent in the Hästholmsfjärden deep. If it does occur, however, it may be so slight that it is not possible to observe with the methods used here.

The anoxic periods are quite short in the Hästholmsfjärden deep; however, they are of sufficient length for strong remobilization of nutrients. If the initiation of remobilization processes in the case of caesium or plutonium were retarded, then the situation may be different in the deep areas of the Baltic Sea where depletion of oxygen has been almost continuous.

Acknowledgements

The project was financially supported by Nordic Nuclear Safety Research

References

Ikäheimonen TK, Mattila J, Klemola S and Ilus E, 1997. A study on the behaviour of caesium and plutonium in the sedimentation process under varying redox-conditions. In: Walderhaug T., Gudlaudsson P.A. (eds), Proceedings of the 11th Ordinary Meeting of the Nordic Radiation Protection Society and the 7th Nordic Radioecology Seminar, Reykjavik, 26-29 August 1996. Geislavarnir rikisins, Reykjavik.

Ilus E. Evaluation of sediment sampling devices and methods used in the NKS/EKO-1 project. Report NKS/EKO-1(96)TR-1. Nordic nuclear safety research, Risö.

Ilus E, Niemistö L and Bojanowski R, 1995. Radionuclides in sediments and suspended particulate matter. In: Radioactivity in the Baltic Sea 1984-1991. Baltic Sea Environment Proceedings No.61: 69-92. Baltic Marine Environment Commission - Helsinki Commission, Helsinki.

Ilus E, Ojala J, Saxen R, Sjöblom K-L, Tuomainen K, 1985. Radionuliders mobilisering ur sediment under varierande redox-förhållanden vid Hästholmsfjärdens fördjupning i Lovisa. Det fjärde nordiska radioekologiseminriet, Gol, Norge.

Launiainen J, 1977. Studies on energy exchange between the air and the sea surface on the coastal area of the Gulf of Finland. Finnish Marine Research 246: 3-110, Helsinki.

Rantavaara A, Klemola S, Saxen R, Ikäheimonen TK, Moring M, 1994. Radionuclide analysis of environmental field trial samples at STUK. Report STUK-YTO-TR 75, Helsinki.

Taipale T.K and Tuomainen K, 1985. Radiochemical determination of plutonium and americium from seawater, sediment and biota samples. Report STUK-B-VALO 26, Helsinki.

Sedimentation rate in the Baltic Sea

Erkki Ilus¹, *Jukka Mattila¹*, *Seppo Klemola¹*, *Tarja K. Ikäheimonen¹ and Lauri Niemistö²* ¹STUK-Radiation and Nuclear Safety authority, Finland, ²Finnish Institute of Marine Research

Introduction

Determination of sedimentation rates plays an important role in material balance and model calculations of seas and other bodies of water. The Baltic Sea offers an exceptionally good opportunity to study processes in sediments and sedimentation rates with radioecological methods, because the concentration peak of Pu-239,240 caused by nuclear weapons tests during the 1960s and the Cs-137 peak caused by the Chernobyl accident in 1986 are easily detectable in corresponding layers of its bottom sediments. In addition, the rate of sedimentation is much higher in the Baltic Sea than in the oceans and in most other coastal seas, and the lack of benthic animals in large bottom areas, due to the poor oxygen conditions there, results in the formation of an undisturbed sedimentary package, enabling the sampling of sediment laminae in an undisturbed historical order.

A considerable fraction of radioactive substances, once entering a body of water, is adsorbed over time onto suspended particulate material and deposited in sediments. With the passage of time, this material is covered by fresher particles, and the contaminated particles are buried in deeper sediment layers. After accidents or fallout situations, it may be necessary to know how rapidly the released radionuclides are buried so deeply in the sediment that they can no longer take part in chemical processes at the sediment surface or are no longer available for benthic organisms in the contaminated area. Furthermore, it is important to know the quantities and variability of radionuclides in Baltic Sea sediments.

Traditionally, sedimentation rate has been evaluated with the Pb-210/Po-210 method; however, the results obtained with this method have often deviated from those evaluated on the basis of the Pu and Cs peaks. The aim of the present project has been to evaluate sedimentation rates in various parts of the Baltic Sea by using alternative methods and to consider reasons for eventual differences in results. At the same time, we have aimed at obtaining a reliable picture of the variability of sedimentation rate in the Baltic Sea.

Material and Methods

Sampling

The project proceeded according to schedule; most of the samplings were performed in 1995 and 1996 aboard the RV ARANDA of the FIMR (Table I, Fig. 1). The samples at Loviisa and Olkiluoto were taken using the STUK research boat.

In 1995, sediment samples were taken at 8 stations in the Gulf of Finland and at Olkiluoto. The samples were taken with a GEMINI Twin Corer, such that 4 parallel tubes (2 hauls) were taken at every station. The cores were sliced into 1-cm slices down to a depth of 20 cm; in addition, five 1-cm slices were taken randomly between depths of 20 and 33 cm. The parallel slices were combined and the samples were frozen and freeze-dried before analysis.

In 1996, samples were taken on 3 cruises of the RV ARANDA from 43 sampling stations situated in the Baltic Proper, Bothnian Bay, Bothnian Sea and Gulf of Finland. The samples were taken with the GEMINI Twin Corer, as before, but only 1 core was sliced for analyses. This enabled us to accelerate sample pretreatment and made sampling possible at an additional number of stations. The cores were sliced into 1-cm slices down to depths of 16-20 cm (8 stations) or to 10 cm (35 stations); the rest of the core was sliced at 2-cm intervals to a depth of about 30 cm.

Table I. List of sampling stations in 1995 and 1996.

The Only of	j Domma			
Station	Date	Lat N	Lon E	Depth m
C VI	17.6.1996	65°14.02'	23°34.05'	68
C V	17.6.1996	64°59.99'	23°14.99'	87
RR3	17.6.1996	64°56.00'	22°21.00'	94
RR6	17.6.1996	64°47.99'	23°28.99'	85
F9	18.6.1996	64°42.00'	22°04.00'	122
BO3	17.6.1996	64°18.02'	22°21.05'	109
SM3	18.6.1996	63°59.00'	21°45.98'	78
F15	16.6.1996	63°31.00'	21°31.05'	48
F18	16.6.1996	63°19.01'	20°17.03'	105
US6b	18.6.1996	62°35.99'	20°15.98'	82
US5b	18.6.1996	62°35.18'	19°58.22'	209
OLK12	28.6.1995	61°13.90'	21°23.00'	16
SR5	15.6.1996	61°05.03'	19°35.00'	125
SR6	19.6.1996	61°03.05'	20°16.01'	102

The Gulf of Bothnia

The Gulf of Finland

Station	Date	Lat N	Lon E	Depth m
F41	25.4.1995	60°07.04'	28°03.86'	51
F42	13.6.1996	60°08.00'	27°28.03'	63
XV1	26.4.1995	60°15.00'	27°15.03'	64
LOV3A	8.6.1995	60°22.20'	26°23.10'	18
LL3a	12.6.1996	60°04.05'	26°20.98'	68
LL4a	13.6.1996	60°00.96'	26°04.50'	66
GF2	27.4.1995	59°50.30'	25°51.60'	84
LL 6a	27.5.1996	59°54.88'	25°02.17'	72
GF1	28.4.1995	59°42.30'	24°41.11'	83.5
JML	29.4.1995	59°34.90'	23°37.80'	80
LL11	14.6.1996	59°34.99'	23°18.08'	68
HankoBay	17.8.1995	59°50.60'	22°54.18'	74
LL 12	28.5.1996	59°29.00'	22°54.00'	82

The Baltic Proper

roper			
Date	Lat N	Lon E	Depth m
14.6.1996	59°46.92'	19°56.02'	189
2.6.1996	59°11.00'	21°45.01'	130
28.5.1996	58°00.61'	19°54.00'	195
28.5.1996	57°59.50'	20°25.01'	101
29.5.1996	57°59.00'	21°05.00'	81
29.5.1996	57°19.00'	20°02.01'	237
29.5.1996	57°18.01'	20°32.00'	115
30.5.1996	56°56.21'	18°49.61'	87.5
30.5.1996	56°56.30'	19°48.60'	178
31.5.1996	56°57.00'	20°16.00'	133
31.5.1996	56°57.01'	20°24.60'	86
1.6.1996	56°29.51'	18°50.03'	99
31.5.1996	56°29.00'	19°34.00'	144
31.5.1996	56°29.00'	19°58.00'	102
1.6.1996	55°32.99'	18°24.00'	90
	Date 14.6.1996 2.6.1996 28.5.1996 29.5.1996 29.5.1996 29.5.1996 30.5.1996 30.5.1996 31.5.1996 31.5.1996 31.5.1996 31.5.1996 31.5.1996 31.5.1996 31.5.1996 31.5.1996 31.5.1996 31.5.1996 31.5.1996 31.5.1996	Date Lat N 14.6.1996 59°46.92' 2.6.1996 59°11.00' 28.5.1996 58°00.61' 28.5.1996 57°59.50' 29.5.1996 57°59.00' 29.5.1996 57°19.00' 29.5.1996 57°19.00' 29.5.1996 57°19.00' 29.5.1996 57°56.21' 30.5.1996 56°56.21' 30.5.1996 56°57.00' 31.5.1996 56°57.00' 31.5.1996 56°29.00' 31.5.1996 56°29.00' 31.5.1996 56°29.00' 31.5.1996 56°29.00' 31.5.1996 56°29.00' 31.5.1996 56°29.00' 31.5.1996 56°29.00' 31.5.1996 56°29.00'	DateLat NLon E14.6.199659°46.92'19°56.02'2.6.199659°11.00'21°45.01'28.5.199658°00.61'19°54.00'28.5.199657°59.50'20°25.01'29.5.199657°59.00'21°05.00'29.5.199657°19.00'20°02.01'29.5.199657°18.01'20°32.00'30.5.199656°56.21'18°49.61'30.5.199656°56.30'19°48.60'31.5.199656°57.00'20°16.00'31.5.199656°29.51'18°50.03'31.5.199656°29.00'19°34.00'31.5.199656°29.00'19°58.00'1.6.199655°32.99'18°24.00'

Stations in special studies of sedimentation basins

Suutons in s	speciai siaaies	o oj seuimenio	anon busins	
Station	Date	Lat N	Lon E	Depth m
LL17	23.4.1996	59°02.16'	21°04.84'	173
LL17 A	23.4.1996	59°02.17'	21°05.21'	180
LL17 B	23.4.1996	59°02.16'	21°05.17'	180
LL17 C	23.4.1996	59°02.16'	21°05.14'	180
JML	24.4.1996	59°34.92'	23°37.79'	80
JML A	24.4.1996	59°34.90'	23°37.78'	80
JML B	24.4.1996	59°34.90'	23°37.72'	80
JML C	24.4.1996	59°34.87'	23°37.64'	80
GF2	27.4.1995	59°50.30'	25°51.60'	84
GF2 D	26.4.1996	59°50.47'	25°52.48'	84

Stations in special study of the River Neva estuary

Station	Date	Lat N	Lon E	Depth m
SL2	14.5.1996	60°03.52'	29°11.94'	28
SL6	15.5.1996	60°07.95'	28°38.83'	39
SL8	16.5.1996	60°14.49'	28°23.49'	38
SL11B	17.5.1996	60°13.99'	27°43.29'	50



Figure 1. Location of the sampling stations in 1995 and 1996. Local variability of sedimentation rate was studied in 3 sedimentation basins indicated with squares. The stations situated in the estuary of the Neva River are not shown in the map.

Analyses

The total number of vertically sectioned sediment slices was about 1200. The samples were analysed gammaspectrometrically for the presence of Cs-137 and Pb-210; about 80 samples were analysed separately for Po-210 and about 90 for Pu-239,240. In the initial phase of the project an application was developed for Pb-210 determination from gamma-ray spectra (Klemola et al., 1997). The application proved to be very useful, and it has significantly reduced the workload of the project by enabling us to substitute the traditional Po-210 method with gamma-ray analysis. When developing the gammaspectrometric application, Pb-210 activities were measured at 3 stations by using the traditional Po-210 method (e.g. Häsänen, 1977) modified at our laboratory, and these results were compared with those obtained by gamma-ray spectrometry.

The Pb-210 activities were analysed by gamma-ray spectrometry, accounting for the selfabsorption of gamma rays in samples of varying density and height (Klemola op cit.). When the unsupported part of Pb-210 was calculated, Ra-226 activity (supported Pb-210) was subtracted from the total Pb-210 activity measured. Ra-226 activities were obtained using the Bi-214 (609.3 keV), Pb-214 (295.2 keV) and Pb-214 (351.9 keV) photon intensities measured by gamma-ray spectrometry. Pu analyses were performed according to the method of Taipale and Tuomainen (1985), and Cs-137 was measured by gamma-ray spectrometry at the same time as the Pb-210 and Ra-226.

Determination of sedimentation rate

Pb-210-based methods

CF:CS-model (Constant Flux : Constant Sedimentation Rate-model)

Basic assumptions (Robbins, 1978):

- the sedimentation rate is constant
- the Pb-210 activity flux to the sediment is constant

The model in practice:

- When the unsupported Pb-210 concentrations are plotted on a logarithmic scale against the cumulative dry mass (mass depth), the resulting Pb-210 profile will be nearly linear according to the assumptions. The mass flux can be determined from the mean slope of the profile using the least-squares fit procedure (e.g. Oldfield and Appleby, 1984).
- To find the most optimal mean slope and to estimate the error for this slope, the tools of regression analysis can be used effectively. It is also possible to calculate the coefficient of determination for this linear regression model.
- Calculations are principally based on the equation (Robbins, 1978; Oldfield and Appleby, 1984)

(1)
$$C(x) = C(o)e^{\frac{-\lambda_{210} \times m}{r}}$$
 where

C(o) = the unsupported Pb-210 concentration at the sediment/water interface [Bq kg⁻¹],

- C(x) = the unsupported Pb-210 concentration in the sediment at depth x [Bq kg⁻¹],
- λ_{210} = Pb-210 decay constant,
- r = the sedimentation rate $[g \text{ cm}^{-2} \text{ y}^{-1}]$ and
- m = the mass depth $[g \text{ cm}^{-2}]$ at depth x [cm].

Slope b of the least-squares fit is then

(2)
$$b = \frac{\lambda_{210}}{r}$$

from which sedimentation rate r can be resolved. It is possible to estimate the error for sedimentation rate by using the standard error of slope b.

If the logarithmic concentration profile of unsupported Pb-210 is divided into 2 or more linear segments and the slope of each segment is used to estimate an accumulation rate of that part of the core, then the assumptions of the CIC-model are also fulfilled (Appleby and Oldfield, 1992). This practice is different and more averaging than that given for the CIC-model later in this report (p. 7). In this report this practice is called CF:CS method.

CRS-model (Constant Rate of Supply-model)

Basic assumptions (Appleby and Oldfield, 1978; Oldfield and Appleby, 1984):

- the sedimentation rate can be variable
- the Pb-210 activity flux to the surface of the water column is constant **and** the transfer of Pb-210 activity from water to sediment is also constant.

This means that the unsupported Pb-210 concentration in the settling material varies with the amount of material. Therefore it is assumed that the measured activity profile of unsupported Pb-210 in sediment is due to changes in the sedimentation rate and to the radioactive decay of Pb-210.

The CRS-model in practice:

- The concentration of unsupported Pb-210 in sediment must be measured at each layer of the sediment down to that depth at which the concentration is near zero. Age estimation of a sediment layer is based on the total activity of unsupported Pb-210 in the sediment profile and the activity of unsupported Pb-210 below the sediment layer to be dated.
- CRS-model calculations are based on the equation (Appleby and Oldfield, 1978)

(3)
$$A(x) = A(o)e^{-\lambda_{210} \times t}$$
 where

A(o) = total residual activity of unsupported Pb-210 in the sediment column [Bq cm⁻²],A(x) = the cumulative residual activity of unsupported Pb-210 in sediments below depth x[Bq cm⁻²]. Age t [y] of the sediment layer at depth x is then

(4)
$$t = \frac{1}{\lambda_{210}} \times \ln \left[\frac{A(o)}{A(x)}\right]$$

and it is possible to calculate sedimentation rate r $[g \text{ cm}^{-2} \text{ y}^{-1}]$ from (Robbins, 1978)

(5)
$$r = \frac{m}{t}$$
 where

m = mass depth [g cm⁻²] of the dated sediment layer. It is possible to count an error for age t (Binford, 1990), which can be used when counting error for sedimentation rate r.

CIC-model (Constant Initial Concentration-model)

Basic assumptions (e.g. Oldfield and Appleby, 1984):

- the sedimentation rate can be variable
- the Pb-210 activity flux to the surface of the water column is constant **but** the transfer of Pb-210 activity from water to sediment is directly proportional to the amount of settling particles.

According to these assumptions, the sinking matter should always have the same initial concentration, and therefore the measured activity of unsupported Pb-210 should decline unambiguously with depth of the sediments.

The CIC-model in practice (e.g. Oldfield and Appleby, 1984):

- the concentration of unsupported Pb-210 in sediment must be measured at each layer of the sediment
- CIC-model calculations are based on the equation

(6)
$$C(x) = C(o)e^{-\lambda_{210}t}$$
 where

- C(o) = the unsupported Pb-210 concentration at the sediment/water interface [Bq kg⁻¹],
- C(x) = the unsupported Pb-210 concentration in the sediment at the depth x [Bq kg⁻¹],
- λ_{210} = Pb-210 decay constant,

t = the age [y] of the sediment layer at depth x, which can be calculated with the equation

(7)
$$t = \frac{1}{\lambda_{210}} \times \ln \left[\frac{C(o)}{C(x)} \right]$$

As in the CRS-model, it is possible to count an error for age t (Binford, 1990), which can be used when counting error for sedimentation rate r. When estimating sedimentation rate r under the assumptions of the CIC-model, it is possible to use the same method as in the CF:CS-model, after which it is possible to estimate age t of a sediment layer by using Equation 3.

Cs-137-based method

Basic assumptions:

- the observed activity peak of Cs-137 at any depth of the sediment profile corresponds to 1986, the year of the Chernobyl accident.
- the sedimentation rate has been constant between 1986 and the sampling year.

The Cs-137 method in practice:

- Cs-137 concentrations are measured in a sediment profile. Mass depth of the highest Cs-137 concentration in the sediment profile corresponds to the year 1986.
- calculation of sedimentation rate $r [g cm^{-2} y^{-1}]$ is based on the equation

(8)
$$r = \frac{m}{t}$$
 where

m = mass depth $[g \text{ cm}^{-2}]$ of the Cs-137 peak and

t = time [y] between sampling and the year 1986.

Here the minimum and maximum sedimentation rates $r [g \text{ cm}^{-2} \text{ y}^{-1}]$ have been calculated using the mass depths of the upper and lower edges of the sediment slice, or a broader sediment layer in which the peak concentration exists (Ilus et al., 1997).

Pu-239,240-based method

Basic assumptions:

- the observed Pu-239,240 activity peak at any depth of the sediment profile corresponds to 1963, the year when maximum global fallout occurred.
- the sedimentation rate has been constant between 1963 and the sampling year.

The Pu-239,240 method in practice:

- Pu-239,240 concentrations are measured in a sediment profile. Mass depth of the highest Pu-239,240 concentration in the sediment profile corresponds to the year 1963.
- calculation of sedimentation rate r [g cm⁻² y⁻¹] and its error is similar to that of the Cs-137 method (Ilus et al., 1997).

The sedimentation rates $[mm y^{-1}]$ were calculated from the dry matter accumulation rates, using calculated porosities at depths of 0-1 cm and 9-10 cm and an assumed value for dry matter density (see e.g. Berner, 1978). Calculation of porosities was based on the water content measured in the sediments. For dry matter density the commonly accepted value of 2.5 g cm⁻³ was used. In those cases in which sedimentation rate was very high and the millimetre value was clearly overestimated, a graphical method was used in which mass depth was plotted against slice depth.

Results and Discussion

Vertical distribution of radionuclides in sediment profiles

Fig. 2 illustrates some extreme examples of Cs-137, Pu-239,240 and unsupported Pb-210 concentrations in the sediment profiles analysed. At Station LL3a the Cs-137 marker of the Chernobyl accident is easily detectable, enabling accurate determination of sedimentation rate with the Cs-137 method. On the other hand, at Station US5b the maximum concentrations are spread out over a very broad sediment layer, leading to great uncertainty in dating of sediments.

Correspondingly, the Pu-239,240 peak of 1963 is very distinct, at Station BCSIVb4, but at Station US6b occurrence of the Pu peak in the uppermost sediment layer makes it difficult to estimate an accurate sedimentation rate. The maximum value at the surface may have been caused by e.g. slow or unstable sedimentation processes, bioturbation or other mixing of sediments as a consequence of natural processes or disturbance during sampling. The sedimentation rate estimated from the same samples with the CF:CS method, however, is as low as that obtained with the Pu-239,240 and the Cs-137 methods (Table II). In these cases, it is recommended that more than one independent method be used in the estimations.

At Station F9 the vertical distribution of unsupported Pb-210 is exponential, and the CF:CS method fits this type of observation very well; thus it is possible to use the model for a wide depth range from the surface to deep, old layers of sediment, and the estimate describes the mean sedimentation occurred over a long period of time. The good fit of the model can be seen from the small error in sedimentation rate and the high coefficient of determination (Table II).

In the case of Station LF2 the vertical distribution of unsupported Pb-210 is not exponential in the uppermost layers of the sediment, but only in the deeper layers. This can be due to mixing of surface sediments, considerable changes in the flux of unsupported Pb-210, significant increase in sedimentation rate, etc. The surface layers, therefore, should be omitted in fitting of the CF:CS method, because the reason for the non-exponentiality is unknown and this type of profile does not fulfil the assumptions of the model. If the surface layers were to be accounted for, it would result in considerably higher values of sedimentation rate.



Figure 2. Vertical distribution of Cs-137, Pu-239,240 and unsupported Pb-210 [Bq kg⁻¹ d.w.] at some Baltic Sea sampling stations.

Evaluated sedimentation rates in various subregions of the Baltic Sea

Sedimentation rates evaluated for various sampling stations with the Cs-137, Pu-239,240, CF:CS and CRS methods are presented in Tables II-X. Evaluations based on Pu-239,240 were made for only 7 stations and those based on the CRS model for 5 stations situated in the Gulf of Finland. The sedimentation rates are reported as mass accumulation rates [g cm⁻² y⁻¹] (Tables II-IV) and as sedimentation rates [mm y⁻¹] to the surface of the sediment (Tables V-VII) and to deeper, more compact layers of the sediment (Tables VIII-X). Sedimentation to the surface of the sediment describes the recently settled fresh, uncompacted material, while that to the more compact layers describes the process in the long run.

The examples given previously (p. 8) show that certain limits of error are always included in all estimates of sedimentation rate, therefore, we have considered it necessary to give minimum and maximum sedimentation rate values for each sampling station. Consequently, the closer the minimum and maximum values are to each other, the better is the reliability of the estimate.

In general, the sedimentation rates $[g \text{ cm}^{-2} \text{ y}^{-1}]$ were highest at the Bothnian Sea sampling stations, but the average was dominated by extremely high values at 2 stations (F18 and US5b) in the northernmost part of the sea area (Table II). In the Gulf of Finland the sedimentation rates were highest in the eastern part, while in the Bothnian Bay and in the Baltic Proper the rates were in general lower than in the 2 areas first mentioned.

The maximum values estimated with the CF:CS and Cs-137 methods for Station F18 were 0.57..0.90 and 0.54..0.70 g cm⁻² y⁻¹. The corresponding values were 21..29 and 20..24 mm y⁻¹, respectively, when the values were estimated graphically on the basis of the uppermost sediment layer (cf. Table V), or 14..23 and 14..18 mm y⁻¹, when the porosities of the 9-10-cm sediment layer were used in the calculations (cf. Table VIII).

In the Gulf of Finland the highest sedimentation rate estimated with the CF:CS method was $0.18..0.20 \text{ g cm}^{-2} \text{ y}^{-1}$ at Station XV1, and that estimated with the Cs-137 method 0.28..0.31 g cm⁻²y⁻¹ at Station LL3a (Table III). The corresponding values were 17..20 and 23..24 mm y⁻¹, respectively, when the values were estimated graphically on the basis of the uppermost sediment layer (Table VI), or 12..14 mm y⁻¹ and 15..17 mm y⁻¹, respectively, when the porosities of the 9-10-cm sediment layer were used in the calculations (Table IX).

In the northern part of the Baltic Proper the highest sedimentation rate estimated with the Cs-137 method was 0.23..0.45 g cm⁻² y⁻¹ (Table III) corresponding to 11..19 or 7..14 mm y⁻¹, depending on the calculation method (Tables VII and X). In general, the sedimentation rates estimated with the CF:CS method for stations in the Baltic Proper were 0.02..0.12 g cm⁻² y⁻¹ and those estimated with the Cs-137 method 0.01..0.18 g cm⁻² y⁻¹ corresponding to 0.4..3 and 0.2..6 mm y⁻¹, respectively, when the porosities of the 9-10-cm sediment layer were used in the calculations (Table X).

Table II. Sedimentation rate $[g \text{ cm}^{-2} \text{ y}^{-1}]$ at Gulf of Bothnia sampling stations evaluated with the Cs-137, Pu-239,240 and Pb-210 CF:CS methods. Centimetre values in the case of Cs-137 and Pu-239,240 methods describe the depth range of the highest Cs-137 and Pu-239,240 activities. In the case of the CF:CS method the centimetre values describe the depth range used in the calculations, and the value of R² is the coefficient of determination.



	Cs-137			Pu-23	9,240		Pb-21	CS			
	[g cm ⁻²	y ⁻¹]		[g cm ⁻²	y ⁻¹]		[g cm ⁻²	y ⁻¹]			
Station	min	max	[cm]	min	max	[cm]	aver.	min	max	[cm]	\mathbf{R}^2
CVI	-	0.058	0-2	0.029	0.042	3-4	0.027	0.024	0.031	1-7	0.94
CV	-	0.043	0-2	-	-	-	0.047	0.045	0.050	0-12	0.98
RR3	0.076	0.139	3-5	-	-	-	0.051	0.047	0.055	6-20	0.96
RR6	-	0.056	0-3	-	-	-	0.032	0.030	0.034	2-12	0.97
F9	0.024	0.040	2-3	0.025	0.032	5-6	0.033	0.031	0.035	0-14	0.95
BO3	0.079	0.104	4-5	-	-	-	0.105	0.077	0.166	0-5	0.71
							0.039	0.036	0.041	5-20	0.97
SM3	-	0.025	0-1	-	-	-	-	-	-	-	-
F15	0.205	0.249	8-9	-	-	-	0.205	0.171	0.257	2-12	0.78
							0.078	0.072	0.085	12-30	0.96
F18	0.535	0.697	14-18	-	-	-	0.695	0.566	0.901	12-28	0.76
US6b	-	0.029	0-1	-	0.021	0-2	0.016	0.014	0.020	0-5	0.91
US5b	0.278	0.541	9-17	-	-	-	0.478	0.431	0.538	0-36	0.77
OLK12	0.140	0.221	6-9	-	-	-	0.154	0.144	0.166	6-31	0.90
							0.084	0.078	0.090	22-31	0.97
SR5	0.022	0.211	1-7	0.102	0.116	10-11	0.119	0.102	0.143	1-15	0.75
SR6	-	0.191	0-6	-	-	-	0.074	0.071	0.077	5-18	0.99

Table III. Sedimentation rate $[g \text{ cm}^{-2} \text{ y}^{-1}]$ at Gulf of Finland sampling stations evaluated with the Cs-137, Pu-239,240, Pb-210 CF:CS and Pb-210 CRS methods. Centimetre values in the case of the Cs-137 and Pu-239,240 methods describe the depth range of the highest Cs-137 and Pu-239,240 activities. In the case of the CF:CS method the centimetre values describe the depth range used in the calculations, and the value of R² is the coefficient of determination. In the case of the CRS method the results are given as an average value for the previous 60 years with the limits of error.



Cs-137 Pu-239,240					9,240	Pb-210 CF:CS					Pb-210 CRS			
	[g cm ⁻²	y ⁻¹]		[g cm ⁻²	y ⁻¹]		[g cm ⁻²	y ⁻¹]			$[g cm^{-2} y^{-1}]$			
Station	min	max	[cm]	min	max	[cm]	aver.	min	max	[cm]	\mathbf{R}^2	aver.	min	max
F41	0.117	0.140	7-8	0.048	0.067	9-11	0.121	0.105	0.142	0-10	0.85	0.077	0.073	0.082
							0.075	0.072	0.080	10-33	0.94			
F42	0.088	0.147	5-7	-	-	-	-	-	-	-	-	-	-	-
XV1	0.011	0.037	1-3	-	-	-	0.183	0.171	0.198	0-30	0.87	-	-	-
LOV3a	0.080	0.096	7-8	0.062	0.067	15-16	0.074	0.072	0.076	10-31	0.98	0.077	0.072	0.082
LL3a	0.278	0.310	16-18	-	-	-	0.100	0.086	0.120	26-40	0.88	-	-	-
LL4a	-	0.043	0-3	-	-	-	0.029	0.026	0.032	1-9	0.95	-	-	-
GF2	-	0.076	0-4	-	-	-	0.062	0.059	0.065	0-25	0.94	0.067	0.063	0.071
LL6a	0.036	0.114	2-5	-	-	-	0.033	0.032	0.034	5-18	0.99	-	-	-
GF1	0.110	0.139	4-5	-	-	-	0.053	0.050	0.056	6-23	0.96	0.066	0.063	0.069
JML	-	0.039	0-2	-	-	-	0.047	0.044	0.049	0-23	0.96	0.045	0.043	0.048
LL11	0.021	0.043	1-2	-	-	-	0.031	0.027	0.037	0-8	0.86	-	-	-
Hanko	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Bay														
LL12	0.012	0.050	1-3	-	-	-	0.025	0.023	0.028	2-16	0.91	-	-	-

Table IV. Sedimentation rate $[g \text{ cm}^{-2} \text{ y}^{-1}]$ at the Baltic Proper sampling stations evaluated with the Cs-137, Pu-239,240 and Pb-210 CF:CS methods. Centimetre values in the case of the Cs-137 and Pu-239,240 methods describe the depth range of the highest Cs-137 and Pu-239,240 activities. In the case of the CF:CS method the centimetre values describe the depth range used in the calculations, and the value of \mathbb{R}^2 is the coefficient of determination.



	Cs-13	7		Pu-23	9,240		Pb-21				
	[g cm ⁻²	y ⁻¹]		[g cm ⁻²	y ⁻¹]		[g cm ⁻²	y ⁻¹]			
Station	min	max	[cm]	min	max	[cm]	aver.	min	max	[cm]	\mathbf{R}^2
F69	0.231	0.452	8-14	-	-	-	-	-	-	-	-
LL15	0.007	0.051	2-5	-	-	-	0.075	0.070	0.082	20-36	0.96
F80	0.013	0.021	2-3	-	-	-	0.028	0.027	0.030	1-22	0.96
LF4	0.006	0.015	1-2	-	-	-	0.020	0.017	0.023	0-9	0.85
LF2	0.018	0.178	1-7	-	-	-	0.100	0.088	0.117	5-14	0.90
BCSIVb4	0.011	0.017	2-3	0.009	0.012	5-6	0.017	0.016	0.018	3-12	0.97
BCSIVb6	0.010	0.039	1-3	-	-	-	0.035	0.030	0.041	3-16	0.85
HA1	-	0.027	0-1	-	-	-	0.032	0.028	0.038	2-10	0.88
HA5	0.012	0.020	2-3	0.011	0.014	5-6	0.017	0.015	0.019	1-13	0.89
HA8	-	0.018	0-2	-	-	-	0.034	0.030	0.040	0-20	0.77
HA9	-	0.045	0-2	-	-	-	0.034	0.030	0.040	2-12	0.87
HL1	-	0.016	0-1	-	-	-	-	-	-	-	-
HL4	-	0.013	0-1	-	-	-	-	-	-	-	-
HL6	-	0.017	0-1	-	-	-	-	-	-	-	-
BCSIII10	-	0.088	0-4	-	-	-	0.073	0.064	0.085	1-15	0.80

Table V. Sedimentation rate $[mm y^{-1}]$ at Gulf of Bothnia sampling stations evaluated with the Cs-137, Pu-239,240 and Pb-210 CF:CS methods. In the calculations porosities of the 0-1-cm sediment layer were used or the values have been estimated graphically (*italic*-font) using mass depth against slice depth. Centimetre values in the Cs-137 and Pu-239,240 methods describe the depth range of the highest Cs-137 and Pu-239,240 activities. In the CF:CS method the centimetre values describe the depth range used in the calculations, and the value of R² is the coefficient of determination.



	Pu-239,240				Pb-210 CF:CS						
	[mm y	¹]		[mm y	⁻¹]		[mm y ⁻¹]			
Station	min	max	[cm]	min	max	[cm]	aver.	min	max	[cm]	\mathbf{R}^2
CVI	-	3.2	0-2	1.6	2.3	2-3	1.5	1.3	1.7	1-7	0.94
CV	-	2.9	0-2	-	-	-	3.2	3.0	3.3	0-12	0.98
RR3	5.0	9.1	3-5	-	-	-	3.3	3.1	3.6	6-20	0.96
RR6	-	4.7	0-3	-	-	-	2.7	2.5	2.9	2-12	0.97
F9	2.6	4.4	2-3	2.7	3.5	5-6	3.6	3.4	3.9	0-14	0.95
BO3	6.3	8.3	4-5	-	-	-	8.4	6.1	13.3	0-5	0.71
							3.1	2.9	3.3	5-20	0.97
SM3	-	1.4	0-1	-	-	-	-	-	-	-	-
F15	17	15	8-9	-	-	-	15	13	18	2-12	0.78
							7	7	8	12-30	0.96
F18	20	24	14-18	-	-	-	24	21	29	12-28	0.76
US6b	-	1.2	0-1	-	0.9	0-2	0.7	0.6	0.8	0-5	0.91
US5b	14	24	9-17	-	-	-	22	20	24	0-36	0.77
OLK12	8	13	6-9	-	-	-	9	9	10	6-31	0.90
							5	5	6	22-31	0.97
SR5	1.5	14.0	1-7	6.8	7.7	10-11	7.9	6.8	9.5	1-15	0.75
SR6	-	10.1	0-6	-	-	-	3.9	3.7	4.1	5-18	0.99

Table VI. Sedimentation rate $[mm y^{-1}]$ at Gulf of Finland sampling stations evaluated with the Cs-137, Pu-239,240, Pb-210 CF:CS and Pb-210 CRS methods. In the calculations porosities of the 0-1-cm sediment layer were used or the values have been estimated graphically (*italic*-font) using mass depth against slice depth. Centimetre values in the Cs-137 and Pu-239,240 methods describe the depth range of the highest Cs-137 and Pu-239,240 activities. In the CF:CS method the centimetre values describe the depth range used in the calculations, and the value of R² is the coefficient of determination. In the case of the CRS method the results are given as an average value for the previous 60 years with the limits of error.



	Cs-13	7		Pu-23	39,240 Pb-210 CF:CS							Pb-210 CRS			
	[mm y	⁻¹]		[mm y	⁻¹]		[mm y ⁻¹]				[mm y ⁻¹]				
Station	min	max	[cm]	min	max	[cm]	aver.	min	max	[cm]	\mathbf{R}^2	aver.	min	max	
F41	11	13	7-8	5	6	9-11	11	10	13	0-10	0.85	7	7	8	
							7	7	7	10-33	0.94				
F42	7	11	5-7	-	-	-	-	-	-	-	-	-	-	-	
XV1	1	4	1-3	-	-	-	19	17	20	0-30	0.87	-	-	-	
LOV3a	13	15	7-8	11	12	15-16	12	12	13	10-31	0.98	13	12	13	
LL3a	23	24	16-18	-	-	-	10	9	12	26-40	0.88	-	-	-	
LL4a	-	4.3	0-3	-	-	-	2.9	2.7	3.2	1-9	0.95	-	-	-	
GF2	-	5.4	0-4	-	-	-	4.4	4.1	4.6	0-25	0.94	4.7	4.4	5.0	
LL6a	2.6	8.4	2-5	-	-	-	2.4	2.3	2.5	5-18	0.99	-	-	-	
GF1	5.8	7.4	4-5	-	-	-	2.8	2.7	2.9	6-23	0.96	3.5	3.3	3.7	
JML	-	2.4	0-2	-	-	-	2.9	2.8	3.1	0-23	0.96	2.8	2.7	3.0	
LL11	1.3	2.6	1-2	-	-	-	1.9	1.6	2.3	0-8	0.86	-	-	-	
Hanko Bav	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
LL12	1.0	4.0	1-3	-	-	-	2.0	1.8	2.3	2-16	0.91	-	-	-	

Table VII. Sedimentation rate $[mm y^{-1}]$ at the Baltic Proper sampling stations evaluated with the Cs-137, Pu-239,240 and Pb-210 CF:CS methods. In the calculations porosities of the 0-1-cm sediment layer were used or the values were estimated graphically (*italic*-font) using mass depth against slice depth. Centimetre values in the Cs-137 and Pu-239,240 methods describe the depth range of the highest Cs-137 and Pu-239,240 activities. In the CF:CS method the centimetre values describe the depth range used in the calculations, and the value of R² is the coefficient of determination.



	Cs-13	7		Pu-23	9,240		Pb-21	CS			
	[mm y	1]		[mm y	⁻¹]		[mm y ⁻¹	¹]			
Station	min	max	[cm]	min	max	[cm]	aver.	min	max	[cm]	\mathbf{R}^2
F69	11	19	8-14	-	-	-	-	-	-	-	-
LL15	2	14	2-5	-	-	-	18	17	20	20-36	0.96
F80	2.5	4.2	2-3	-	-	-	5.6	5.3	6.0	1-22	0.96
LF4	1.0	2.9	1-2	-	-	-	3.7	3.2	4.4	0-9	0.85
LF2	1.3	12.5	1-7	-	-	-	7.0	6.2	8.2	5-14	0.90
BCSIVb4	2.7	4.1	2-3	2.2	3.0	5-6	4.1	3.9	4.4	3-12	0.97
BCSIVb6	1.3	5.2	1-3	-	-	-	4.6	4.0	5.4	3-16	0.85
HA1	-	1.3	0-1	-	-	-	1.6	1.4	1.9	2-10	0.88
HA5	2.7	4.5	2-3	2.5	3.1	5-6	3.8	3.4	4.3	1-13	0.89
HA8	-	2.1	0-2	-	-	-	4.0	3.4	4.7	0-20	0.77
HA9	-	3.1	0-2	-	-	-	2.3	2.0	2.7	2-12	0.87
HL1	-	1.2	0-1	-	-	-	-	-	-	-	
HL4	-	1.2	0-1	-	-	-	-	-	-	-	-
HL6	-	1.4	0-1	-	-	-	-	-	-	-	-
BCSIII10	-	5.6	0-4	-	-	-	4.6	4.0	5.4	1-15	0.80

Table VIII. Sedimentation rate $[mm y^{-1}]$ at Gulf of Bothnia sampling stations evaluated with the Cs-137, Pu-239,240 and Pb-210 CF:CS methods. In the calculations porosities of the 9-10-cm sediment layer were used. Centimetre values in the Cs-137 and Pu-239,240 methods describe the depth range of the highest Cs-137 and Pu-239,240 activities. In the CF:CS method the centimetre values describe the depth range used in the calculations, and the value of R^2 is the coefficient of determination.



	Pu-239,240				Pb-21	CS					
	[mm y	¹]		[mm y	⁻¹]		$[\mathbf{mm}\mathbf{y}^{-1}]$	1			
Station	min	max	[cm]	min	max	[cm]	aver.	min	max	[cm]	\mathbf{R}^2
CVI	-	1.2	0-2	0.6	0.9	2-3	0.6	0.5	0.6	1-7	0.94
CV	-	1.0	0-2	-	-	-	1.1	1.0	1.1	0-12	0.98
RR3	2.8	5.1	3-5	-	-	-	1.9	1.7	2.0	6-20	0.96
RR6	-	1.4	0-3	-	-	-	0.8	0.8	0.9	2-12	0.97
F9	0.7	1.3	2-3	0.8	1.0	5-6	1.0	1.0	1.1	0-14	0.95
BO3	3.2	4.2	4-5	-	-	-	4.3	3.1	6.7	0-5	0.71
							1.6	1.5	1.7	5-20	0.97
SM3	-	0.5	0-1	-	-	-	-	-	-	-	-
F15	4.3	5.2	8-9	-	-	-	4.3	3.6	5.4	2-12	0.78
							1.6	1.5	1.8	12-30	0.96
F18	13.5	17.6	14-18	-	-	-	17.6	14.3	22.8	12-28	0.76
US6b	-	-	0-1	-	0.4	0-2	-	-	-	0-5	0.91
US5b	10.1	19.7	9-17	-	-	-	17.4	15.7	19.6	0-36	0.77
OLK12	5.1	8.0	6-9	-	-	-	5.6	5.2	6.0	6-31	0.90
							3.0	2.8	3.3	22-31	0.97
SR5	0.6	5.7	1-7	2.8	3.1	10-11	3.2	2.8	3.9	1-15	0.75
SR6	-	4.3	0-6	-	-	-	1.7	1.6	1.7	5-18	0.99

Table IX. Sedimentation rate $[mm y^{-1}]$ at Gulf of Finland sampling stations evaluated with the Cs-137, Pu-239,240, Pb-210 CF:CS and Pb-210 CRS methods. In the calculations porosities of the 9-10-cm sediment layer were used. Centimetre values in the Cs-137 and Pu-239,240 methods describe the depth range of the highest Cs-137 and Pu-239,240 activities. In the CF:CS method the centimetre values describe the depth range used in the calculations, and the value of R² is the coefficient of determination. In the case of the CRS method the results are given as an average value for the previous 60 years with the limits of error.



Cs-137 [mm y ⁻¹]			Pu-239,240 [mm y ⁻¹]				Pb-210 CRS							
						[mm y ⁻¹]				$[\mathbf{mm y}^{-1}]$				
Station	min	max	[cm]	min	max	[cm]	aver.	min	max	[cm]	\mathbf{R}^2	aver.	min	max
F41	4.1	4.9	7-8	1.7	2.3	9-11	4.2	3.7	5.0	0-10	0.85	2.7	2.6	2.9
							2.6	2.5	2.8	10-33	0.94			
F42	1.7	2.8	5-7	-	-	-	-	-	-	-	-	-	-	-
XV1	0.8	2.5	1-3	-	-	-	12.5	11.7	13.5	0-30	0.87	-	-	-
LOV3a	4.9	5.8	7-8	3.8	4.1	15-16	4.5	4.4	4.7	10-31	0.98	4.7	4.4	5.0
LL3a	14.8	16.5	16-18	-	-	-	5.4	4.6	6.4	26-40	0.88	-	-	-
LL4a	-	1.1	0-3	-	-	-	0.7	0.7	0.8	1-9	0.95	-	-	-
GF2	-	2.7	0-4	-	-	-	2.2	2.1	2.3	0-25	0.94	2.3	2.2	2.5
LL6a	1.6	5.1	2-5	-	-	-	1.5	1.4	1.5	5-18	0.99	-	-	-
GF1	4.3	5.5	4-5	-	-	-	2.1	2.0	2.2	6-23	0.96	2.6	2.5	2.7
JML	-	1.4	0-2	-	-	-	1.7	1.6	1.8	0-23	0.96	1.7	1.6	1.8
LL11	-	-	1-2	-	-	-	-	-	-	0-8	0.86	-	-	-
Hanko	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Bay														
LL12	0.4	1.5	1-3	-	-	-	0.8	0.7	0.9	2-16	0.91	-	-	-

Table X. Sedimentation rate $[mm y^{-1}]$ at the Baltic Proper sampling stations evaluated with the Cs-137, Pu-239,240 and Pb-210 CF:CS methods. In the calculations porosities of the 9-10-cm sediment layer were used. Centimetre values in the Cs-137 and Pu-239,240 methods describe the depth range of the highest Cs-137 and Pu-239,240 activities. In the CF:CS method the centimetre values describe the depth range used in the calculations, and the value of R^2 is the coefficient of determination.



	Cs-13	7		Pu-23	9,240		Pb-21				
	[mm y ⁻¹]			[mm y	1]		[mm y ⁻¹	¹]			-
Station	min	max	[cm]	min	max	[cm]	aver.	min	max	[cm]	\mathbf{R}^2
F69	7.3	14.4	8-14	-	-	-	-	-	-	-	-
LL15	0.4	3.3	2-5	-	-	-	4.9	4.5	5.3	20-36	0.96
F80	1.4	2.3	2-3	-	-	-	3.2	3.0	3.4	1-22	0.96
LF4	0.2	0.5	1-2	-	-	-	0.6	0.5	0.7	0-9	0.85
LF2	0.6	6.0	1-7	-	-	-	3.4	2.9	3.9	5-14	0.90
BCSIVb4	0.6	0.9	2-3	0.5	0.6	5-6	0.9	0.8	0.9	3-12	0.97
BCSIVb6	0.6	2.3	1-3	-	-	-	2.1	1.8	2.4	3-16	0.85
HA1	-	0.6	0-1	-	-	-	0.7	0.6	0.8	2-10	0.88
HA5	0.6	0.9	2-3	0.5	0.7	5-6	0.8	0.7	0.9	1-13	0.89
HA8	-	0.7	0-2	-	-	-	1.3	1.2	1.6	0-20	0.77
HA9	-	0.6	0-2	-	-	-	0.5	0.4	0.5	2-12	0.87
HL1	-	0.3	0-1	-	-	-	-	-	-	-	-
HL4	-	0.6	0-1	-	-	-	-	-	-	-	-
HL6	-	0.2	0-1	-	-	-	-	-	-	-	-
BCSIII10	-	2.7	0-4	-	-	-	2.3	2.0	2.7	1-15	0.80

Useability of dating methods

One of the advantages of the Pb-210-based methods is that they give information on sedimentation rate over longer periods of time than the Cs-137 and Pu-239,240 methods. In contrast to the Pu-239,240 method, Pb-210 can be analysed gammaspectrometrically; however, the gammaspectrometric method for Pb-210 is very demanding both for the equipment and the staff.

At least in the case of our material, the CF:CS method appeared to be useable for the Baltic Sea sediments, because

- by using the CF:CS method it is possible to omit the mixed surface layer and its impact on the results.
- the very small activity concentrations of unsupported Pb-210 at the deep sediment layers, which can be difficult to analyse, can be omitted when using the CF:CS method.
- the CF:CS method is an averaging method that results in mean values over long periods of time.

Since no exact data are available on the constancy of Pb-210 flux into the Baltic Sea sediments, the basic assumptions of the CRS method are not necessarily fulfilled there. In contrast to the CF:CS method, mixing of the uppermost sediment layers and the low activity concentrations in the deep layers could have impact on results in the CRS method. The CIC method was not used in this study, because the basic assumption of constant concentration in the surface layer of sediment is not fulfilled in the Baltic Sea. For our material, especially, which consists of 1-cm slices of surface sediment, the model is less suitable.

The advantages of the Cs-137 method are that Cs-137 is relatively quick and easy to measure, and its activity concentrations in sediments are easily detectable in all regions of the Baltic Sea. On the other hand, the Cs-137 peak is still today very often located relatively near the sediment surface, because only 11 years have elapsed since the Chernobyl accident. The soft surface sediments are in general very loose and susceptible to diffusion and errors in sampling. Except for diffusion, the mobility of particles can affect the depth profile of caesium, which can lead to situations in which the Cs peak is difficult to distinguish, but the high concentrations are found over a broad depth range.

The Pu-239,240 peak in the Baltic Sea sediments is caused by the nuclear weapons tests of the 1960s and occurs, therefore, at much greater depths than the Chernobyl peak of Cs-137. At most stations the Pu peak is already at a depth at which the sediment is relatively packed and solid, which makes it less susceptible to errors in sampling. In addition, Pu has proved to be more firmly bound to particles than Cs, but if the particles are mobile it may also affect the results of this method. A clear disadvantage of the Pu method is that the analyses are demanding, slow and expensive.

In principle the sediment-trap method differs totally from those mentioned previously, because it is based on direct dry weight measurement of particulate material collected by traps. Factors affecting the results obtained with the traps include suspension-resuspension processes in the sediments and overtrapping or undertrapping design of the traps themselves. Of course, the results obtained with the traps also represent much shorter time periods of sedimentation than those obtained with the other methods.

Comparison of the sedimentation rates obtained with various methods

The results obtained with the Pb-210/Po-210 method and the gammaspectrometric Pb-210 method were in good agreement (Fig. 3). This indicates that the concentrations of Pb-210 analysed by our application of gamma-ray spectrometry are suitable for estimation of sedimentation rate.

At all Gulf of Bothnia stations where sedimentation rate was estimated with the 3 independent methods (Cs-137, Pu-239,240 and CF:CS), no systematic differences were observed among the results, but their ranges overlapped. In the Gulf of Finland, the methods representing longer sedimentation periods (Pu-239,240, CF:CS, CRS) resulted in smaller estimates of sedimentation rate than the Cs-137 method. This is probably due to increased sedimentation in the eastern Gulf of Finland during recent years. The results obtained with the methods first mentioned were very similar. In the Baltic Proper, the Pu-239,240 method resulted in slightly smaller values than the CF:CS and Cs-137 methods, although the differences were in general small.



Figure 3. Unsupported Pb-210 activities [Bq kg-1 d.w.] based on gammaspectrometric measurements and radiochemical analyses of Po-210 in logarithmic scale at Sampling Station LOV3a.

At many stations the sedimentation rates calculated with the Cs-137 method were somewhat higher than those obtained with the CF:CS method. In these cases the values obtained with the CF:CS method represent longer sedimentation periods and were based on older sediment layers formed before the time of Cs-137 deposition; e.g. at Station RR3, the Cs-137 peak is situated at a depth of 3-5 cm, but the CF:CS estimate is based on a depth range of 6-20 cm (Table I). On the other hand, at those stations where it was possible to use the CF:CS method for shorter sedimentation periods, the results were similar to those obtained with the Cs-137 method (e.g. Stations BO3, F15, F41); however, the error limits of these estimates are relatively large. At many stations in the Baltic Proper the CF:CS method resulted in slightly

higher values than the Cs-137 method, but in general both the differences and the level of sedimentation rate were small in this area.

Sediment traps were used at 2 sampling stations for measuring accumulation rate of dry matter [g cm⁻² y⁻¹]. At Station LOV3a the dry weight sum of the sampling periods of 1996 was 0.21 g cm⁻², whereas the values obtained with the Cs-137 and CF:CS methods were 0.08..0.10 and 0.07..0.08 g cm⁻²y⁻¹, respectively. At Station OLK12 the dry weight sum was 0.63 g cm⁻² and the sedimentation rates obtained with the above-mentioned methods were 0.14..0.22 and 0.14..0.17 g cm⁻²y⁻¹. The reason for the 3-4 times higher values obtained with the traps may be due to the fact that they represent only a one year period and most probably are also affected by resuspension

Test samplings performed in some sedimentation basins of the Gulf of Finland have shown that sedimentation processes can be different even at stations situated very near to each other. Local variation in of sedimentation processes and sedimentation rate has been studied in 3 sedimentation basins (8 stations) in cooperation with the FIMR and the Geological Survey of Finland. The study may give important information on the general applicability of single sedimentation rate estimates. In addition, samples taken from the area near St. Petersburg in 1996 will result in information on sedimentation processes in the estuary of the River Neva.

Conclusions

The results obtained in this project show that in the Baltic Sea the use of more than 1 parallel methods in estimation of sedimentation rate is recommended. None of the methods is necessarily suitable for routine use, and it is always important to ensure that the basic assumptions of the methods are fulfilled. In those cases where the Cs-137 or Pu-239,240 peak is distinct, sharply defined and at sufficient depth, these methods may result in the best estimates. On the other hand, at those stations where the peaks are spread out over a broad range of depths, the methods based on Pb-210 may give more accurate results.

In addition, the results show that the accumulation rates of dry matter may vary between 0.006 and $0.90 \text{ g cm}^{-2}\text{y}^{-1}$ at different sampling stations of the Baltic Sea and the sedimentation rates between 0.2 and 29 mm y⁻¹ depending on the sedimentation itself and the method used in calculation. This is a considerable range in results, considering that all of the sampling stations were located in areas of soft sediment bottoms. The differences among the results obtained with various methods varied unsystematically; thus it was not possible to predict that anyone of the methods would always give higher results than any of the others or *vice versa*.

In the sedimentation rate studies the importance of undisturbed and high-quality samples is especially pronounced. The loss of soft surface sediments during sampling may significantly affect the results when using the Cs-137 and Pu-239,240 methods.

In comparing the methods, the sedimentation rates should be presented as accumulation rates of dry matter $[g \text{ cm}^2 \text{ y}^{-1}]$ to avoid the error caused by compaction of the sediment and its impact on the results. Furthermore, the time scale of the estimation should always be considered.

The project has markedly increased our knowledge of sedimentation rates in various subregions of the Baltic Sea, and in addition it has provided further data on vertical distribution of Cs-137 and Pu-239,240, as well as on the total inventory of Cs-137 in Baltic Sea sediments.

Acknowledgements

The project was financially supported by Nordic Nuclear Safety Research.

References

Appleby P.G. and Oldfield F., 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported Pb-210 to the sediment. Catena. 5: 1-8.

Appleby P.G. and Oldfield F., 1992. Application of lead-210 to sedimentation studies. -In Ivanovich M. and Harmon R.S.(eds), Uranium-series Disequilibrium: Applications to Earth, Marine and Environmental Sciences: 731-778. 2nd edition. Clarendon Press, Oxford, 1992.

Berner R.A., 1978. Principles of Chemical Sedimentology. McGraw-Hill Book Company. p. 240.

Binford M. W., 1990. Calculation and uncertainty analysis of ²¹⁰Pb dates for PIRLA project lake sediment cores. J. Paleolimn., 3: 253-267.

Häsänen E., 1977. Dating of sediments, based on Po-210 measurements. Radiochem. Radioanal. Letters 31(4-5): 207-214.

Ilus E, Mattila J, Klemola S and Ikäheimonen TK, 1997. Evaluation of sedimentation rate at two sampling stations in the Gulf of Finland based on Pb-210, Cs-137 and Pu-239,240 profiles in sediments. -In: Ilus E.(ed.), Proceedings of the Seminar: Dating of sediments and determination of sedimentation rate, Helsinki 2-3 April, 1997. Report STUK-A145, STUK, Radiation and Nuclear Safety Authority, Helsinki. (in print).

Klemola S., Mattila J. and Ikäheimonen TK., 1997. Determination of Pb-210 in sediment samples by gamma ray spectrometry.-In: Walderhaug T, Gudlaugsson E.P.(eds), Proceedings of the 11th Ordinary Meeting of the Nordic Radiation Protection and the 7th Nordic Radioecology Seminar, Reykjavik 26-29 August, 1996. Geislavarnir rikisins, Reykjavik.

Oldfield F. and Appleby P. G., 1984. Empirical testing of 210Pb-dating models for lake sediments. -In: Haworth E. Y. and Lund J. W. G. (eds.), Lake Sediments and Environmental History: 93-124. Leicester University Press.

Robbins J. A., 1978. Geochemical and geophysical applications of radioactive lead. - In: Nriagu J. O. (ed.), Biogeochemistry of Lead in the Environment: 285-393. Elsevier. Holland.

Taipale T.K. and Tuomainen K., 1985. Radiochemical determination of plutonium and americium from seawater, sediment and biota samples. STUK-B-VALO 26.

Run-off and sedimentation processes over the continental shelf along the European-Siberian Tundra coast

Dan Josefsson University of Lund, Sverige

Introduction

The anthropogenic radioactivity in the arctic seas is composed from releases from many different sources, with the most important being fallout from atmospheric nuclear bombs test in the 1950's and 60's, releases from European nuclear reprocessing and debris from the accident at the Chernobyl nuclear power plant. Most of the bomb test fallout were transported to the Arctic with the currents from the Atlantic Ocean, and the liquid discharges from the Sellafield and La Hague reprocessing plants are transported to the North Sea and then via the Norwegian Coastal Current (NCC) to the Arctic. Also the Chernobyl related radioactivity is primarily transported to the Arctic Ocean via the NCC, and only a smaller part was deposited directly after the accident. Outside Norway at about 65 °N the NCC meets the Atlantic Ocean current and together they enter the arctic ocean. About one third of the combined current is transported west of Spitsbergen and then turn east, following the Siberian shelf slope. The remaining two thirds are passing across the Barents Sea further to the east and enters the central Arctic Ocean east of Frans Joseph's Land. Due to their higher density, both branches will mainly enter the arctic ocean below the lighter surface layer and constitute an easily identified high salinity, high temperature water mass at approximately 150 to 1000 metres depth. Part of the water masses will though remain in the upper layer and mix with the arctic ocean mixed layer or be transported further to the east on the shelf.

The sediment deposition rate in the central arctic ocean is very low because of the low biological activity and the long distance to river mouths. On the shelves, on the other hand a high seasonal biological activity may appear, and together with the sediment output from the big rivers this causes a high amount of suspended load in the water column. Because of the shallow waters, the shelf sediment is affected by the ice and ice formation which may cause disturbance and mixing.

The sampling for the SE-3 project has been performed during two arctic expeditions. In 1994 the Swedish-Russian expedition, Tundra Ecology -94, passed the Siberian shelf seas, from Barents Sea in the west to East Siberian Sea in the east. The expedition was mainly focused on terrestrial ecology, but since it used a large research ship as logistic base, we could participate to get marine samples. The other expedition took place in the summer of 1996 when the Swedish icebreaker Oden were used in the Swedish Arctic Ocean -96 expedition which was mainly concentrated to the central Arctic Ocean. The expedition crossed the Barents Sea and entered the Arctic proper at the St. Anna Trough. The main part of the expedition was concentrated to the Amundsen Basin and the North Lomonosov Ridge. The return route passed the North Pole and went south along 10° E to Spitsbergen.

Materials and methods

The sampling methods differ a little between the two expeditions. During the Tundra Ecology -94 expedition sea water were sampled at two depths, surface and near bottom water. Surface water were collected with a ship stationary pump at 3 metres depth while for the near bottom water we used a separate pump attached to a hose which was lowered from the rail of the ship. Sediment were collected by either a HAPS corer or a Box corer. For the determination of the ¹³⁴Cs/¹³⁷Cs activity ratio large amounts of sea water were passed through 10 inch cotton wound cartridge filters impregnated with CuFC (Cu₂Fe(CN)₆), an efficient caesium adsorber.

At the Arctic Ocean -96 expedition sea water was sampled at many different depths down to 2000 metres. Surface water was sampled at 8 metres depth by a ship stationary pump and the deep water sampling was performed using a 100 litre Go-Flow bottle. At most stations the sampling started with a CTD profile enabling us to chose appropriate sampling depths. The standard sampling profile consisted of a surface sample, an Atlantic water sample at temperature maximum around 250-300 metres and one deep sample at 850-1000 metres. At some stations sampling was also performed in the halocline and occasionally at other depths. Sediment was collected with a multiple corer. The sampling for the ¹³⁴Cs/¹³⁷Cs activity ratio was done as described above.

At both expeditions the treatment of the samples were the same. For the determination of 137 Cs we normally used 200 litre water samples which were preconcentrated on the ship by CuFC precipitation after addition of 134 Cs as yield determinant. Back at the laboratory the precipitate was further concentrated and the activity was measured by use of a HPGe detector. At the laboratory the filters for the 134 Cs/ 137 Cs activity ratio determination were ashed and measured on a Ge(Li) detector. By oxalate precipitation also the strontium samples were preconcentrated at the ship. The typical volume were 150 to 200 litres. At the laboratory the strontium were extracted and measured in a beta counter.

The sediment samples were sliced in 0.5 or 1 cm slices, grounded and measured on a gamma counter.

Results and discussion

The standard deviations (1 SD) for the ¹³⁷Cs concentrations in water are below 10 % and for sediment results and ¹³⁴Cs and ⁹⁰Sr in water below 20%.

The Norwegian Sea

The ¹³⁷Cs activity distribution along the Norwegian coast show decreasing levels towards the north, both in 1994 and 1996. In 1994 it decreases from 9.7 Bq/m³ outside Bergen to 8.8 outside Trondheim and 6.4 outside Tromsoe. The same figures for 1996 are 7.0, 3.9 and 3.1 Bq/m³. The reason for this decrease is most probably a dilution when the Atlantic water mixes with the NCC. Observed activity levels along the Norwegian coast are approximately 30 % lower in 1996 compared with 1994. No sediment samples were obtained in this area.


Figure 1. Sampling stations at the Tundra -94 expedition.

The Eurasian Arctic shelf seas

A map over the sampling stations in the Eurasian arctic shelf seas is shown in Figure 1. The ¹³⁷Cs activity distribution in 1994 as a function of longitude along the Siberian coast is illustrated in Figure 2. A trend with increasing activity concentrations from eastern Barents Sea to western Laptev Sea is observed in the surface water, going from 5.3 to 10 Bq/m³, and is more pronounced in the near bottom layer raising from 6.4 to 15 Bq/m³. Since the overall transport in the area is eastward along the coast this means that the total ¹³⁷Cs inflow from the Norwegian Coastal Current has decreased during the beginnings of the 1990's.

The caesium ¹³⁴Cs/¹³⁷Cs activity ratio in the same area is almost constant in both surface and bottom waters. Since the release ratio from the Chernobyl accident in 1986 is known to be about 0.57 and the ¹³⁴Cs influence from Sellafield releases were low in 1994 we may calculate the Chernobyl contribution to the total caesium content. The measured mean ratio 0.014 correspond with 30 % Chernobyl caesium, and we conclude that also the inflow of Chernobyl derived caesium has decreased in the 1990's. The fallout derived ¹³⁷Cs constitute a more or less constant background concentration at 2.5 Bq/m³ in the North Atlantic and Arctic waters. If that amount, and the calculated Chernobyl contribution is subtracted from the total activity, the remaining activity is likely to be Sellafield released caesium which will show the same increase towards east.

At 150 $^{\circ}$ E a sharp gradient is observed and in the East Siberian Sea both surface and near bottom water ¹³⁷Cs activities are significantly lower, 1-3 Bq/m³. These concentrations are approximately in level with the fallout background and this water is therefor supposed to originate from the Pacific Ocean. Further support for this theory is given from the strontium measurements presented below.

The surface water along the coast is strongly influenced around the mouths of the rivers Ob, Yenisej and Lena were the ¹³⁷Cs activities decrease together with the salinity. The analysis of fresh water samples from six rivers in the Kara, Laptev and East Siberian Sea show low ¹³⁷Cs activities, around 1 Bq/m³, and are assumed to consist of runoff of old fallout radiocaesium.



Figure 2. Cs-137 in surface and near bottom water in the Eurasian arctic shelf seas.



Figure 3. Sr-90 in surface and near bottom water in the Eurasian arctic shelf seas.

The strontium activity distribution is shown in Figure 3. The above mentioned increase for the ¹³⁷Cs activity between the Kola Peninsula and the Laptev Sea are also observed, but not as obvious, for the ⁹⁰Sr activity. East of 150 °E the surface water show decreasing activities. The decrease is not so large as for caesium which can be explained by a mixing with runoff water, that have a lower ¹³⁷Cs/⁹⁰Sr ratio than sea water.

Due to the shallow waters at the sampling stations on the shelf, ice formation in the autumn are likely to disturb and mix the bottom sediment. Also biological activity may cause disturbance. All analysed sediment cores from the shelf showed mixed profiles. However two of them reached below the maximum dept of ¹³⁷Cs which enabled us to calculate the integrated ¹³⁷Cs activity. At station 9 west of the Yamal peninsula in the Kara Sea the deposition is 650 Bq/m², and at station 21 west of the New Siberian Island it is 840 Bq/m². The fast mixing of the sediment prevent exchange equilibrium between sediment and water and the K_d will get underestimated. K_d factors were calculated at stations 7, 8, 9 and 21 to be 370, 103, 226 and 1170 Bq kg⁻¹/Bq l⁻¹ respectively. Mixing is assumed to have a large impact

on these K_d 's, regarding that the activity profile from the core that gave the lowest K_d showed high mixing, with ¹³⁷Cs-concentrations strongly increasing with depth.

The central arctic ocean

The sampling stations are presented in Figure 4. In the Arctic interior the highest surface activities in 1996 are found at the north Lomonosov Ridge and at the Gakkel Ridge at 10 °E, reaching 10.2 and 10.6 Bq/m³ respectively. Lower activities are found in the Nansen Basin and the east Amundsen Basin. Compared to earlier measurements in the same area in 1991 and 1994 we note a continued decrease. In 1991 Roos and Holm (1993) observed the highest ¹³⁷Cs activities, 14-19 Bq/m³, in the central Amundsen Basin and north Lomonosov Ridge and Ellis *et al.*(1995) reported a maximum of 14.7 Bq/m³ in 1994 in the same area. The activity origins are, however, somewhat different. The Chernobyl related ¹³⁷Cs in 1991 was low, 0.3-1 Bq/m³ (Roos and Holm, 1993), while the content in 1994 was approximately 30 % (Ellis *et al.*, 1995). Our measured ¹³⁴Cs/¹³⁷Cs activity ratios in the Arctic proper are in the range 2.3 - 7.2 ‰ which correspond to a Chernobyl content of 10-30 %. Highest ratios are found at approximately the same stations as the highest surface ¹³⁷Cs.

The overall surface distribution pattern is reflecting the transpolar drift, which transfer surface water from the shelf seas Laptev and East Siberian Sea, towards the north pole and on down to the waters between Svalbard and Greenland. The estimated total transport time is about three years. The ¹³⁷Cs measurements along the Eurasian shelf in 1994 showed highest activities in the Laptev Sea, with a Chernobyl contribution around 30 %. This is similar to observed levels in the high activity region at the Lomonosov Ridge and around the North Pole in 1996.

In Figure 5 and 6 some of the ¹³⁷Cs activity profiles are displayed. At all stations the warm



Figure 4. Arctic Ocean -96 expedition route.

Atlantic core shows lower ¹³⁷Cs activities than the surface layer, but slightly higher than the deep water samples. The spatial distribution pattern of the Atlantic and deep layer concentrations follows approximately the surface layer distribution, with higher values on the Lomonosov Ridge and at the Gakkel Ridge at 10 °E. Maximum concentrations are found on the latter with 7.2 and 6.1 Bq/m³ in the two layers respectively. In the northern Makarov Basin the only 2000 metre sample was obtained giving the concentration 1.1 Bq/m³. The halocline layer on the Lomonosov Ridge and in the Makarov Basin show elevated concentrations compared to the surface and Atlantic layer. On the Gakkel ridge station at 10 °E, the concentrations are, however, lower in the halocline than in the surface water. This is probably an effect of the different transport pathways for the different layers.

In the Amundsen and Nansen Basin the ⁹⁰Sr depth distribution show similarities with caesium with slightly decreasing activities with depth. Mean concentration in the surface layer is about 3.3 Bq/m³, 3.0 in the Atlantic core and 2.2 at 850 metres depth. At the Lomonosov Ridge and in the Makarov basin the mean activities are slightly higher, 3.7, 2.7 and 2.4 Bq/m³ in the corresponding layers. However, ⁹⁰Sr do not show any peak in the halocline layer as did ¹³⁷Cs.

The different sedimentation rates result in sediment activities in the central arctic much lower compared to the shelves. Integrated ¹³⁷Cs activities are in the range 15 to 80 Bq/m² with the highest values on the Lomonosov Ridge. Most sediment samples from the arctic interior lack a corresponding water sample due to the large depths. However, three K_d's at the Lomonosov Ridge, at a total depth of around 1000 metres and with water samples at 850 metres, were possible to calculate. At 86° 23' N K_d equals 1857 Bq kg⁻¹/Bq l⁻¹, at 87° 11' N 1027 and at 88° 49' N 1352.



Figure 6. Cs-137 depth distribution on the Lomonosov Ridge and in the Makarov Basin



Figure 5. Cs-137 depth distribution in the Amundsen and Nansen Basins

Conclusions

The contribution of anthropogenic radionuclides from the European sources to the arctic seas have decreased in the first half of the 1990's. This is reflected in the measured activities in the different arctic seas which all show lower concentrations compared to earlier measurements. The influence from the Chernobyl accident were about one third of the total surface activity of ¹³⁷Cs at the Eurasian continental shelf in 1994 and between 10-30 % in the central Arctic Ocean in 1996. The obtained results give no indication of any large extra sources for anthropogenic activity besides the well known fallout from atmospheric nuclear bombs test, discharges from European reprocessing plants and the Chernobyl accident releases. However smaller or local contributions from e.g. the dumped nuclear material in the Kara Sea and releases by the Siberian river from Russian nuclear facilities are not possible to exclude in this investigation.

Acknowledgements

This project has received financial support from the Nordic Nuclear Safety Research, The Swedish Radiation Protection Institute, The European Community and the Swedish Natural Science Research Council.

References

Ellis, K.M., J.N. Smith, R.P. Nelson, L. Kilius, R. Macdonald, E.C. Carmack, and B. Moran, 1995. Distribution of Artificial Radionuclides in the Arctic Ocean from the 1994 Arctic Ocean Section. In: P. Strand and A. Cooke (Eds.): Environmental Radioactivity in the Arctic, Østerås, 1995.

Roos, P. and E. Holm, 1993. Distribution of Radiocaesium and Plutonium in Arctic Water and Sediments, Results from the Swedish Oden-Expedition 1991. In: P. Strand and E. Holm (Eds.): Environmental Radioactivity in the Arctic and Antarctic Østerås, 1993.

Radioactivity contamination of the Russian Arctic Seas

Kristina Rissanen¹, Tarja K. Ikäheimonen², Dmitri Matishov³ and Gennady G. Matishov³

¹STUK Radiation and Nuclear Safety Authority, Rovaniemi, Finland, ²STUK Radiation and Nuclear Safety Authority, Helsinki, Finland, ³Murmansk Marine Biological Institute, Murmansk, Russia

Introduction

STUK Radiation and Nuclear Safety Authority participated during 1993 - 1996 in scientific expeditions organized by the Murmansk Marine Biological Institute (MMBI) on the Russian Arctic Seas. The aim of the joint work carried out by STUK and MMBI has been to obtain reliable data on the levels of transuranics and other antropogenic radionuclides in the sea areas and ecosystems of the northwestern part of the former Soviet Union. MMBI was responsible for organizing the expeditions, obtaining the necessary permits and for the physical work involved in sample collection. STUK was responsible for all the radioactivity determinations.

The Barents Sea and the Kara Sea are not a part of Fennoscandia but, in the case of an accident, radioactive contamination would also spread into the Norwegian and Icelandic Sea areas. Information about the radioactive waste dumped in the area etc. has already caused great concern among the population of the North.

STUK's research on the Russian Arctic Sea areas is a part of the EU-project "Radioecological assessment of the consequences of contamination of Arctic waters. Modelling of key processes controlling radionuclide behaviour under extreme conditions" (ARMARA). Because STUK's main task in ARMARA is to investigate the accumulation of radionuclides in the arctic food chains, the sampling was orientated towards surface sediment and biota samples. Sediment cores useful for studying the sedimentation processes were obtained in only a few locations.

Sources

There are several sources of the anthropogenic radioactivity levels currently detectable in the northwestern Arctic Seas of Russia:

- the global fallout caused by atmospheric nuclear weapons testing in the 50's and 60's - marine transport from the European reprocessing plants at Shellafield, Cap de la Hagua, Dounreya

- fallout derived from the Chernobyl nuclear reactor accident
- transport from the Baltic Sea (Chernobyl)
- dumped liquid radioactive waste
- river transport to the Kara Sea (Ob and Jenisey Rivers)

There are also several potential sources for the release of radioactive materials into the environment in the future:

- dumped high-level, solid radioactive waste in the Kara Sea
- dumped medium- and low-level, solid radioactive waste in the Kara Sea and Barents Sea

- spent fuel assemblies and radioactive waste stored in wrecked submarines, storage vessels and facilities close to the sea in harbours and military bases in North Russia.

Russia has planned to use floating nuclear reactors as energy sources for the Stockmanovskaya gas field in the Barents Sea, to establish an industrial decommission enterprise for nuclear submarine in the Archangels area in the White Sea and to use Novaya Zemlya or the Kola Peninsula as the final storage site for high radioactive waste.

Materials and Methods

Sediment sampling

STUK participated during 1993 - 1995 in the collection of sediment samples at 74 locations. In 1993 sampling was carried out in the Barents, Pechora and Kara Sea, in 1994 in the Barents, Pechora and White Sea, and in 1995 in the Kola Bay. Additional top-layer sediments were collected at 72 locations by scientists from MMBI during expeditions to the Stohkmanovskaya gas field, to the northern part of the Barents sea near Franz Josefs Land and St.Anna Trough, and to the east coast of Novaya Zemlja. Top-layer sediment samples were also obtained during the Laptev Sea expedition of the icebreaker "Polarstern" of Alfred Wegener Institute. The sampling locations of the sediments analysed by STUK are presented in Fig 1.



Fig 1. Locations of MMBI & STUK sediment sampling during 1993-1995. STUK participated in sampling at the locations marked with dots, and the locations sampled by MMBI are marked with triangles.

In 1996 the Russian Seas were closed to all foreign radioactivity scientists. Since then, no new sediment samples have been obtained. Radioactivity research is nowadays again classified as a matter of national security in Russia.

Most of our sediment samples represent the 0 - 2 cm layer collected with a spoon or spatula from a van Veen grab or Russian Ocean grab. More quantitative samples were collected with a box corer. These samples were sliced with a large spatula. A Niemistö gravity corer (diameter of the corer 5 cm) was also used during the Barents, Pechora and White Sea expedition in 1994 and a Gemini twin corer (diameter 8-cm) during the Kola Bay expedition in 1995. The sediment cores were cut into 2-cm slices for the first 10-cm, and thereafter into 5 cm slices. One Gemini corer was lost during the White Sea expedition in 1994.

Radioactivity determination

Before the analyses the sediment samples were dried at 105°C and homogenized. All the samples were measured gammaspectrometrically at STUK's regional laboratory in Rovaniemi with a high purity germanium semiconductor and a multichannel pulse-high analyser. The measurement geometry was either 550-ml Marinelli containers or 35 ml or 100-ml plastic jars, and the measurement time 1000-5000 min. The results were analysed using STUK's own computer programs.

Radiochemical analyses of the Pu-isotopes, ²³⁸Pu and ^{239,240}Pu, were carried out on selected samples in collaboration with Tarja K Ikäheimonen, STUK Helsinki, using a method developed at STUK with an internal ²⁴²Pu tracer. After wet ashing and acid leaching of the residue, the plutonium isotopes were separated by means of anion exchange and then electrodeposited onto a stainless steel disc in nitric acid media. Alpha activity was measured either in STUK's laboratory in Helsinki or in Rovaniemi with semiconductor detector - multichannel analyser equipment. For quality assurance the analysis series also contained reagent blanks. Plutonium analyses on the samples are continuing.

Results and Discussion

Barents, Pechora, Kara and Laptev Seas

The ¹³⁷Cs concentrations of the surface sediments in the Barents, Pechora, Kara and Laptev Seas were very low, 0.2 - 40 Bq/kg dry weight (Fig 2). Higher concentrations were measured only in the estuary of River Yenisey, where 80 Bq/kg ¹³⁷Cs were found in a badly mixed sediment box core (Table 1). One 53-cm long Niemistö corer sample from the same place, but discarded by AguaPlan Niva, TromsØ, had similar ¹³⁷Cs and ⁶⁰Cs levels. No ¹³⁷Cs was detected below 28 cm, and the 23-28 cm layer contained only 1 Bq/kg d.w. Minor amounts of ⁶⁰Co and ¹³⁴Cs were also found in other sediment samples collected outside the Ob and Jenisey estuaries.

sample depth cm	¹³⁷ Cs	⁶⁰ Co	^{239,240} Pu	²³⁸ Pu
0 - 2 cm	81	5.8	0.74	0.026
2 - 5 cm	75	5.1	0.65	0.029
5 - 8 cm	76	4.0	1.1	0.042
8 - 11 cm	70	2.3	1.1	0.040
11 - 14 cm	67	1.8	1.2	0.041
14 - 17 cm	75	1.8	0.72	0.032

Table 1. Radionuclide concentrations, Bq/kg d.w. in a box corer sediment sample collected in the Jenisey estuary in 1993.



Fig 2. ¹³⁷Cs concentrations, Bq/kg d.w., in surface sediment layers in the Russian Arctic Seas. MMBI expeditions 1993-1995, radioactivity determinations by STUK.

 137 Cs concentrations of the quantitative surface sediment samples varied from 10 - 200 Bq/m², with an average 100 Bq/m². In the Yenisey estuary the 0-3 cm sediment layer was calculated to contain 580 Bq/m² and the 0 - 17 cm layer 5200 Bq/m² (Fig 3).



Fig 3. Amount of ¹³⁷Cs, Bq/m², in surface sediment layers in the Russian Arctic Seas, 1993 - 1995.



Fig 4. ^{239,240}Pu concentrations, Bq/kg d.w. in surface sediment layers in the Russian Arctic Seas, 1993-1995.

The plutonium concentrations of the surface sediment layers were very low; ²³⁸Pu varied from <0.02 to 0.53, and ^{239,240}Pu from 0.14 to 4.4 Bq/kg d.w. ^{239,240}Pu concentrations over 3 Bq/kg were detected south of Novaya Zemlya and at one site in the Barents Sea. STUK's results for the ^{239,240}Pu levels in the Russian Arctic Seas are represented in Figure 4.

At 14 of these sites the sediments were sampled quantitatively with a box corer or gravity corer which enables the amount of plutonium to be calculated per square metre. The amounts of ^{239,240}Pu were very low varying from 2.5 to 46 Bq/m². Amounts over 25 Bq/m² were detected at only one location, - 46 Bq/m² at the sampling site south of Novaya Zemlja,. The plutonium activity ratio, ²³⁸Pu/^{239,240}Pu, was calculated for sediment samples with measurable amounts of ²³⁸Pu. The ratio varied from 0.23 to 0.083.



Fig 5. Amount of ^{239,240}Pu, Bq/m², in surface sediment layers in the Russian Arctic Seas. MMBI expeditions 1993 - 1995, radioactivity determination by STUK.

The White Sea

The only known potential source of anthropogenic radioactivity in this less-studied arctic sea is the "Sevmash" enterprise in Severodvinsk on the south coast of the White Sea near the city of Archangels.

 137 Cs and 239,240 Pu concentrations, Bq/kg d.w., of twelve 0-2 cm surface sediment samples are presented in Fig 6. The calculated Bq/m² amounts of 137 Cs varied from 120 to 260, 239,240 Pu from 2.48 to 16.8 and 238 Pu 0.19 - 0.95. The 238 Pu/ 239,240 Pu ratio was in most cases 0.025 - 0.055, but 0.117 in location 24. Traces of 134 Cs were detected in some of the samples, and 1.7 Bq/kg of 60 Co, in the surface layer in Kandalaksh Bay (location 22).



Fig 6. ¹³⁷Cs and ^{239,240}Pu concentrations, Bq/kg d.w., in the 0-2 cm surface sediment layer in the White Sea 1994. MMBI expedition, radioactivity determinations by STUK.

The vertical distribution of ¹³⁷Cs and ^{239,240}Pu at three locations in the White Sea are presented in Fig. 7. In the Kandalaksh Bay (location 22) and in the open White Sea (location 32), both the 137Cs and ^{239,240}Pu concentrations decreased steadily from the surface down to a depth of 10 - 15 cm which, according to the sedimentation rate calculations of Riso National Laboratory, Denmark, corresponds to about 30 - 40 years of sedimentation. ¹³⁷Cs and ^{239,240}Pu were not detected in deeper layers. At the Dvina estuary (location 30), the sediment layers were badly mixed.



22. Kandalaksh Bay N 66°30.5' E 34°12.6', depth 290 m Niemistö corer 23.7.94



Fig 7. Vertical distribution of ¹³⁷Cs, ⁶⁰Co, ²³⁸Pu and ^{239,240}Pu in pooled sediment cores, White Sea 1994. The sampling locations are marked in Figure 6. MMBI expedition, radioactivity determinations by STUK.

The total ¹³⁷Cs radioactivity load per square metre in the 10 cm surface layer was calculated to be 570 in the Kandalaksh Bay, 420 in the open White Sea and 2650 Bq/m² in the Dvina estuary, the ^{239,240}Pu load being 64.5, 31.4 and 23.5, respectively. The 20 cm-long column collected in the Dvina estuary contained 5800 Bq ¹³⁷Cs and 59 Bq ^{239,240}Pu per square metre. The ¹³⁷Cs/^{239,240}Pu ratio of the Dvina estuary sediment was 105, indicating an excess of radiocesium input via riverine transport from the large catchment area, while in all the other White Sea locations the ratio varied from 9 to 22. A similar high ¹³⁷Cs/^{239,240}Pu ratio was earlier reported in the Yenisey River estuary in the Kara Sea, where the total cesium load was also about the same order of magnitude as that in the Dvina estuary.

The ¹³⁷Cs concentrations measured in the White Sea are higher than those measured in sediments in the Barents, Petshora, Kara and Laptev Seas. The "Mediterranean" White Sea is surrounded by land and affected by fresh water transport from several rivers. The excess of radioactive cesium in the sediments of the Dvina river estuary is transported from the large catchment area of the river. The riverine transport of fallout radionuclides from the 50's and 60's, and from the Chernobyl accident, is one of the main sources of the radioactivity nowadays measured in the White Sea.

Releases from the "Sevmash" enterprisce in Severodvinsk was not noticed, but all the samples of this study were collected in unrestricted areas. The origin of the activation product ⁶⁰Co

found in the Kandalaksh bay and the high ²³⁸Pu/^{239,240}Pu ratio in sediment sampling location 24 is unknown. According to the Yablokov report (1) one dumping place for liquid radioactive waste is located between our sampling locations 24 and 25.

Kola Bay

The purpose of the expedition in May 1995 was to study the level of radioactive pollution in the Kola Bay where several potential sources are located. The civilian nuclear icebreaker base "Atomflot" with liquid waste purification plant and the storage vessels "Lepse" and "Imandra" are located in Murmansk town area. Military nuclear submarine bases and Naval shipyards are located in Sevmorput, Severomorsk, Polarnyy, Pala Bay, Olenaya Bay etc. with storage for fuel assemblies, solid and liquid radioactive waste in ships and on land.



Fig 8. Sediment sampling locations in the Kola Bay in 1995.

Sediment samples were collected from the 16 locations (marked in Figure 8) with a Gemini gravity corer, a box corer or a van Veen grab during an expedition that started from Murmansk and ended at Kildin Island in the Barents Sea.

The results of the gammaspectrometric measurements and plutonium analyses are presented in Figures 9 and 10 and in Table 2. Figure 9 represents the concentrations (Bq/kg) of 137 Cs, 60 Co and 125 Sb and the concentrations of 238 Pu and $239,2^{40}$ Pu in the corresponding surface (0 - 2 cm)

sediment layers of sampling locations 1 - 16 in the Kola Bay. The average ¹³⁷Cs concentration of the surface sediment was 11 Bq/kg, varying from 5 to 18 Bq/kg. The amount of cesium per square metre were 120 Bq/m² for the 0 - 2 cm surface layer, and about 300 Bq/m² for the 0 - 5 cm surface layer. 0.2 - 2 Bq/kg ⁶⁰Co was detected in all the surface sediments between "Atomflot" and the Barents Sea. Traces of ¹³⁴Cs were detected in locations 1, 6 and 11 and small ¹³⁷Cs particles near the "Atomflot".



Fig.9. Gammanuclide and plutonium isotope concentrations, Bq/kg d.w., in surface sediment in the Kola Bay in 1995. MMBI expedition, radioactivity determinations by STUK.

Figure 10 illustrates the vertical distribution of the ¹³⁷Cs, ⁶⁰Co and ¹²⁵Sb concentrations in sliced Gemini corer samples from locations 2-6 and 9-10 in the Kola Bay. One 0 - 6 cm Gemini corer was also collected at "Atomflot" and measured in a 550 ml Marinelli geometry. This large volume sample contained 23 Bq/kg of ¹³⁷Cs, 0.3 ¹³⁴Cs, 2.1 ⁶⁰Co, 0.5 ⁹⁵Zr, 2.6 ¹⁵⁴Eu, and 1.9 ¹⁵²Eu.

The plutonium levels were low (Table 2), but elevated ²³⁸Pu/^{239,240}Pu ratios were found in four locations: south of Murmansk city, in deeper layers upstream from the nuclear icebreaker fleet "Atomflot", in front of the "Atomflot" and in the sediment collected in the outlet of the Kola Bay in the Barents Sea.

Because of the mixed sediment layers and the particles, determination of the sedimentation rate was not possible.



Vertical distribution of Pu-238 and Pu-239,240

concentrations, Bq/kg d.w., in sediment, Kola bay 1995,

2

2,0

2.0

2,0

2

2

2,5

2,5

2.5

2,5

2,5

2,5

2,5

Vertical distribution of gammanuclide concentrations, Bq/kg d.w., in sediment, Kola bay 1995, sampling with a gemini or box corer

Fig.10. Vertical distribution of the gamma nuclides ¹³⁷Cs, ⁶⁰Co, ¹²⁵Sb and plutonium isotopes ²³⁸Pu and ^{239,240}Pu in sediments from the Kola Bay, pooled samples of 5 - 6 cores. MMBI expedition in May 1995, radioactivity determinations by STUK.

Location	²³⁸ Pu	^{239,240} Pu	²³⁸ Pu/ ^{239,240} Pu
1	0,044 (23)	0,37 (8)	0,118
2	0,051 (12)	0,73 (4)	0,070
3	0,046 (19)	0,69 (6)	0,067
4	0,072 (11)	1,17 (4)	0,062
5	<0,025	0,48 (7)	
6	0,11 (12)	0,95 (4)	0,116
7	0,026 (20)	0,48 (5)	0,054
8	0,048 (15)	0,90 (5)	0,053
9	0,13 (9)	1,56 (4)	0,083
10x	0,12 (30)	1,78 (6)	0,067
11x	0,12 (10)	2,42 (5)	0,050
12	0,058 (17)	0,76 (6)	0,076
15x	0,14 (30)	1,99 (10)	0,070
16	0,046 (25)	0,89 (6)	0,052
13x	0,10 (14)	0,84 (6)	0,119
14x	0,08 (15)	1,01 (5)	0,079

Table 2. ²³⁸Pu and ^{239,240}Pu concentrations, Bq/kg d.w., and ²³⁸Pu /^{239,240}Pu activity ratios in 0-2 cm surface sediment samples collected in 1995 from the Kola Bay ($\pm 1 \delta \%$)

(x marked samples 0-5 cm)

The ¹³⁷Cs levels measured in this study in the Kola Bay are similar to those found in the open Barents Sea sediments if the ¹³⁷Cs particles are excluded. The appearance of the corrosion product ⁶⁰Co-60 (half-life 5.3 y) in all sediment samples between "Atomflot" and the Barents Sea, the other anthropogenic radionuclides detected and the increased ²³⁸Pu/^{239,240}Pu ratio in sediment from outside the "Atomflot" and in the outlet of the Kola Bay, indicate some fresh release from the nuclear icebreaker facility or storage vessels lying in front of it. However, considering the abundance of military and civilian nuclear activities in the Kola Bay, the measured concentrations are low.

Conclusion

The levels of anthropogenic radionuclides in the Russian Arctic Seas are low compared to the potential sources of pollution, and mainly originate from global fallout, Chernobyl fallout and from the nuclear fuel reprocessing plants in Western Europe. Fresh release of radioactivity was noticed in this study only in the Kola Bay and in two sampling locations in the White Sea. The increased ¹³⁷Cs concentrations measured in the estuaries of the River Dvina and River Yenisey are caused by riverine transport from the large catchment area.

The sediments in the Russian Arctic Seas are hard. Unmixed, sufficiently long cores for determination of the sedimentation rate were obtained in only two locations in the White Sea. All the cores from river estuaries were badly mixed.

Acknowledgement

The authors are grateful to the crew of the scientific expedition and to the experts from MMBI in identifying the sediment types.

The work was financed by the Finnish Ministry of Foreign Affairs, by the Ministry of the Environment, by the EC project ARMARA, Contract No. F14P-CT95-00335 (DG 12-WSME), by the Nordic Council of Ministers and by the Nordic Nuclear Safety Research (NKS-EKO-1). Without the support of the employment authorities in Rovaniemi the time consuming preliminary treatment of the sediment and biological samples would not have been possible.

Refenences

(1) Yablokov A.V., Karasev V.K., Rumyantsev V.M., Kokeyev M. Ye., Petrov O.I., Lystsov V.N., Yemelyanenkov A.F., Rubtsov P.M., Facts and Problems Related to Radioactive Waste Disposal in Seas Adjacent to the Territory of the Russian Federation, Office of the President of the Russian Federation, English Edition by Small World Publishers, Alberquerque 1993.

STUK:S Publications on Radioactivity Levels in Russian Arctic Seas

Rissanen K., Matishov D., Matishov G., Radioactivity levels in Barents, Petshora, Kara, Laptev and White Sea. In "Environmental Radioactivity in the Arctic". Ed. Per Strand, Andrew Cooke, Østerås 1995, p.208-214.

Rissanen K., Ikäheimonen T.K., Matishov D. and Matishov G.G., Radioactivity levels in fish, benthic fauna, seals and sea birds in the Northwest Arctic of Russia. Radioprotection - Colloques, 32, C2 (1997) 323-331.

Ikäheimonen T.K., Rissanen K., Matishov D., Matishov G., Plutonium in fish, algae, and sediments in the Barents, Petshora, and Kara Sea. The Science of the Total Environment 202 (1997) 79-87.

Rissanen K., Ikäheimonen T.K., Nielsen S.P., Matishov D.G. and Matishov G.G., Gammanuclide and plutonium concentrations in the White Sea. Extended abstracts of the Third International Conference on Environmental Radioactivity in the Arctic, Tromsø, Norway June 1-5, 1997 p. 222-224.

Rissanen K., Ikäheimonen T.K., Matishov D. and Matishov G.G., Radioactivity levels in Kola Bay. Radiation Protection Dosimetry 75(1998)223-228.

Radionuclides in marine sediments – Distribution and processes

Anne Liv Rudjord¹, Deborah Oughton², Tone D. Bergan³, Gordon Christensen³ ¹Norwegian Radiation Protection Authority, ²Agricultural University, Ås, ³IFE

1. Introduction

As a result of the Russian-Norwegian investigations (1992-94) of the dumped radioactive waste in the Kara Sea, it was recognized that more information on sediment processes was needed in order to improve the assessements of long term consequences following releases of radioactivity to the marine environment. It has been shown that the results of model calculations used in the assessements are sensitive to parameters like sedimentation rates and distribution coefficients.

Information on the sources of the actual radioactive contamination in sediments and sea water can be obtained by studying isotope ratios. Primary sources of contamination include global weapons' fallout, fallout from the Chernobyl accident, discharges of reprocessing wastes (Sellafield, La Hague) and leakage's from sea-dumped radioactive waste.

Sediments can act as both sinks and sources of radionuclides in the marine environment. Following an input to marine systems, sediments represent the major sink for many radionuclides. However, when the primary sources have ceased or been greatly reduced, remobilization of radionuclides from previously contaminated sediments may increase in importance as a diffuse secondary source (G.J. Hunt et al.,1990, D.H. Oughton et al.,1997). Secondary sources also include mobilisation from contaminated land-based areas. In addition to soluble species in surface run-off from terrestrial ecosystems, two main sources of sediment to marine waters can occur under episodic events: the transport of suspended sediments with flood waters and the transport of sediments incorporated within "dirty" ice (S.L. Pfirman et al.,1996; D. Meese et al.,1995). In both cases, freshwater sediments are transferred into marine waters, thus are subject to changes that can influence mobility of associated radionuclides.

The partitioning of radionuclides between water and sediments is represented by the distribution coefficient or K_d (ml/g):

 $K_d = \frac{Bq/g \text{ sediment}}{Bq/ml \text{ water}}$

 K_d is one of the major parameters determining the fate of radionuclides in the environment: the higher the K_d , the greater the proportion of contaminant that will be found in sediments. It follows that the mobility of any radionuclide in a water-sediment system will be limited by the strength of sorption to the sediment, the reversibility of the sorption mechanism and the kinetics of the sorption/desorption processes. These factors will in turn depend upon the physical and chemical properties of the radionuclide, the water and the sediment. Radionuclides can be transported from the water to the sediment phases by physical (e.g. sedimentation), chemical (e.g. ion-exchange, polymerisation, colloid aggregation) and biological (e.g. detris) processes (Fig 1.1). Physical remobilization of contaminants from sediments to water can occur due to natural or anthropogenic resuspension of the sediments, e.g. during flooding, erosion or estuary dredging; chemical mobilisation includes ion-exchange, leaching and dissolution. Biological processes can effect both chemical and physical mobilisation (eg. bioturbation).

The radionuclide speciation and interaction with sediment components determines the degree to which contaminants will be transported to other parts of the ecosystem (B. Salbu et al., 1995). Hence, parameters which cause a variation in K_d subsequently influence radionuclide transport.



Figure 1.1

In this project, an attemt has been made to obtain data both empirically by radionuclide analysis of surface sediment and sediment cores, and by laboratory tracer experiments using sediments collected simultaneously. The aim of the laboratory experiments was to provide some information on the kinetics of radionuclide water-sediment interactions, and to determine which parameters can influence sorption processes, K_ds and kinetics.

1.1 Sources of marine radioactive contamination

There are several sources of radioactive contamination in the marine environment of the Nordic countries. The major contributors are:

- Fallout from atmospheric nuclear weapons testing in the fifties and sixties.
- Fallout from the Chernobyl accident in 1986.
- Transport of radionuclides discharged from reprocessing plants (Sellafield and Dounreay in the United Kingdom, La Hague in France, Mayak PA and Tomsk-7 in Russia).

In addition to the radionuclides already released to the environment, there are areas were there exist potential risks for future releases. The major potential sources to radioactive contamination in Nordic and Arctic waters, are assumed to be:

- Transport of radioactive contamination with river transport by Ob and Yenisey, from landbased nuclear installations and from accidental releases.
- Dumped solid radioactive waste and spent nuclear fuel in the Kara Sea.
- Civilian and military nuclear installations on the Kola Peninsula.
- (Continued) runoff of Chernobyl fallout from land to especially the Baltic Sea.

The atmospheric nuclear weapons testing is the main source of radioactive contamination in the Arctic region. It is estimated that approximately 75% of ¹³⁷Cs and 95% of ⁹⁰Sr inventories in the North Atlantic are coming from global fallout as a result of atmospheric nuclear weapons testing (A.Aarkrog, 1989). In the early sixties nuclear weapons testing was also carried out underwater close to Novaya Zemlya. In the Chernaya Fjord high local contamination is assumed to be due to these detonations (Smith et al.).

One of the main sources of radiocaesium, strontium, plutonium, americium, iodine and tritium discharges to the North Atlantic and the North Sea, have been the reprocessing facilities in Sellafield, UK. But after the mid-seventies the releases of radiocaesium from Sellafield have decreased considerably. However, the operation of the Thermal Oxide Reprocessing Plant (THORP) and the Enhanced Actinide Removal Plant (EARP), which started operating in 1994, is expected to increase discharges of some long lived radionuclides like ¹³⁷Cs, ⁶⁰Co, ⁹⁰Sr and especially ⁹⁹Tc. From the late sixties until the mid-eighties, the releases of radiocaesium from Sellafield were up to a factor 100 higher than the releases from Dounreay and Cap de la Hague.

The Chernobyl accident took place in Ukraine April 1986 and was the most serious accident of nuclear reactor operation in the history. Radionuclides were released to the atmosphere and contaminated large areas of Europe. The fallout from the Chernobyl in the marine area west of Norway, in the Baltic Sea, and the run-off from contaminated land areas have influenced the Nordic marine environment.

From 1959 to 1991 Soviet nuclear waste was dumped in the Barents and Kara Seas. The waste ranged from low level liquid waste to spent nuclear fuel. A Joint Russian-Norwegian Expert Group has investigated the present contamination at the dumpsites and the potential for future releases. The investigation concludes that enhanced levels of artificial radionuclides in sediments collected in the close vicinity of localised dumped objects demonstrate that leakages do occur. However no contribution from dumped radioactive waste can be observed in the open sea. Preliminary assessments of the total releases from dumped nuclear waste indicate a very small dose to the population (JRNEG, 1997).

Radioactive releases from several former Soviet nuclear installations enter the drainage areas of the Ob River (Tomsk and Mayak) and of the Yenisey River (Krasnoyarsk). Both rivers have their outflow to the Kara Sea. It is difficult to estimate the impact on the Arctic waters from these sources, since the data in the open literature are inconsistent. Observations carried out by Roshydromet (Vakulovsky,1993) indicate that the amount of ⁹⁰Sr and ¹³⁷Cs transported by the rivers during 1961-1989 is about 1 PBq and 0.1 PBq, respectively.

In addition to the radionuclides transported to the Kara Sea by river run-off, approximately 200 TBq of ⁹⁰Sr and 20 TBq of ¹³⁷ Cs have been transported to the Barents Sea by the rivers Pechora, Onega and Severnaya Dvina (Vakulovsky, 1993).

2. Materials and Methods

2.1 Collection of samples

The sediment samples were collected under a number of different research expeditions, and includes sediments from the open Kara Sea, the Stepovogo Fjord (Novaya Zemlya), the Ob estuary, the Yenisey estuary, the «mix» area north of the Ob-Yenisey estuary mouths, sediments collected from dirty ice north of the Ob-Yenisey estuary mouths as well as samples from the Norwegian coast and the Irish Sea.

The locations of the sampling stations are given in Fig.2.1.

Core profiles of marine and estuarine sediments were taken from box core samples, and sectioned after freezing. Bulk samples for use in tracer experiments were collected by scraping surface sediments from the box corer.

The dirty ice sediment was collected from a melting pool on the surface of the floating pack ice. All samples apart from Stepovogo Fjord were frozen after collection.

Further details of the sample collection are given in elsewhere (JRNEG, 1997; Grøttheim, 1998; Karex 94).

2.2 Radionuclide analysis

The sediment samples were freeze-dried prior to analysis of gamma-emitting radionuclides using high resolution HPGe-detectors. For tracer experiments, a NaI 3 x 3" detector was used. Strontium-90 was determined by chemical separation followed by low-level liquid scintillation counting (Bjørnstad et al, 1992). Plutonium isotopes and ²⁴¹Am were determined by radiochemical separation from other transuranics using ion-exchange, followed by electrodeposition and alpha-spectrometric measurement on semiconductor silicon-detectors (Clacher,1995; Chen et al, 1991).

Sediments from the Kara Sea, the estuaries of Ob and Yenisey and from the Norwegian Sea have been dated by analysis of ²¹⁰Po and ²¹⁰Pb. ²¹⁰Pb and ²²⁶Ra have been analysed by n-type germanium detector and the amount of unsupported ²¹⁰Pb have been used to determine sedimentation rates.

The total amount of ²¹⁰Pb in the sample has been detected directly by n-type HPGe detector γ -spectrometry. As ²¹⁰Pb emits γ -rays with an energy of 46.5 keV, it is important to correct for self absorption in the sample. Each sample has therefore been analysed both with an external ²¹⁰Pb point source on top of the sample and without. The self absorption has been corrected for according to Cutshall et al.(1983). The total uncertainty for individual samples is about 30 %.

Alternatively ²¹⁰Po has been analysed by chemical separation and α -spectrometry. A sediment sample of 1 - 2 g was treated with hot, conc. HCl for several hours. The solution was evaporated nearly to dryness, then water was added to the precipitate and the mixture stirred

well. The supernatant was decanted and filtered, and the precipitate washed with 0.5 N HCl. The new supernatant was filtered and added to the first. Polonium was then auto-electroplated onto a prewashed (with 1 N HCl) Ni-disc. For determination of the chemical yield, ²⁰⁸Po or ²⁰⁹Po was added to the sediment at the start of the procedure. Assuming radioactive equilibrium between ²¹⁰Po and ²¹⁰Pb, the ²¹⁰Pb activity is equal to the found ²¹⁰Po activity. Precision tests showed an overall uncertainty in the determinations of ²¹⁰Po in individual samples of 33%.



Figure 2.1 EKO-1/No-1 sediment sampling stations collected during the R/V Gauss expedition in 1995. In addition, sediments from the Irish Sea, the Kara Sea, the Stepovogo Bay and from the Ob and Yenisey estuaries have been studied.

2.3 Determination of sedimentation rates

The radionuclide ²¹⁰Pb and its daughter ²¹⁰Po are often used for dating of sediments and determine sedimentation rates. They have half lives of 22.3 years and 138.4 days, respectively. Both are daughter nuclides of ²²²Rn which is produced from ²²⁶Ra. ²²²Rn is a gas and is therefore partly released to the atmosphere. The daughter products of ²²²Rn are subsequently washed out of the atmosphere by precipitation, and in aquatic systems they are adsorbed to sedimenting particles in the water phase. The adsorbed amount of ²¹⁰Pb is called «unsupported», distinguishing it from the «supported» ²¹⁰Pb originating from the sediment particles themselves.

Sedimentation rates have been calculated based on determination of the amount of unsupported ²¹⁰Pb in the different layers of sediment cores. This has been done by two different analytical methods described below.

In addition to the analytical errors, there are other uncertainties connected to the determination of sedimentation rates. In marine environments, the rates are usually low, and a layer of 1 cm may represent 5-10 years or more. Biological activity in the sediments can lead to a mixing of the upper layers, and thus the analytical results are difficult to interpret. The largest uncertainty is however from the sediment sampling itself. The sediment core is often compressed, usually there is larger friction along the edges of the sampling device, and a new compression can occur when the core is pressed out of the tube to be sliced.

A method of sediment compression (density) correction has been used, as described by Tadjiki et al. (1994). Differences in density between the samples were compensated corewise by adjusting the thickness of the slices below 2 cm depth relative to the 0-2 cm slice. The calculations were based on the relation between sample dry weight and sample water weight; thereby determining the porosity of the samples.

For most cores, the ²¹⁰Pb or ²¹⁰Po activity approached a constant value at a certain depth. This represents the amount of supported ²¹⁰Pb in the sediments of the core. Otherwise, the supported ²¹⁰Pb is determined by analysis of ²²⁶Ra (or ²¹⁴Pb or ²¹⁴Bi if in radioactive equilibrium with ²²⁶Ra). The sedimentation rate was then calculated using exponential curve fit based on determinations of the content of unsupported ²¹⁰Po in density corrected core slices.

2.4 Sediment characterisation

Dry weight (105°C), organic content by loss on ignition (LOI, 550°C), pH, cation exchange capacity (CEC), trace element concentrations, surface area, and mineral type were determined on sediment sub-samples.

Cation exchange capacity (CEC) determination was carried out by an NH₄Ac extraction method. An aliquot (5-10 g) of the washed (distilled water), freeze-dried sediment is extracted with 1M NH₄Ac (pH 7.00, 150 ml) and the macro cation (Na, K, Mg, Ca) concentrations in the extract determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (A. Øien et al., 1987). Trace element concentrations were determined on whole sediment samples using neutron activation analysis (NAA) (D.H. Oughton et al., 1993). Organic content was estimated by ashing freeze-dried samples at 550°C and determining the weight loss (LOI). Total carbon (TC) was determined by ashing freeze-dried sediments in a carbon analyser (EC-12). Extracting freeze-dried sediments with 2M HCl and then ashing in the carbon analyser gives total inorganic carbon, TIC. The total organic carbon, TOC, = TC - TIC. Determination of sediment surface area (m^2/g) was carried out by the nitrogen method. The pressure difference between a null sample and the freeze-dried sediment (measured by condensing N₂ gas on the surface) is used to calculate the surface area of the sediment.

2.5 Tracer experiments: general conditions

Tracer studies using the gamma-emitting radioisotopes 134 Cs (t_{1/2} 2.1 years, 605 and 795 keV) and 85 Sr (t_{1/2} 65 days, 514 keV) were used to investigate the kinetics of radionuclide adsorption and desorption. All experiments were carried out under aerobic, dark conditions at 4°C, using wet sediments. Seawater in all experiments was Oslo Fjord seawater (pH 8.2, salinity 34 ‰); the riverwater used was collected from Oslo Akerselv, just below Maridalsvann (pH 5.8). Both waters have been well characterised with respect to chemical composition. It must be stressed that tracer experiments should be seen as operationally-

defined investigations into processes and controlling parameters, rather than an attempt to mimic natural conditions.

2.6 Time dependent changes in K_d: sediment-seawater tracer studies

Rates of change in K_d (ml g⁻¹) were measured as a function of contact time in static seawatersediment tank studies. Wet sediments, equivalent to about 10g dry weight (DW), were added to 2.0 l seawater and allowed to "equilibrate" for 2 weeks in dark, aerobic conditions at 4°C. The area of the sediment/seawater contact surface was 300 cm² and sediment-water tanks were set up in duplicate for each sampling site. After two weeks, the ¹³⁴Cs and ⁸⁵Sr tracer solution (1.0 ml in 0.5 mM HCl) containing 50 kBq of each radioisotope was added to the seawater and the water was stirred gently in order to mix the tracer solution into the seawater without disturbing the sediment. The aliquots did not alter the pH of the seawater, and the added Cs and Sr concentrations (< 0.01 g) were insignificant compared to the levels in seawater (Sr 8 mg/l and Cs 0.3 g/l). Samples of water (20 ml) were collected and ¹³⁴Cs and ⁸⁵Sr concentrations determined throughout the 1 year period. In order to check for sorption to container walls and removal of the radiotracers by precipitation out of solution, a control solution was prepared by adding the tracer solution to 2.0 l seawater without sediment.

2.7 Sequential extraction of tracer labelled marine sediments

Radionuclide mobilisation from sediments was studied using a series of batch studies, wherein sediments were subjected to sequential extraction after different contact times with labelled seawaters. Seawater (20 ml, ca. 500 Bq ¹³⁴Cs and ⁸⁵Sr) was added to wet sediments (equivalent to ca. 1 g) in 50 ml centrifuge tubes, shaken on a rolling table for 1 hour, and then allowed to stand in aerobic conditions at 4°C. After the appropriate contact time (1 hour, 1 day, 1 week and 1 month) the seawater was separated from the sediment using high speed centrifugation (10 000 rpm, 30 min) and the labelled sediments subject to sequential extraction. The extraction agents included: seawater (1 hr at RT); 1M NH₄Ac (pH 7, 2 hr at room temperature); 1M NH₄Ac (pH 5, 2 hr at room temperature); and 7M HNO₃ (6 hr at 85°C). Supernatants were separated from the solids using high speed centrifugation, and then filtered through 0.45 um filters into 20 ml counting vials. Extracts, filters and residues were counted using a NaI detector.

2.8 Sequential extraction of environmentally labelled marine sediments

In samples having high enough "natural" contamination levels (i.e., Irish Sea and Stepovogo) the distribution of ¹³⁷Cs and ⁹⁰Sr between sediment extraction fractions was compared with that of the ¹³⁷Cs and ⁸⁵Sr tracers. Both Irish Sea and Stepovogo Fjord sediments show considerable variation in radionuclide levels: maximum activity levels in the Irish Sea samples are found at a depth of 10 -30 cm (H. Fjelldal et al., 1995) and the activities in Stepovogo Fjord sediments are very inhomogenous due to localised leakage from dumped waste containers (P. Børretzen et al., 1995). Hence, in addition to extraction studies on surface sediment samples used in tracer studies, studies were also carried out on selected "high activity" samples from the same location.

2.9 Change in K_d after transfer of labelled sediments from freshwater to seawater

The potential for mobilisation of radionuclides from sediments following transfer from a freshwater to a seawater environment was studied. Labelled river waters (20 ml, 500 Bq 134 Cs and 85 Sr) were added to Ob-II and «dirty ice» sediment samples (equivalent to ca. 1 g dry weight). After 1 week contact time, the water was separated from the sediment using high speed centrifugation. The labelled sediments were then extracted sequentially with river water (3 x 20 ml) and seawater (3 x 20 ml): shaken for 1 hour, then separated by high-speed

centrifugation. Distribution coefficients ($K_d m l g^{-1}$) were measured in the fresh water and seawater extraction's.

3. Results and Discussion

3.1 Radionuclides in surface sediments

In Table 3.1 the concentration of radionuclides in surface sediment (0-2 cm) are listed.

In the «Norwegian» surface sediments, the ¹³⁷Cs concentrations varied in the range 3.0- 24.7 Bq/kg. ¹³⁴Cs was detected at station 26 only. The observed ¹³⁴Cs/¹³⁷Cs ratio was 0.032-0.035, similar to what would be expected for pure Chernobyl radiocesium (0.03) in 1995. These results indicate that fallout from the Chernobyl accident is an important source to the contamination of the sediments at station 26, probably as a result of direct deposition to the sea surface. It has been reported earlier that Chernobyl fallout in the Norwegian Sea was rapidly removed to the sediments (Baumann, 1989). Chernobyl origin is also supported by the fact that the activity ratio ¹³⁷Cs/^{239,240}Pu is about 40 at this station, while at all other stations this ratio is less than 20.

The ^{239,240}Pu concentration in the «Norwegian» surface sediments are in the range 0.6-2.77 Bq/kg. The observed ²⁴¹Am concentrations are in the same order of magnitude, 0.29-0.98 Bq/kg.

 238 Pu/ 239,240 Pu ratios in the sediments are in the range 0.03-0.10. At stations 11 (Skagerak/Kattegat) and 16 (North Sea) some influence from Sellafield plutonium is suggested, as the plutonium ratio is significantly higher (0.08-0.10) than would be expected from global fallout (0.03).

3.2 ¹³⁷Cs in sediment cores and sedimentation rate

In Fig. 3.1 the ¹³⁷Cs activity profiles of the cores are shown.

Results for the determination of sedimentation rates are given in Table 3.2. Plots of ²¹⁰Po (supported and unsupported) vs. depth are given in Figure 3.2

As mentioned in chapter 2, there are many uncertainties connected to the determination of sediment rates in addition to the analytical errors. Biological activity in the upper layers are one of these. The ideal core gives a ²¹⁰Pb activity curve which approaches a background value at a certain depth. Here the activity represents supported ²¹⁰Pb only. Subtracting this background value from the total activity gives a nice straight line in a semi logarithmic plot, the slope of which determines the sedimentation rate.

The cores from the locations 46 and 56 are approximately such "ideal" ones, and the rate can be determined with reasonable confidence (see Figure3.3b)). Table 3.2 shows that the sedimentation rate is about 0.1 cm/year at these locations in the Barents Sea and northern part of the Norwegian Sea. Relatively high values of Cs-137 as deep as 6-10 cm, representing 60-100 years old sediment, cannot be explained by input from any of the major known sources mentioned above if the found sedimentation rate is correct. If it was due to bomb fallout, the rate should have been about 0.25 cm/year.

Sample	¹³⁷ Cs (Bq/kg)	⁹⁰ Sr	²³⁸ Pu	^{239,240} Pu	²⁴¹ Am
		(Bq/kg)	(Bq/kg)	(Bq/kg)	(Bq/kg)
Irish Sea	480 <u>+</u> 24 (3200*)	250 <u>+</u> 12 (2000*)	na	43 <u>+</u> 3 (245*)	na
11 Skagerak/ Kattegat	10.5 <u>+</u> 2.0	na	0.28 <u>+</u> 0.03	2.77 <u>+</u> 0.18	0.98 <u>+</u> 0.07
16 North Sea	13.1 <u>+</u> 1.3	na	0.12 <u>+</u> 0.02	1.60 <u>+</u> 0.11	0.97 <u>+</u> 0.07
26 Norwegian Sea	24.7 <u>+</u> 1.0	na	0.030 <u>+</u> 0.007	0.61 <u>+</u> 0.05	0.29 <u>+</u> 0.04
34 Komsomolets	22.2 <u>+</u> 2.2	na	0.040 <u>+</u> 0.010	1.16 <u>+</u> 0.08	0.86 <u>+</u> 0.06
39 North of Finnmark	3.0 <u>+</u> 0.6	na	0.019 <u>+</u> 0.005	0.64 <u>+</u> 0.05	0.29 <u>+</u> 0.03
46 Barents Sea	6.7 <u>+</u> 2.1	na	0.074 <u>+</u> 0.009	1.92 <u>+</u> 0.12	0.74 <u>+</u> 0.05
Norway 56a West of Svalbard	8.5 <u>+</u> 0.7	na	0.054 <u>+</u> 0.010	1.01 <u>+</u> 0.07	0.85 <u>+</u> 0.06
Kara Sea	3.0 <u>+</u> 0.2	< 2	na	0.7 <u>+</u> 0.07	na
Stepovogo	110 ± 6 (120.000*)	14 <u>+</u> 1	na	na	na
Ob-I Ob-II	< 0.5	5 <u>+</u> 0.5	na	na na	na
Yenisey	< 0.5	3 <u>+</u> 0.3	na	na	na
Mix	< 0.5	2 <u>+</u> 0.2	na	na	na
Dirty Ice	< 0.5	4 <u>+</u> 0.4	na	0.7 <u>+</u> 0,07	na

Table 3.1 Concentration of radionuclides in surface sediments (0-2 cm)

na not analysed

* high activity level samples used in sequential extraction studies

Further south, outside Mid-Norway (26) and in the North Sea (16), the rates are lower, about 0.03-0.04 cm/year. These cores are also approximately "ideal" ones.

In Skagerak, however, the found sedimentation rate is higher, about 0.25 cm/year. The rate is however somewhat uncertain, as can be seen from Figure 3.2 a). There has probably been some disturbance of the upper layers. The supported ²¹⁰Pb had to be determined from the ²²⁶Ra content of the sediment (65 Bq/g) and may be too high. But even if a background value of 36.5 Bq/kg (the ²¹⁰Pb content of the lowest core layer) is used instead, the rate would have been 0.31 cm/year or only about 20 % higher. Omitting the first and fourth core layers from the curve fit will not alter the slope of the straight line much. Thus the value of 0.25 cm/year is probably nevertheless a good approximation of the actual value. The maximum of the ¹³⁷Cs profile at this location is at about 9 cm depth (density corrected), representing 30-40 years old sediment and indicating that this ¹³⁷Cs is mostly from bomb fallout.



Figure 3.1 Concentrations of ¹³⁷Cs (Bq/kg) in sediment profiles.

It is rather surprising to find such a low sedimentation rate (0.05 cm/year) in the Yenisey Bay. Figure 3.2c) however shows a rather nice plot indicating no disturbance of the upper layers and a rather well defined background of supported ²¹⁰Pb. It can be questioned if this ²¹⁰Pb method is adequate for such an estuarine zone where also the ice covers the area most of the year. For location 32 in the Northern Kara Sea, a similar value (0.06 cm/year) was found. This

may be less surprising, however. For this core the supported lead had to be determined by the 226 Ra content of the sediment layers.



11-1 "Skagerak/Kattegat"







Figure 3.2a) Total and unsupported ²¹⁰Po concentrations in sediment cores from station 11-1 and 16-1.



Figure 3.2.b) Total and unsupported ²¹⁰Po concentrations in sediment cores from station 26-1 and 34-1





Figure 3.2 c) Total and unsupported 210 Po concentrations in sediment cores from the Kara Sea and from the mouth of Yenisey

Site/Core	Supported ²¹⁰ Po	Coefficient	Sedimentation rate		
	Bq/kg		cm/year	g/(m ² year)	
11-1 "Skagerak/Kattegat"	64.5	0.116	0.27	1500→748	
16-1 "North Sea"	20.9	1.084	0.03	463→231	
26-1 "Norwegian Sea"	25.0	0.845	0.04	919 → 460	
34-1 "Komsomolets"	40.0	0.270	0.12	1130→562	
46-1 "Barents Sea"	21.3	0.253	0.12	1218→609	
56a-2 "West of Svalbard"	73.8	0.325	0.10	N/A	
Karex 94 no. 32	22.0	0.556	0.06	N/A	
Karex 94 no. 84	32.3	0.582	0.05	N/A	
Stepovogo Bay	43.5	0.479	0.06	N/A	

Table 3.2 Sedimentation rates.

N/A – not calculated:

3.3 Distribution coefficients

It is rather difficult to obtain representative values for the distribution coefficient K_d based on field data. One of the reasons is the lack of exchange equilibrium between the sediment and the water phase. However, an attempt has been made to calculate distribution coefficients for ^{137}Cs , $^{239,240}Pu$ and ^{241}Am based on the analysis of surface sediments (0-2 cm) and data on sea water collected near bottom at the same locations.

Results from analysis of sea water sampled during the R/V Gauss cruise in the North Sea, Norwegian Sea and Barents Sea in the summer 1995 are given in Table 3.3. The samples have been analysed by the Federal Maritime and Hydrographic Agency, Hamburg and Rostock [Ni97a, Ni97b, He98].

In Table 3.4 the calculated distribution coefficients are listed. At station 11 Skagerak/Kattegat, only surface water data was available. At station 16, sea water measurements from 150 m depth was used (Grøttheim, 1998).

Station	Lat.	Long.	Date	Depth (m)	Tot.	¹³⁷ Cs	Err.	⁹⁰ Sr	Err.
				,	depth (m)	(Bq/m^3)	(%)	(Bq/m^3)	(%)
11	58.30	9.30	19.06.95	0	535	25.5	2.2	-	-
16	58.30	4.30	19.06.95	0	283	-	-	5.6	3.0
16c	58.30	4.30	19.06.95	280	283	-	-	1.6	3.8
26	66.30	10.00	23.06.95	0	268	4.6	4.3	-	-
26c	66.30	10.00	23.06.95	250	268	2.6	5.1	-	-
34	73.43	13.15	29.06.95	0	1679	2.6	6.1	1.5	3.3
34h	73.43	13.15	29.06.95	1615	1679	0.77	11.0	0.4	5.0
46	74.00	35.00	06.07.95	0	288	3.4	8.4	-	-
46c	74.00	35.00	06.07.95	260	288	3.4	8.6	-	-
56k	77.50	7.30	12.07.95	3270	3200	0.42	10.8	-	-

Table 3.3 Radionuclides in sea water samples collected during the R/V Gauss cruise in the summer 1995 (H. Nies et al., 1997; H. Nies et al., unpublished; J. Hermann et al., 1998).

- no data

For ¹³⁷Cs, the empirical K_d value varies from 390 at station 11 Skagerak/Kattegat to 28.800 at station 34 Komsomolets. At station 26 direct deposition of Chernobyl fallout in the sediment may influence the result. At the two deep sea stations no.34 and 56, the high K_d value reflect the low concentrations of ¹³⁷Cs in the water.

Apart from at station 11, the K_d values obtained for plutonium varied by less than an order of magnitude (i.e. $0.4 - 1.0 \times 10^5$). Slightly higher values were obtained for ²⁴¹Am (in the range $0.8 - 4.0 \times 10^5$).

 K_d for ¹³⁷Cs was also studied in the laboratory experiments (see chapter 4). In general, it is observed that the rough empirical values obtained here are higher than the values obtained in laboratory experiments. This may be due to the fact that the 2 cm surface sediment in most cases has accumulated over many years, carrying contamination from a period when levels of ¹³⁷Cs in the sea water were higher, for instance due to the influence of Sellafield releases. The ¹³⁷Cs in the sediment is now fixed, or being remobilized only very slowly. Burial of the contamination by sedimentation may also make it unavailable for exchange with free water masses.

Table 3.4 «Distribution coefficient» K_d (Bq kg ⁻¹ /Bq l ⁻¹)
derived from surface sediment and near bottom sea water measurements.

Site/core	Depth	¹³⁷ Cs (Bq kg ⁻¹ /Bq l ⁻¹)	²³⁹ Pu (Bq kg ⁻¹ /Bq l ⁻¹)	$\frac{^{241}Am}{(Bq kg^{-1} /Bq l^{-1})}$
11-1 Skagerak	535	390 (surface water)	$7.2 ext{ x10}^{5}$ (surface water)	6.8 x 10 ⁵ (surface water)
16-1 North Sea	283	1.870 (150 m water)	-	-
26-1 Norw. Sea	268	9.500	0.4 x 10 ⁵	0.8 x 10 ⁵
34-1 Komsomolets	1679	28.800	0.7 x 10 ⁵	4.0 x 10 ⁵
46-1 Barents Sea	288	1.700	1.0 x 10 ⁵	3.4×10^5
56a-2 West of Svalbard	3200	20.200	-	-

4. Water- sediment interactions: Laboratory studies

4.1 Sediment Characteristics

The sediments utilised in the tracer studies varied in terms of organic content, CEC and stable element concentration, although, as expected for marine sediments they showed similar pH (Table 4.2). Apart from Irish Sea and Stepovogo sediments, the radionuclide concentrations were low and within the range of levels reported from other surveys of the areas (H. Fjelldal et al., 1995; P.Børretzen et al., 1995; JRNC, 1994; D.L. Sparks, 1988). It should be stressed that the sediments used in these studies represent a single sample taken from each location, thus are unlikely to be categorically representative of the site in question. The experiments utilised the different samples merely to obtain a range of sediment characteristics that might be found in Northern Seas.

	PH	Dry	LOI	CEC ^a	Surface	Со	Cs	Fe	Rb	Sc	Zn
	(H ₂ O)	Wgt (%)	(%)	(meq/ 100g)	(m ² /g)	$(\mu g/g)$	$(\mu g/g)$	(mg/g)	$(\mu g/g)$	(µg/g)	(µ g/g)
Irish Sea	7.6	77.5	3.3	25		7	3.3	25.9	65	5	69
Kara	7.8	55.3	9.9	68		28	5.4	94.4	90	12	153
Stepo- vogo	8	53	5	46		21	6.1	64.4	91	14	260
Mix	7.9	38.4	7.2	84		19	3.6	65.4	75	12	nd ^b
Dirty Ice	7.8	39.4	10.6	120		21	4.3	76	79	13	nd
Ob-I Ob-II	5.5 5.6	48.5 59.8	8.5 na ^c	74 na		18	3.7	63.3	87	11	nd
Yeni- sey	7.9	57.7	3.8	24		16	1.8	49.6	52	13	nd
Nor-16	7.5	45.1	11	29	15.9						
Nor-26	7.4	62.6	4.4	27	7.7						
Nor-34	7.4	45.7	9.8	32	17.4						
Nor-39	7.4	62.5	4.0	23	6.2						

Table 4.1 Chemical characteristics and tracer element concentrations in marine surface sediments (0-2 cm) used in tracer tank and batch studies. Error on values \pm 5% (\pm 20% on CEC).

^a the method can overestimate CEC for marine sediments because of high Na concentration in sea water ^b- not detected; ^c - not analysed

4.2 Time Dependent Changes in Kd: Sediment-Seawater Tracer Studies

Distribution coefficients K_d (ml g⁻¹) were calculated from:

$$K_{d} = \frac{V(C_{c} - C_{t})}{mC_{t}}$$

where C_c and C_t are the count rates (cpm/ml) of the control and experimental solutions at time t, respectively, V is the solution volume (ml) and m the dry weight mass of sediment (g). The results of the static tank experiment showed clearly how K_d for ¹³⁷Cs varies both with contact time and with sediment type (Fig. 4.1, Table 4.2.)



Figure 4.1 Variation in K_d for Cs-134 as a function of time and sediment type Table 4.2 Distribution coefficients (K_d) for ¹³⁴Cs tracer in seawater-sediment systems. Average \pm SD (n = 2)

	K_d 1 week (ml g ⁻¹)	K_d 1 year (ml g ⁻¹)	CEC meq/100g
Mix	430 ± 30	1680 ± 30	84
Ob-I	380 ± 40	1520 ± 80	74
Kara	300 ± 10	1480 ± 20	68
Irish Sea	190 ± 10	740 ±10	25
Stepovogo	160 ± 100	980 ± 40	46
Yenisey	260 ± 10	900 ± 70	24
Dirty Ice	390 ± 20	na	120
Norway-16	120 ± 10	460 ± 20	29
Norway-26	70 ± 10	150 ± 10	32
Norway-34	100 ± 10	280 ± 10	23
Norway-39	80 ± 10	170 ± 10	27

¹³⁴Cs activity levels in seawater decreased with sediment contact time, giving K_d values of between 150 and 1680 after 1 year. This is equivalent to 61-95 % of the added tracer being adsorbed to the sediment. For ⁸⁵Sr, no significant sorption to sediment (K_d < 50) could be observed during the 1 year contact time. K_d for ¹³⁴Cs showed a rather good correlation with the estimated sediment cation exchange capacity for the different sediments, suggesting that the primary interaction mechanism is cation exchange (Table 4.2). At one week, K_d = 3.5 CEC + 51 (R² = 0.69) and at one year, K_d = 19.8 CEC (R² = 0.77). Particle size distribution was not determined, and surface area (m²/g) was not measured in all sediments. However,
since one would expect cation exchange capacity to be correlated with surface area and inversely correlated with particle size, either one of these variables might influence K_d .

Results from batch studies showed that gentle shaking increased binding rates of ¹³⁴Cs by a factor of 10 compared to the static experiments. This is expected as shaking reduces the time needed for the hydrated cation to diffuse through the water layer and come in contact with the exchange sites on the sediment (Børretzen et al, 1997). After 1 month contact time, however, there was reasonable agreement between K_d in static and shaken water-sediment systems. Batch studies (excluding Norwegian samples) verified that after 1 month contact time K_d for ⁸⁵Sr (11 ± 2 ml g⁻¹) was much lower than for ¹³⁴Cs (950 ± 350 ml g⁻¹).

4.3 Sequential Extraction of Tracer and Environmentally Labelled Marine Sediments

Sequential extraction studies of sediments labelled with tracers showed that ¹³⁴Cs was rapidly and strongly fixed to sediment components (Fig. 4.1 a). The distribution pattern was very similar for all sediments, variations were within 10%. After only 1 hr, more than 70% of the ¹³⁴Cs was found in the HNO₃ and residual fractions. A small fraction of ¹³⁴Cs (1-10%) remained in the easily exchangeable fraction (NH₄Ac). The decrease in the exchangeable fraction with time probably reflects long-term fixation of ¹³⁴Cs by sediment components.

Comparison of ¹³⁴Cs tracer distributions with results from extraction studies on ¹³⁷Cs in Irish Sea and Stepovogo sediments (i.e., environmentally labelled sediments) gave similar distributions for the two Cs isotopes (Fig. 4.1c). The percentage of ¹³⁷Cs in the mobile fraction was < 1%, suggesting increased fixation of caesium ions with longer contact time. The Stepovogo sediments showed a rather high fraction of ¹³⁷Cs in the residue.

Sequential extraction of ⁸⁵Sr tracer showed that ionic Sr associated with sediments could be easily mobilised; more than 99% of the adsorbed ⁸⁵Sr could be displaced with the NH₄Ac extraction at pH 7 (Fig 4.1b). Again, the distribution pattern for the ⁸⁵Sr tracer was very similar for all sediments. However, sequential extraction of ⁹⁰Sr from environmentally labelled Irish Sea and Stepovogo sediments indicated that ⁹⁰Sr was rather less mobile than the ionic ⁸⁵Sr tracer (Fjelldal et al, 1995;Børretzen et al,1995), showing a significantly higher extraction into NH₄Ac (pH 5) than was observed for the tracer (Fig. 4.1d). This could reflect a time-dependent incorporation of ⁹⁰Sr in the carbonate or amorphous fraction in marine sediments. However, differences between the ionic, experimental tracer and the environmental ⁹⁰Sr may also indicate different ⁹⁰Sr species in the discharge (i.e. non-ionic). Finally, other water-to-sediment removal mechanisms besides ion-exchange and surface sorption (e.g. biogeochemical cycles) are likely to exist in the natural environment.



Figure 4.1 Tracer study showing sequential extraction of a) 134 Cs and b) 85 Sr tracers associated with the «mix» marine sediment as a function of contact time, and c) 137 Cs and d) 90 Sr associated with Irish Sea and Stepovogo sediments.

4.4 Modelling of Caesium Sediment-Water Interactions

The rate of decrease of ¹³⁴Cs activity levels in seawater could be resolved into a fast and a slow component, probably represented by relatively fast interaction with sediments by electrochemical surface sorption or ion exchange followed by slow removal to "irreversibly" fixed sites -- probably diffusion into clay mineral lattices. The kinetics of the water-sediment water interactions of the ionic ¹³⁴Cs tracer have been modelled using a simple box model (Modelmaker, SB Technology Ltd, 1994). Although the model cannot give absolute rate constants for the chemical processes, it is a useful tool in parameterising the sorption rates so that the different sediments can be compared. Two models were tested: a 3 box and a 4 box model (Figs.4.2 and 4.3). Although the 3-box model is quite capable of describing the rate of decrease in seawater, the 4-box model (wherein the "fixed" compartment is divided into a "slow-reversible" and "irreversible" compartment) is more consistent with changes in sequential extraction studies. Optimisation of the model gave similar rate constants for uptake and removal from water to the "exchangeable" pool for the 10 different sediments, $k_1 0.17 \pm 0.03 d^{-1}$ and $k_2 0.09 \pm 0.05 d^{-1}$. These results suggest that the rate determining step probably reflects diffusion of the ion through the solution microlayer surrounding sediment particles followed by surface sorption [13], rather than a mechanism which is strongly dependent upon sediment characteristic. Rate constants for transfer to the "fixed"pool varied between the different sediments: k_3 from 0.0003 to 0.001 d⁻¹. No correlation with CEC or LOI could be found. It was not possible to calculate rate constants for removal from the fixed pool with any degree of certainty, optimisation gave large uncertainties for k₄ but half-lives seemed to be in the order of decades.



Figure 4.2 Simple box models describing sorption of ¹³⁴Cs tracer to marine sediments



Figure 4.3 Model of ¹³⁴Cs tracer to marine sediment (4-box model, Kara Sea sediment) ■ - data points and errors (n=2)

4.5 Change in Kd after Transfer of Labelled Sediments from Freshwater to Seawater

Experiments using Ob and dirty ice sediments labelled with ¹³⁴Cs and ⁸⁵Sr tracers in freshwater showed that K_d varied considerably between freshwater and seawater: K_d in freshwater being a factor of 100 higher than in seawater (Fig. 4.4). This indicates a significant potential for mobilisation of Cs and Sr on transfer of sediments from a freshwater to a saltwater environment. In agreement with the previous studies, K_d for Sr was a factor of 10 -100 lower than for Cs in both media. The mobilisation of ¹³⁴Cs and ⁸⁵Sr after transfer of sediments from freshwater to seawater may reflect the effect of increased pH, ionic strength, salinity and/or concentration of exchangeable elements (i.e., alkali or alkaline earth metals). However, reducing the pH of seawater to 5.0 decreased K_d for both ¹³⁴Cs and ⁸⁵Sr by a factor of 2, and K_d returned to its original level after increasing pH back to 7. So pH is unlikely to be a major controlling factor. In the case of ⁸⁵Sr, high stable Sr concentrations in seawater (8 mg/l) will promote mobilisation through isotopic exchange. If Sr is not present as an exchangeable form (e.g., carbonate forms, or fuel particles), mobilisation may be less extensive. It should also be noted that the high stable Sr concentrations in seawater will reduce the specific activity of ⁹⁰Sr in seawater and, despite any increase in ⁹⁰Sr mobility, should result in reduced concentration factors in biological food chains as compared to freshwater environments.



Figure 4.4 Change in K_d following sequential extraction of labelled Ob and dirty ice sediments with fresh water and seawater. (n=3, STD< 5%)

4.6 Time Dependent Changes in Kd: Sediment-Freshwater Tracer Studies

Studies were also carried out on freshwater sediments collected from Heimdalen (Norway) and Losjøen (Sweden) Lakes. These studies were intended to act as a link between EKO-1 and EKO-2. Results confirmed that after 1 year contact time K_d s were higher in freshwater-sediment than in seawater-sediment systems. However, the data indicated that the sorption process were considerably slower in the freshwater system as compared to the seawater systems (Fig 4.5). This might reflect an effect of high ionic strength on colloid aggregation and particle precipitation in seawater systems. Cs sorption kinetics were best described by the 3 box model used in seawater. Sr sorption kinetics were well described by a 2-box model representing water and reversibly-bound components (Fig. 4.6). Sequential extraction of sediments confirmed that ⁸⁵Sr bound to sediments was easily exchangeable.



Figure. 4.5. Model of Cs-134 sorption to Heimdalen sediment in freshwater (pH 5). n - data points and errors (n=2)



Figure 4.6. Model of Sr-85 sorption to Loppesjö sediment in freshwater (pH 5). n - data points and errors (n=2)

5. Conclusion

In the «Norwegian» surface sediments, the 137 Cs concentrations varied in the range 3.0- 24.7 Bq/kg.

The 239,240 Pu concentration in the «Norwegian» surface sediments are in the range 0.6-2.77 Bq/kg. The observed 241 Am concentrations are in the same order of magnitude, 0.29-0.98 Bq/kg.

 238 Pu/ 239,240 Pu ratios in the sediments are in the range 0.03-0.10. At stations 11 (Skagerak/Kattegat) and 16 (North Sea) some influence from Sellafield plutonium is suggested, as the plutonium ratio is significantly higher (0.08-0.10) than would be expected from global fallout (0.03).

At station 26 (Norwegian Sea) the sediments seem to be influenced by radiocesium from the Chernobyl accident. This may be due to direct fallout deposition to the sea surface and followed by a rapid sinking and sedimentation.

At station 16 (North Sea) some influence from Sellafield plutonium is suggested, as the plutonium ratio is significantly higher (0.08-0.10) than would be expected from global fallout (0.03).

Sedimentation rates based on analysis of ²¹⁰Pb or ²¹⁰Po varied between 0.05 cm/year - 0.25 cm/year. A suprisingly low sedimentation rate was found in the Yenisey Bay (0.05 cm/year). It is possible that the dating method is less suited in this area.

In the laboratory experiments, distribution coefficients ($K_d ml g^{-1}$) for ¹³⁴Cs in seawatersediment systems varied with contact time, mixing conditions, sediment type, and salinity, and appeared to be correlated with cation exchange capacity. After 1 year contact time under static conditions, K_d for ¹³⁴Cs ranged from 150 to 1680 ml g⁻¹. Extraction studies showed that the majority of ¹³⁴Cs was strongly bound to sediment components, although a small fraction (1-10%) was easily displaced and remained in dynamic equilibrium with soluble species. In general, the rough estimates on K_d values for ¹³⁷Cs obtained empirically are higher than K_d values obtained from experiment. This may be due to the fact that the 2 cm surface sediment in most cases has accumulated over many years, carrying contamination from the early eighties when levels of ¹³⁷Cs in the sea water were higher. The ¹³⁷Cs in the sediment is now fixed, or being remobilized only very slowly. Burial of the contamination by sedimentation may also make it unavailable for exchange with free water masses.

Kinetic modelling using a simple box model indicated that the uptake of ionic Cs to sediments could be described by a two-component function. The relatively fast component probably reflects diffusion through the sediment-water microlayer followed by surface sorption to sediment (ion exchange). Rate constants for transfer between seawater and the exchangeable fraction were similar for the different sediments, $0.17 \pm 0.03 \text{ d}^{-1}$ for uptake and $0.09 \pm 0.05 \text{ d}^{-1}$ for removal. The slow component is thought to represent strong fixation within the mineral lattice; rate constants for fixation showed greater variation, ranging from 0.0003 to 0.001 d⁻¹. Ionic ⁸⁵Sr was rather conservative in seawater, showing little transfer to sediments: K_d was 11 $\pm 2 \text{ ml g}^{-1}$. Furthermore, ⁸⁵Sr bound to sediments by ion exchange was easily displaced. Sequential extraction of Irish Sea and Stepovogo sediments indicated, however, that ⁸⁵Sr was rather less mobile than the ionic tracer. This might reflect the presence of different ⁹⁰Sr species in the discharge (i.e. non-ionic) or a different water-sediment interaction mechanism in the natural environment. For both radionuclides, K_d in freshwater was a factor of 100 higher than in seawater, indicating that ¹³⁷Cs and ⁹⁰Sr can be mobilised if freshwater sediments are transferred to the marine environment. Further studies of water-sediment interactions for these and other radionuclides is necessary for a better understanding of processes in estuarine mixing zones. Investigations of the variables responsible for the relatively slow sorption rate of ¹³⁴Cs and ⁹⁰Sr to freshwater sediments could be relevant to studies on the ecological half-life of radionuclides in such systems.

Laboratory studies can offer some important insights into the underlying processes which influence the transport of contaminants in the environment. For example, knowledge on the types of parameters which can result in variations in K_d s are useful for assessment of model predictions and sensitivity.

References

Baumann,M., M. Segl, G. Wefer, and B. Von Bodungen, Chernobyl derived radiocesium in the Norwegian Sea: Flux between water column and sediment, in: W. Feldt (Ed.) The Radioecology of Natural and Artificial Radionuclides, proceedings IRPA congress (XV) (1989) p. 318-323

H.E. Bjørnstad, H.N. Lien, Y. Yu-fu and B. Salbu, Determination of ⁹⁰Sr in environmental and biologicalmaterials with combined HDEHP solvent. J. Radioanal. Nuc. Chem. 156 (1992) 165-173.

P. Børretzen, H. Fjelldal, H. Lien, D.H. Oughton, and B. Salbu, Mobility of radionuclides in sediments from Abrosimov and Stepovogo Fjords, in P. Strand and A. Cooke (Eds), Environmental Radioactivity in the Arctic. NRPA, Østerås, 1995, pp 168-172.

P.Børretzen, D.H. Oughton, and B. Salbu, Mobility of radionuclides in sediments from Abrosimov and Stepovogo Fjords, in Tromsø conference 1997

Chen et al. Determination of Plutonium in Environmental Samples by controlled Valence in Anion Exchange. Denmark: Risø National Laboratory, RISØ-M-2856, 1991.

A. Clacher, Development and Application of Analytical Methods for Environmental Radioactivity. Ph.D. Thesis, Univ. of Manchester, 1995.

Cutshall, I.L. Larsen and C.R. Olsen, Direct analysis of ²¹⁰Pb in sediment samples: Selfabsorption corrections. Nuclear Instruments and Methods 206 (1983) p.309-312

S. Grøttheim Radionuclides in Norwegian Seas (in preparation)

H. Fjelldal, H. Lien, D.H. Oughton, and B. Salbu, Mobility of radionuclides in Irish Sea sediments, in P. Strand and A. Cooke (Eds), Environmental Radioactivity in the Arctic. NRPA, Østerås, 1995, pp 245-249.

Häsänen, Dating of sediments, based on ²¹⁰Po measurements. Radiochem. Radioanal Letters 31(4-5)(1977) p.207-214

Herrmann, J., Nies, H. and Goroncy, I. *Plutonium of the deep layers of the Norwegian and Greenland Sea*. Rad. Prot. Dosim. (1998) (accepted for publ.).

G.J. Hunt and P.J. Kershaw, Remobilisation of artificial radionuclides from the sediment of the Irish sea, J. Radiol. Prot., 10, 147-152, 1990.

D. Meese, L. Cooper, I.L. Larsen, W. Tucker, E. Reimnitz, and J. Grebmeier, Cesium-137 contamination in Arctic Sea Ice, in P. Strand and A. Cooke (Eds), Environmental Radioactivity in the Arctic. NRPA, Østerås, 1995, pp 195-198.

Nies, H., Bahe, C., Dethleff, D., Harms I., Karcher, M.J. and Kleine, E. *Transport and dispersion of artificial radioactivity in the Arctic Ocean - model studies and observations*. Radioprotection - Colloques, **32** (C2) (1997) 407-416.

Nies, H. and Herrmann, J., Federal Maritime and Hydrographic Agency, Hamburg and Rostock (unpublished data).

D.H. Oughton and J.P. Day, Determination of cesium, rubidium and scandium in biological and environmental materials by neutron activation analysis. J. Radioanal. Nuc. Chem.174 (1993) 177-185.

Joint Russian-Norwegian Collaboration (JRNC) Radioactive contamination at dumping sites for nuclear waste in the Kara Sea: results from the Russian-Norwegian expedition to the Kara Sea. NRPA, Østerås, 1994.

Karex 1994

D.H. Oughton, P. Børretzen, B. Salbu, E. Trondstad. Mobilisation of ¹³⁷Cs and ⁹⁰Sr from Sediments: Potential Sources to Arctic Waters. Sci Tot. Environ. 1997. 202: 155-165.

S.L. Pfirman, J.W. Køgeler, and B. Anselme, Transport of radionuclides from the Kara Sea: Potential "Shortcuts" in space and time, in P. Strand and A. Cooke (Eds), Environmental Radioactivity in the Arctic. NRPA, Østerås, 1995, pp 191-194.

B.Salbu and D.H. Oughton, Processes affecting the uptake of radioactive species into the environment. Rad. Prot. Dosimetry, 62, 1-4, 1995.

D.L. Sparks, Kinetics of Soil Chemical Processes, Academic Press, London, 1988, p103-105. Tadjiki, S and Erten, H.N. *Radiochronology of sediments from the Mediterranean Sea using natural 210Pb and fallout 137Cs*. J. Radioanal. and Nucl. Chem., Articles, 181 (1994) 447-459.

A. Øien and T. Krogstad, Øvelser i jordanalyser, Institute for Soil Science, Agricultural University of Norway, Ås, 1987. (In Norwegian)

Radionuclides in sediment in Icelandic waters and their use for the determination of sedimentation rates

Sigurður Emil Pálsson¹, Magnús Danielsen², Elísabet D. Ólafsdóttir¹ ¹Geislavarnir ríkisins (Icelandic Radiation Protection Institute) ²Hafrannsóknastofnunin (Marine Research Institute), Iceland

Introduction

This report describes the results of the Icelandic part of the NKS / EKO-1 project, in the project period 1994-1997.

The sea bottom around Iceland has a very uneven topology. This is understandable due to Iceland being a part of the Mid-Atlantic Ridge. Iceland is also at the junction of warm and cold ocean currents (Stefánsson and Ólafsson 1991). This contributes to create rich fishing grounds around Iceland. Over the years there has been considerable oceanographic research in Iceland and there has been some sediment research. Measurement of radiocaesium in the ocean around Iceland has been carried out regularly by the Icelandic Radiation Protection Institute since 1989 (Ólafsdóttir et al. 1999). Prior to the start of the EKO-1 project there had, however, been no studies of radionuclides in sediments carried out in this area.

The aim of this study was to sample sediments near some of the places that are regularly used for sampling by the Marine Research Institute. Seawater was to be sampled as well. Key parameters such as temperature and salinity were measured in the sea above the sampling sites so that the water masses could be identified. Gamma spectrometric analyses were to be performed on all samples, with main emphasis on ¹³⁷Cs. Additionally the sediment samples were to be analysed for ²¹⁰Pb and ²²⁶Ra. With these radionuclides it is possible to estimate the sedimentation rate.

Materials and methods

Sampling sediments proved to be much more difficult than anticipated. Attempts were made at 35 stations around Iceland, repeatedly at most of them. The stations where sampling was attempted are shown in figure 1. Due to the very difficult conditions good quality sediment cores were just obtained in four areas. These are shown in figure 2.



Figure 7. The 35 stations where sampling was attempted (shown as dots)



Figure 2. Stations were sediment cores were obtained, labelled a-d. In area b two sediment cores were obtained at different times.

The sediment sampler used was the "Little Gravity Corer" based on a design from the Woods Hole Oceanographic Institute, USA. This is a gravity corer with an inner plexiglas tube. The total length is 80 cm but the length of the tube is 50 cm. The inner diameter of the tube is 62 mm and the sampled area is 30 cm². The sectioning interval used was 2.5 cm and 5 cm. The total weight of the sampler is 8 kg. Additional weights of up to 20 kg can be used. The sampler is closed by closing an upper closing valve. This means that the sample is held in place without any support from below. This can increase the risk of loosing sample material, especially after the sampler has been hoisted above the sea surface. The light weight of this corer can also cause difficulties when sampling in deep waters in rough weather. These limitations of the sampler contributed to the difficulties encountered during the sampling attempts. Additional weights were used in the later attempts and that improved the situation somewhat. The various problems associated with sediment sampling are discussed in an EKO-1 report by Erkki Ilus (1996)

The ²¹⁰Pb in the sediment originates from two sources. Part of it comes from the decay of ²²⁶Ra in the sediment (the supported fraction) and the other part comes from the flux of particles settling on the sediment surface (the excess lead or unsupported fraction). It is possible to estimate the sedimentation rate from the ²¹⁰Pb profile of a sediment core. The concentration of unsupported ²¹⁰Pb in each slice can be estimated by assuming that the supported ²¹⁰Pb is in equilibrium with the ²²⁶Ra in the sediment. The concentration of unsupported ²¹⁰Pb is then equal to the total concentration of ²¹⁰Pb minus the concentration of ²²⁶Ra.

$$[^{210}Pb]_{unsupp} = [^{210}Pb]_{tot} - [^{226}Ra]$$

If there is a constant influx of ²¹⁰Pb to the sediment surface, then the concentration of unsupported ²¹⁰Pb can be expected to fall exponentially with depth due to the physical decay of the radionuclide (half-life 22.3 years). A more detailed description of the use of the ²¹⁰Pb method for dating sediments can be found in the section "Methods used in estimation of the sedimentation rates", in the EKO-1 final report, NKS(97)FR4 and in scientific publications (e.g. Robbins, 1978; Oldfield and Appleby, 1984).

The ¹³⁷Cs found in the sea around Iceland is mainly due to fallout from the atmospheric nuclear weapons testing in the late fifties and early sixties. Some increase, mostly due to the nuclear reprocessing plant at Sellafield, can be found west, north and northeast of Iceland. Fallout from the Chernobyl accident was very limited in comparison to the already mentioned sources. It is therefore possible to use ¹³⁷Cs as a marker when dating sediments from the sea bottom near Iceland.

The distribution coefficient (K_d) is the ratio of concentration of a radionuclide in sediment to that in seawater. The K_d describes the ability of sediments to bind radionuclides from seawater and it is an important parameter when modelling the behaviour of radionuclides in seawater and sediments.

The ²¹⁰Pb influx to the sediment surface mentioned earlier is an interesting parameter in itself. It has been used for process studies and an extensive compilation of data from which world

wide sediment studies has been made. The influx can be calculated assuming a steady state condition in the sediment column and that ²¹⁰Pb is deposited at the same rate as it decays. Then:

 $dA/dt = F - \lambda A = 0$ => $F = \lambda A$ where:

A : total inventory of unsupported ²¹⁰Pb per unit area in the column (unit: Bq m⁻²)

F : influx of ²¹⁰Pb (unit: Bq m⁻² y⁻¹)

 λ : physical decay rate of ²¹⁰Pb (unit: y⁻¹)

Results and discussion

General gamma spectrometric analysis was performed at the Icelandic Radiation Protection Institute. Analysis for ²¹⁰Pb and ²²⁶Ra was done at Risø National Laboratory in Denmark. Conditions at the five sampling stations are summarised in table 1.

Station	Area	Position		Depth	Date of	Temp	Salinity
no.		latitude	longitud e	111	sampi.	ť	700
1	а	66°15'N	23°17'W	106	Sep. '95	7.78	34.86
2	b	66°36'N	23°59'W	210	Sep. '95	5.77	35.03
3	b	66°36'N	23°59'W	215	May '97	4.19	34.97
4	с	65°45'N	25°39'W	256	Sep. '95	5.65	35.05
5	d	67°35'N	23°56'W	972	Sep. '95	-0.73	34.91

 Table 1. Description of the five sampling stations and conditions at each station

Sedimentation rate determination using ²¹⁰Pb profiles

The sedimentation rate was determined using a ²¹⁰Pb dating method. Linear regression was used to fit a line to the logarithm of the unsupported ²¹⁰Pb data versus mass depth (in g cm⁻²). Each point was assigned weight in the following manner: $w_I = 1 / s_i^2$, where s_I is the standard deviation of counts of point number i.

All the points at the five stations were used for the analysis with the exception of the first point (corresponding to the top layer) at Station 1. The ²¹⁰Pb data with the calculated fitted line are shown in figures 3 - 7. The error bars shown correspond to 95% confidence intervals based solely on the standard deviation of counts.



Figure 3 - Unsupported ²¹⁰Pb as a function of mass depth $[g/cm^2]$ at Station 1, depth 106 m. Estimated sedimentation rate 0.14 g cm⁻² y⁻¹ (3.2 mm y⁻¹)



Figure 4 - Unsupported ²¹⁰Pb as a function of mass depth $[g/cm^2]$ at Station 2, depth 210 m. Estimated sedimentation rate 0.16 g cm⁻² y⁻¹ (3.3 mm y⁻¹)



Figure 5 - Unsupported ²¹⁰Pb as a function of mass depth $[g/cm^2]$ at Station 3, depth 215 m. Estimated sedimentation rate 0.27 g cm⁻² y⁻¹ (3.9 mm y⁻¹)



Figure 6 - Unsupported ²¹⁰Pb as a function of mass depth $[g/cm^2]$ at Station 4, depth 256 m. Estimated sedimentation rate 0.06 g cm⁻² y⁻¹ (1.1 mm y⁻¹)



Figure 7 - Unsupported ²¹⁰Pb as a function of mass depth $[g/cm^2]$ at Station 5, depth 972 m. Estimated sedimentation rate 0.03 g cm⁻² y⁻¹ (0.6 mm y⁻¹)

The results of the analyses for the 5 stations are summarised in table 2.

sediment cores						
Station	Depth	Sedimentation rate		Standard	\mathbf{R}^2	
no.		$(g cm^{-2} y^{-1})$	$(mm y^{-1})$	deviation		
1	106 m	0.14	3.2	5 %	99 %	
2	210 m	0.16	3.3	7 %	98 %	
3	215 m	0.27	3.9	9 %	96 %	
4	256 m	0.060	1.1	15 %	95 %	
5	972 m	0.030	0.6	26 %	94 %	

Table 2 Estimates of sedimentation rates at stations 1 - 5 based on evaluation of unsupported ²¹⁰Pb in sediment cores

The linear sedimentation rate (in mm y^{-1}) was calculated from the mass deposition rate (in g cm⁻² y⁻¹) using the density of the top section of the sediment. The linear sedimentation rate calculated is therefore an estimate for the top layer.

The obtained fit is good in all cases (R^2 ranging from 0.94 to 0.99).

¹³⁷Cs profiles in sediments

The sediment profiles were also analysed for ¹³⁷Cs and the combined results for all stations are shown in figure 8. The last points in series 2, 4 and 5 are lower limits of detection, not measured values.



Figure 8 - Depth distribution of 137 Cs in sediment cores from stations 1 - 5.

The ¹³⁷Cs concentration is seen to increase with depth and then to fall significantly (most often below detection limits) at a certain depth. The main source of ¹³⁷Cs in the sediments is the atmospheric testing of nuclear weapons in the late fifties and early sixties. The Chernobyl accident had a very minor effect in Icelandic waters. At station no. 5 (depth 972 m) input of ¹³⁷Cs from the Sellafield reprocessing plant can be expected. The ¹³⁷Cs concentration can thus be used as a marker to check the validity of the ²¹⁰Pb sediment age determinations.

The following check was done. The age of the slice having maximum ¹³⁷Cs concentration at each station was calculated and the corresponding time period found containing the ¹³⁷Cs maximum. The results are shown in table 3.

Table 3

Station	Depth of ¹³⁷ Cs maximum	Time period	
no.			
1	10 - 15 cm	1948 – 1965	
2	7.5 - 10 cm	1951 – 1965	
3	13 - 17 cm	1947 – 1959	
4	2.5 - 5 cm	1948 – 1973	
5	0 - 2.5 cm	1955 – 1995	

Depth of maximum concentration of 137 Cs in sediment cores from stations 1 - 5 and corresponding time of sedimentation

The time period of sedimentation corresponding to each slice was calculated from the ²¹⁰Pb derived estimate of the mass deposition rate and using depth values corresponding to the upper and lower surface of each slice.

The time period calculated includes in all cases the late fifties that saw the beginning of the large-scale atmospheric tests. The ¹³⁷Cs measurements thus confirm the sedimentation rate determinations obtained with the ²¹⁰Pb method.

²¹⁰Pb influx

The influx of ²¹⁰Pb was estimated assuming steady state conditions using two different methods for estimating the total activity of unsupported ²¹⁰Pb per unit area in the column.

- methods for estimating the total activity of unsupported ²¹⁰Pb per unit area in the column.
 a) Measured in core: Total activity of unsupported ²¹⁰Pb per unit area in the measured core
- b) Model fit: The model fits shown in figures 3 7 were integrated to infinite depths to give the total inventory per unit area.

The flux was subsequently calculated from the inventory as described in the introduction.

Station no.	Depth	²¹⁰ Pb influx Bq m ⁻² y ⁻¹ (measured in core)	²¹⁰ Pb influx Bq m ⁻² y ⁻¹ (model fit)
1	106 m	890	1040
2	210 m	690	770
3	215 m	910	1160
4	256 m	360	410
5	972 m	103	112

Table 4. Estimates of ²¹⁰Pb influx into the sediment

The model fit gives higher values in all cases because the model fit includes the ²¹⁰Pb contribution below the bottom of the core. There is considerable uncertainty in these estimates and variability in local conditions can cause differences in values from the same region. This can e.g. be seen in the table above since stations no. 2 and 3 are in the same area.

Estimation of distribution coefficient for ¹³⁷Cs

The distribution coefficients for ¹³⁷Cs were estimated using the measured concentration in the uppermost slice in each core and the best estimate available for the concentration in the near bottom seawater. In some cases actual measurements were available, but in other cases estimates were used based on knowledge about the type of seawater at the bottom and other measurements of the ¹³⁷Cs concentration in this type of water. The concentration for Atlantic water was assumed to be 2.7 Bq/m³ and the concentration for Atlantic deep water 2.2 Bq/m³. The classification of seawater was based on measured values of salinity and temperature at the sampling sites.

Station	Depth	Sea water type	K _d
no.			
1	106 m	AW	1400
2	210 m	AW	890
3	215 m	AW	1240
4	256 m	AW	930
5	972 m	ADW	3810

Table 5. Estimates of distribution coefficients (K_d) for ¹³⁷Cs

AW: Atlantic Water

ADW: Atlantic Deep Water

The K_d values given here refer to concentration per mass of sediment to concentration in seawater per equal mass. Values can be transformed to (ml/g) by dividing with the density of seawater, 1.03 g/ml. The uncertainty in this estimate is however greater than the effect of this transformation.

Conclusions

Sedimentation rates have been determined for a few sediment cores obtained from the sea bottom near Iceland. Comparison of the two profiles from the same area (no. 2 and 3) demonstrate the variability that can be obtained within a single area. The ¹³⁷Cs measurements confirmed the results obtained with the ²¹⁰Pb dating method.

The EKO-1 project has been important for research in this field in Iceland. Not only have data for the area been obtained, but also valuable experience in sampling under these difficult conditions and in the subsequent interpretation of results.

Acknowledgement

The work described in this paper was supported by the Nordic nuclear safety research. The authors appreciate the assistance provided by the Risø National Laboratory by carrying out analyses of ²¹⁰Pb and ²²⁶Ra in the samples.

References

- Ilus, E., 1996. Evaluation of sediment sampling devices and methods used in the NKS/EKO-1 Project. Report NKS/EKO-1(96)TR-1. Nordic nuclear safety research, Risø, Denmark.
- Oldfield F. and Appleby P.G., 1984. Empirical testing of ²¹⁰Pb-dating models for lake sediments. In: Haworth E. Y. and Lund J.W.G. (eds.), Lake Sediments and Environmental History: 93-124. Leicester University Press.
- Ólafsdóttir E. D., Pálsson S. E., Magnússon S. M. and Guðnason K. 1999. Distribution and origin of Cs-137 in the ocean around Iceland an indicator of man-made radioactivity. Rit Fiskideildar 16, 67:77.
- Robbins J.A., 1978. Geochemical and geophysical applications of radioacitve lead. In: Nriagu J.O. (ed.), Biogeochemistry of Lead in the Environemnt: 285-393. Elsevier. Holland.
- Stefánsson U. & Ólafsson J. 1991. Nutrients and Fertility of Icelandic Waters. Rit Fiskideildar 12, 1:56.

Radionuclides in Sediment Cores From Thule, Greenland

Sven P. Nielsen, Henning Dahlgaard Risø National Laboratory, Denmark

1. Introduction

A number of unique sediment cores taken in 1991 in the Thule accident area (North West Greenland) have been made available in collaboration with the Bedford Institute of Oceanography, Canada. The cores have been sectioned in 1-cm slices. The work on the sediment cores has focused on the following items:

- to analyse the cores for ²¹⁰Pb by gamma spectrometry,
 to analyse the cores for ²³⁹⁺²⁴⁰Pu by alpha spectrometry,
- to compare ²¹⁰Pb and transuranics as tracers for sedimentation and bioturbation processes.
- to determine sedimentation rates and bioturbation parameters of interest in connection with radiological assessments in the Arctic marine environment.

2. Materials and methods

Samples of marine sediments were collected in 1991 from Greenland by the Bedford Institute of Oceanography, Canada, and shared with Risø National Laboratory. The sampling covered the plutonium contamination of the Thule area where a US military aircraft carrying nuclear weapons crashed on the ice in January 1968. Sediment cores (0-50 cm) were sampled and sliced in 1-cm sections. Risø carried out radiometric analyses on 10 cores from the near-zone (within 10 km) of the point of impact (Figure 1) and on 5 cores from the northern part of Baffin Bay. The analyses partly carried out under the EKO-1 project comprised gamma-spectrometric determinations of natural radionuclides including ²¹⁰Pb and the fallout radionuclide ¹³⁷Cs, and radiochemical isolation of the plutonium isotopes followed by the detection of ²³⁹⁺²⁴⁰Pu by alpha spectrometry.

The vertical profiles of the radionuclide concentrations were interpreted in order to obtain information on sediment characteristics of importance for the evolution with time of the plutonium contamination in the Arctic marine environment. Lead-210 in the sediment originates from the natural content of ²²⁶Ra and decay products (supported fraction), and from the flux of ²¹⁰Pb on particles settling from the water column on surface sediments (unsupported fraction). The excess ²¹⁰Pb in surface sediments thus contains a historical record of sedimentation within about two hundred years limited by the physical half life of ²¹⁰Pb of 22 y. An undisturbed sediment profile will show an exponentially decreasing concentration of ²¹⁰Pb where the rate of decrease is determined by the rate of sedimentation and the ²¹⁰Pb half life. Deviations from the exponential decrease of 210 Pb in the surface sediments may be interpreted in terms of mechanical mixing due to biological activity and water flow generated by wind and tidal forces. It is important to understand and quantify the mixing processes because they speed-up and enhance the transfer of radionuclides from the sediment back to the water column from where they may more readily enter into human food chains.

A mathematical compartment model for the activity of radionuclides in sediments was set up considering sedimentation and mixing. The model was based on the work by Christensen

(1982). The model assumes that mixing may be expressed as a diffusive process with gaussian mixing in the upper layer. The diffusion coefficient is thus assumed to decrease with depth from a maximum value at the water-sediment interface following a gaussian function:

$$D = D_0 \cdot e^{-\frac{z^2}{2\sigma^2}},$$

where Do $(\text{cm}^2 \text{ y}^{-1})$ is the diffusion coefficient (mixing rate) at the sediment surface, z (cm) the depth, and σ (cm) the effective mixing depth. There are biological reasons for choosing a gaussian diffusion coefficient, since deposit-feeding animals, like worms, are mainly found in the top sediments and their distributions with depth are close to gaussian. Furthermore, physical mixing generated by water movement also declines rapidly with depth.

For unsupported ²¹⁰Pb, the model simulates continuos deposition for about two hundred years until 1991, and for plutonium isotopes the model starts with a single input of ²³⁹⁺²⁴⁰Pu in 1968 followed by a 23-year simulation without input until 1991. The depth profiles calculated with the model are compared with the observed profiles and the model parameters are selected to minimise the difference.

The parameters used by the model for each sediment core includes the sedimentation rate $(cm^{-1} y^{-1})$, the mixing depth (cm), the mixing rate $(cm^2 y^{-1})$, the continuous ²¹⁰Pb input rate (Bq m⁻² y⁻¹) and the single ²³⁹⁺²⁴⁰Pu input (Bq m⁻²) in 1968

3. Results and Discussion

The concentration profiles of ²¹⁰Pb and ²³⁹⁺²⁴⁰Pu were analysed with the model for each core. The availability of the ²³⁹⁺²⁴⁰Pu profiles proved to be important for the determination of mixing rates. If ²¹⁰Pb profiles were analysed separately, best fits would often result in mixing rates that were very high (above 10 cm² y⁻¹). Such high mixing rates effectively remove any structure in the ²³⁹⁺²⁴⁰Pu sediment profile above the mixing depth, and the comparison between predicted and observed ²³⁹⁺²⁴⁰Pu data thus proved very valuable. It was thus not possible to select values for mixing depths and mixing rates directly from computer optimisation due to the variable and unreliable results produced by this approach. Instead, these values were selected based on best judgement and visual inspection of the agreement between observations and model predictions.

Figure 2 illustrates the result of the analysis of unsupported ²¹⁰Pb and ²³⁹⁺²⁴⁰Pu concentration profiles from one of the sediment cores, Station No. 20, collected in the near-zone of the Thule accident area. For this core the sedimentation rate is determined at a value of 0.26 cm $y^{-1} \pm 9\%$ (1 sd), the mixing depth at a value of 5 cm, the mixing rate at a value of 1 cm² y⁻¹, the ²¹⁰Pb input rate at a value of 220 Bq m⁻² y⁻¹, and the single ²³⁹⁺²⁴⁰Pu input in 1968 at a value of 71 kBq m⁻². Furthermore, the observed ¹³⁷Cs profile for the core is included for comparison.

The sediment parameters estimated from the 10 cores from the Thule accident area are shown in Table 1 listing the mixing depths and mixing rates, the sedimentation rates and the corresponding uncertainties (1 sd), the ²¹⁰Pb input rates, the ²³⁹⁺²⁴⁰Pu inventories and the ¹³⁷Cs inventories. The mixing parameters are generally consistent across all sediment cores with a mixing depth of 5 cm and a mixing rate of 1 cm² y⁻¹. The mean sedimentation rate is 0.3 cm y⁻¹,

varying from 0.2 to 0.4 cm y⁻¹. The ²¹⁰Pb input rate varies from 74 to 460 Bq m⁻² y⁻¹ with a mean value of 261 Bq m⁻² y⁻¹. This value agrees with the average deposition flux of ²¹⁰Pb of about 1 dpm cm⁻² y⁻¹ (= 170 Bq m⁻² y⁻¹) found in sediments at temperate latitudes. The atmospheric flux of ²¹⁰Pb is lower at northern latitudes, but at the Thule area sedimentation is high due to particle transport from land by run off. The ¹³⁷Cs inventories are closely associated with the ²¹⁰Pb input rates for the ten sediment cores: the two sets of data show a strong correlation of 0.9 (P<0.001). Actually both data sets are highly correlated with the rates of sedimentation (correlation coeffficients of 0.8, P<0.01). The ²³⁹⁺²⁴⁰Pu inventories vary significantly from 2 to 71 kBq m⁻² with an arithmetic mean value of 15 kBq m⁻².

4. Conclusions

Analyses of radionuclide profiles in sediment cores collected in 1991 at Thule in Greenland have provided information on processes that occur in the sediments. The radionuclides include the naturally occurring ²¹⁰Pb, ²³⁹⁺²⁴⁰Pu originating from the aircraft accident in 1968, and ¹³⁷Cs originating from nuclear weapons testing. The processes include mixing of the surface sediments mainly from biological activity and burial of sediments due to particle scavenging. These processes influence the time scale and the extent to which the plutonium contamination is in contact with seawater and thus available for further dispersion. The quantified description of these processes is necessary for numerical modelling of the impact of radioactive contamination of the marine environment. These processes are of particular importance for the transuranic elements due to the relatively high radiotoxicity, the long physical half lives and the sediment-reactive properties of these elements.

The radionuclide profiles have been analysed with a numerical model to identify values of parameters describing the sediment processes. The average parameter values for the Thule area are: 0.3 cm y^{-1} for the sedimentation rate, 5 cm for the mixing depth and 1 cm² y⁻¹ for the mixing rate. It was found that the mixing parameters were not correctly identified from the interpretation of the unsupported ²¹⁰Pb profile alone, but that information from the ²³⁹⁺²⁴⁰Pu profile was necessary. This stresses the need for caution when interpreting ²¹⁰Pb profiles where no other information is available.

5. References

Christensen, E. A Model for Radionuclides in Sediments Infuenced by Mixing and Compaction. J. Geophys. Res. 87, p. 566-572; 1982.

Station	Mix.	Mix.	Sedim.	Uncert.	²¹⁰ Pb rate	²³⁹⁺²⁴⁰ Pu	¹³⁷ Cs
No.	depth	rate	rate				
Sample	(cm)	$(cm^2 y^{-1})$	$(cm y^{-1})$	(1 sd, %)	$(Bq m^{-2} y^{-1})$	$({\rm Bq} {\rm m}^{-2})$	$(Bq m^{-2})$
No.							
15-	3	1	0.20	18	140	4400	650
98832							
16-	5	1	0.40	8	460	21000	1720
98834							
17-	5	1	0.18	20	74	2200	80
98836							
18-	5	1	0.18	29	110	2600	320
98838							
19-	5	1	0.22	10	280	5700	1030
98840							
20-	5	1	0.26	9	220	71000	1050
98842							
21-	5	1	0.28	12	350	16000	960
98844							
23-	5	1	0.21	14	330	7600	980
98848							
24-	5	1	0.38	15	370	7300	1130
98850							
25-	5	1	0.34	10	280	12000	1290
98852							
Mean	4.8	1	0.27	15	261	14980	921
SD (%)	13	0	31	44	48	137	51

Table 1. Parameter values from sediment samples collected from the Thule area in 1991.

Figure Legends

Figure 1. Map showing the location of Thule, Greenland.

Figure 2. Locations (station #) for the Thule 1991 sediment samples. *: point of impact.

Figure 3. Observed and calculated radionuclide concentration profiles for sediment core no. 98842 including estimated parameter values (Station No. 20, co-ordinates: 76° 30.79' N, 69° 17.18 W).







Other Work

Since Risø National Laboratory was not able to collect sediment samples during the project period as originally planned, we have carried out radiometric analyses on samples from other project participants covering direct gamma spectrometry for Cs-137 and Pb-210 and radiochemical analyses followed by alpha spectrometry for transuranics. The results of these analyses are not reported here.

Risø has organised and carried out a sediment intercomparison exercise among participants of the EKO projects and other laboratories. The results were reported in 1996.

Risø has contributed to the project on radiological-assessment modelling covering Arctic waters and the Baltic Sea. This is described more detailed in the main text of the EKO-1 report.

Publications from EKO-1 project

Nielsen, S.P. A sensitivity analysis of a radiological assessment model for Arctic waters. In: Proceedings of the 7th Nordic Radioecological Seminar, 26-29 August 1996, Reykjavik, Iceland.

Nielsen, S.P. A Preliminary Assessment of Potential Doses to Man from Radioactive Waste Dumped in the Arctic Sea. Risø-R-841(EN), 1995.

Nielsen, S.P., An Intercomparison Exercise on Radionuclides in Sediment Samples. Risø-R-914(EN), 1996.

Title	Marine Radioecology. Final reports from sub-projects within the Nordic Nuclear Safety Research Project EKO-1
Author(s)	Sigurður Emil Pálsson (editor)
Affiliation(s)	Geislavarnir ríkisins (Icelandic Radiation Protection Institute)
ISBN	87-7893-056-1
Date	April 2001
Project	NKS/EKO-1
No. of pages	132
No. of tables	29
No. of illustrations	60
No. of references	104
Abstract max. 2000 characters	This report contains a collection of eight papers describing research done in the NKS/EKO-1 project. It also contains a preface giving a summary of the results. The EKO-1 project as a whole has been described in the report NKS(97)FR4. The aim of the project was to make a joint Nordic study on radionuclides in sediments and water and the interaction between these two phases. Relatively less emphasis had been put on this factor compared to others in previous Nordic studies on marine radioecology. For some of the participating countries this work was the first of its kind undertaken The project involved field, laboratory and model studies. The work and results helped to highlight the important role of sediments when assessing the consequences of real or possible releases of radionuclides to the marine environment.
Key words	Radioecology; marine radioecology; sediments; distribution coefficient; sedimentation rate; radiocaesium; modelling; doses to man

Available on request from the NKS Secretariat, P.O.Box 30, DK-4000 Roskilde, Denmark. Phone (+45) 4677 4045, fax (+45) 4677 4046, e-mail annette.lemmens@catscience.dk, http://www.nks.org.