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Seasonal variations in activity concentrations of ^{137}Cs, ^{40}K, ^{7}Be, ^{228}Ra, ^{99}Tc, ^{90}Sr, and ^{239,240}Pu in *Fucus vesiculosus* and *Ascophyllum nodosum* from the southeastern coast of Norway

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Abstract. The aim of this study was to compare the indicator properties of *Fucus vesiculosus* and *Ascophyllum nodosum*. Activity concentrations of ^{137}Cs, ^{40}K, ^{7}Be, ^{228}Ra, ^{99}Tc, ^{90}Sr and ^{239,240}Pu were measured in plants of the two species collected monthly in 2002 from one location at the southeastern coast of Norway. For ^{40}K, ^{137}Cs, ^{90}Sr, ^{7}Be and ^{228}Ra the activity concentrations were significantly higher in *Fucus vesiculosus* than in *Ascophyllum nodosum*, whereas the opposite was the case for ^{99}Tc. For ^{137}Cs, ^{90}Sr, ^{7}Be and ^{228}Ra the temporal variations in activity concentrations showed similar pattern for the two species, whereas for ^{99}Tc the temporal pattern was different for the two species. The observed temporal variations in activity concentrations of ^{137}Cs (both species) and ^{90}Sr (only *Fucus vesiculosus*) correlate with expected variations in seawater concentrations. For ^{137}Cs salinity, light conditions, temperature and growth rates seem to work in the same direction as the variations in seawater concentrations. A lack of correlation between salinity and ^{99}Tc concentrations in the algae indicates a slower dynamic in uptake and/or secretion for technetium. The observed differences between the two species may partly be explained by the difference in growth rate and life length between the two species.

1. INTRODUCTION

Brown algae have been proven to be useful indicator organisms for heavy metals and radionuclides in the marine environments due to their ability to concentrate elements from the ambient water. In the North Atlantic region especially *Fucus Vesiculosus* has been used to study radioactive pollutions in the marine environments e.g. [1-8], while other species has been used to a lesser extent. *Ascophyllum nodosum* has though been proven to be an effective indicator organism for ^{99}Tc [3]. The main focus of most studies has been on ^{137}Cs and ^{99}Tc, although detailed studies of uptake of ^{60}Co, ^{54}Mn and ^{65}Zn as well as ^{137}Cs in *Fucus vesiculosus* has been performed by [9-11]. Data for other long-lived anthropogenic nuclides such as ^{90}Sr and Pu, and for natural occurring radionuclides are sparser. The present work is a part of a Nordic research project called INDOFERN, managed by the Nordic Nuclear Safety Research (NKS), to investigate indicator organisms for environmental radioactivity. The aim of this study was to compare the indicator properties of *Fucus vesiculosus* and *Ascophyllum nodosum*, to provide data for some radionuclides that have not been focused on previously and to look at seasonal variations in activity concentrations. Activity concentrations of ^{137}Cs, ^{40}K, ^{7}Be, ^{228}Ra, ^{99}Tc, ^{90}Sr and ^{239,240}Pu were measured in whole plants of *Fucus vesiculosus* and *Ascophyllum nodosum* collected over a period of one year from one location at the southeastern coast of Norway.

The seawater at the sampling location consists of a mixture of high salinity Atlantic Ocean water and low salinity Baltic Sea water. There are great temporal variations in the mixing ratios, leading to relatively large variations in the salinity. The Atlantic Ocean water has a high concentration of ^{99}Tc compared to the Baltic Sea water due to discharges from the reprocessing plant at Sellafield, while the concentrations of ^{137}Cs, ^{90}Sr and Pu are highest in the Baltic Sea water due to the Chernobyl accident. The concentration of these nuclides in the seawater at the sampling location is therefore assumed to vary with the salinity. ^{99}Tc from Sellafield is predominately present in the seawater as TcO_4^-, while the other nuclides in this study are present as cations.

Due to an increasing focus on the release of natural occurring radionuclides (e.g. radium) from the oil and gas industry, there is a large demand for more knowledge about concentration levels and uptake of radium in marine environments. Concentration data for ^{238}Ra in seaweed is provided through measurements of the daughter nuclide ^{228}Ac. ^{228}Ra is reported to exist in a concentration of 0.13-3.4 mBq/l in surface water in the Atlantic Ocean [12]. ^{7}Be is a cosmogenic nuclide that is continuously formed in the atmosphere due to cosmic irradiation of air.

Fucus vesiculosus and *Ascophyllum nodosum* are both commonly found along the coast of Norway, and they often occur together on the middle shore. While the fronds of *Fucus vesiculosus* grow relatively fast and live for only 3-5 years, *Ascophyllum nodosum* is very slow growing and individual fronds become up to 15 years before breakage.

2. SAMPLING AND ANALYSES

Samples of *Fucus vesiculosus* and *Ascophyllum nodosum* were collected every month in 2002 from one location nearby the island Tromøya at the southeastern coast of Norway. The samples consisted of several individual plants, with a mixture of young and old plants, collected along a stretch of 10-20 m. Only plants growing on rocks or big stones were collected. Salinity was measured in water samples taken at the same location in about 20 cm depth.

The samples were dried to constant weight at 105 °C, milled and homogenized before analyses. All samples were measured for gamma emitting nuclides (^{7}Be, ^{40}K, ^{137}Cs and ^{238}Ac) and ^{99}Tc. Samples from every second month were also analysed for ^{90}Sr and ^{239,240}Pu.

Gamma analysis and radiochemical analysis of ^{90}Sr and ^{239,240}Pu were performed at Institute for Energy Technology. Gamma emitting nuclides (^{7}Be, ^{40}K, ^{137}Cs and ^{238}Ac) were measured by gamma spectrometry using HPGe-detectors. ^{238}Ac is assumed to be in equilibrium with the parent nuclide ^{238}Ra, so the concentration of ^{238}Ra can be taken as the same as for ^{238}Ac. ^{90}Sr was analysed by means of chemical separations and measurements of the beta-activity of the daughter product ^{90}Y. The method is based on a modified HASL 300 procedure [13-14]. Following chemical separation of strontium, the samples were left for ingrowth of ^{90}Y. Yttrium was then precipitated as oxalate, collected on a filter, and measured by low level anticoincidence beta counters, model Risø GM-25-5. Chemical yield was determined by ^{85}Sr-tracer and titration of Y with EDTA. Analyses of ^{239,240}Pu were performed by chemical separation and electro deposition of Pu on steel plates. The activity of ^{239,240}Pu was measured by alpha spectrometry using PIPS detectors, and the yield was determined by ^{242}Pu-tracer. The method is based on Chen [15]. The laboratory has an internal quality control system, and participates in intercomparison exercises for these types of analyses at a regular basis.

The ^{99}Tc-analyses were performed by the Department of Radiation Physics at University of Lund, which also participates in intercomparison exercises at a regular basis. Technetium was extracted by TBP from sulphuric acid-hydrogen fluoride media. Back-extraction was done from sodium hydroxide solution from which the technetium was electrodeposited onto stainless steel discs. ^{99m}Tc was used as chemical yield determinant. After decay of the yield determinant, ^{99}Tc was measured by an anticoincidence-shielded GM counter [16].

3. RESULTS AND DISCUSSION

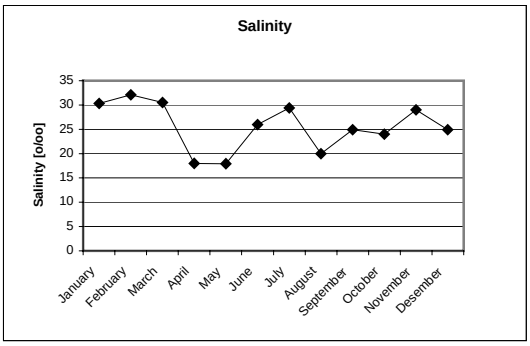
The results are illustrated graphically in *Figure* 1. The error bars represent two standard measurement uncertainties.

The salinity at the sampling location (figure 1 a) varied from 18-32 ‰ due to varying mixing between saline-rich Atlantic Ocean water and saline-poor Baltic Sea water. The salinity was highest in January- March, July and November, which should indicate low concentrations of ^{137}Cs and ^{90}Sr, and high concentrations of ^{99}Tc in these periods. The low salinity in April, May and August should indicate relatively high concentration of ^{137}Cs and ^{90}Sr, and low concentrations of ^{99}Tc during these periods.

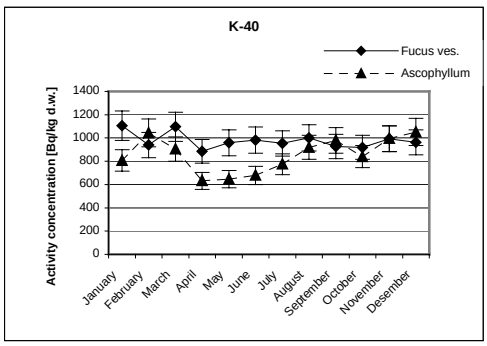
The concentrations were in average higher in *Fucus vesiculosus* than in *Ascophyllum nodosum* for all the measured radionuclides except ^{99}Tc. For ^{99}Tc the concentrations were in average higher in *Ascophyllum nodosum* than in *Fucus vesiculosus*. The data show that there were great seasonal variations in the concentrations of the measured radionuclides. For ^{137}Cs, ^{90}Sr, ^{228}Ra and ^{7}Be the temporal variations in activity concentrations showed the same pattern for the two species, whereas for ^{99}Tc the temporal pattern was completely different for the two species.

The ^{40}K-concentrations varied from 890-1110 Bq/kg dry weight (d. w.) in *Fucus vesiculosus*, and from 630-1050 Bq/kg d. w. in *Ascophyllum nodosum*. The concentrations were in average 20 % higher for ^{40}K in *Fucus vesiculosus* compared to *Ascophyllum nodosum*. The difference is statistical significant at a 95 % confidence level (two sided paired students t-test gives p = 0.011). There were little pronounced temporal variations in the activity concentrations for ^{40}K, which could be expected because the uptake of K is homeostatic regulated in most organisms.

The ^{137}Cs-concentrations varied from 0.86-7.3 Bq/kg d. w. in *Fucus vesiculosus*, and from 0.73-3.9 Bq/kg d. w. in *Ascophyllum nodosum*. The concentrations were in average 50 % higher in *Fucus vesiculosus* than in Ascophyllum nodosum. The difference is statistical significant (p = 0.014 for student t-test). The temporal pattern was similar for the two species (figure 1 c), with the highest ^{137}Cs concentrations during the spring and early summer. The variations were however larger for *Fucus vesiculosus* than for *Ascophyllum nodosum*. There was a significant negative correlation between salinity and concentrations of ^{137}Cs for both species (Pearson correlations significant at a 0,05 level). The correlations are illustrated in figure 2 a. The correlation was strongest for *Fucus vesiculosus*. The negative correlation may at least partly be explained by higher water concentrations of ^{137}Cs due to high Baltic outflow in the periods with low salinities. The salinity has also been shown to influence the uptake of ^{137}Cs in *Fucus vesiculosus* [10], with a higher uptake in low salinity water. This may also contribute to the negative correlation between salinity and ^{137}Cs-concentrations seen in our data. Significant effects of temperature and light on the initial rate of uptake of ^{137}Cs in *Fucus vesiculosus* have been reported [11], high temperatures and light giving higher uptake. Increasing water temperatures and improving light conditions in spring and early summer might therefore also explain the increased concentrations in this period. Part of the decrease in ^{137}Cs concentrations in July and August may be explained by growth dilution because of rapid growth in this period as well as lower ^{137}Cs concentrations in the seawater (high salinity). The actual loss of caesium from *Fucus vesiculosus* has been reported to be in the same order of magnitude as the growth dilution [11].



a)



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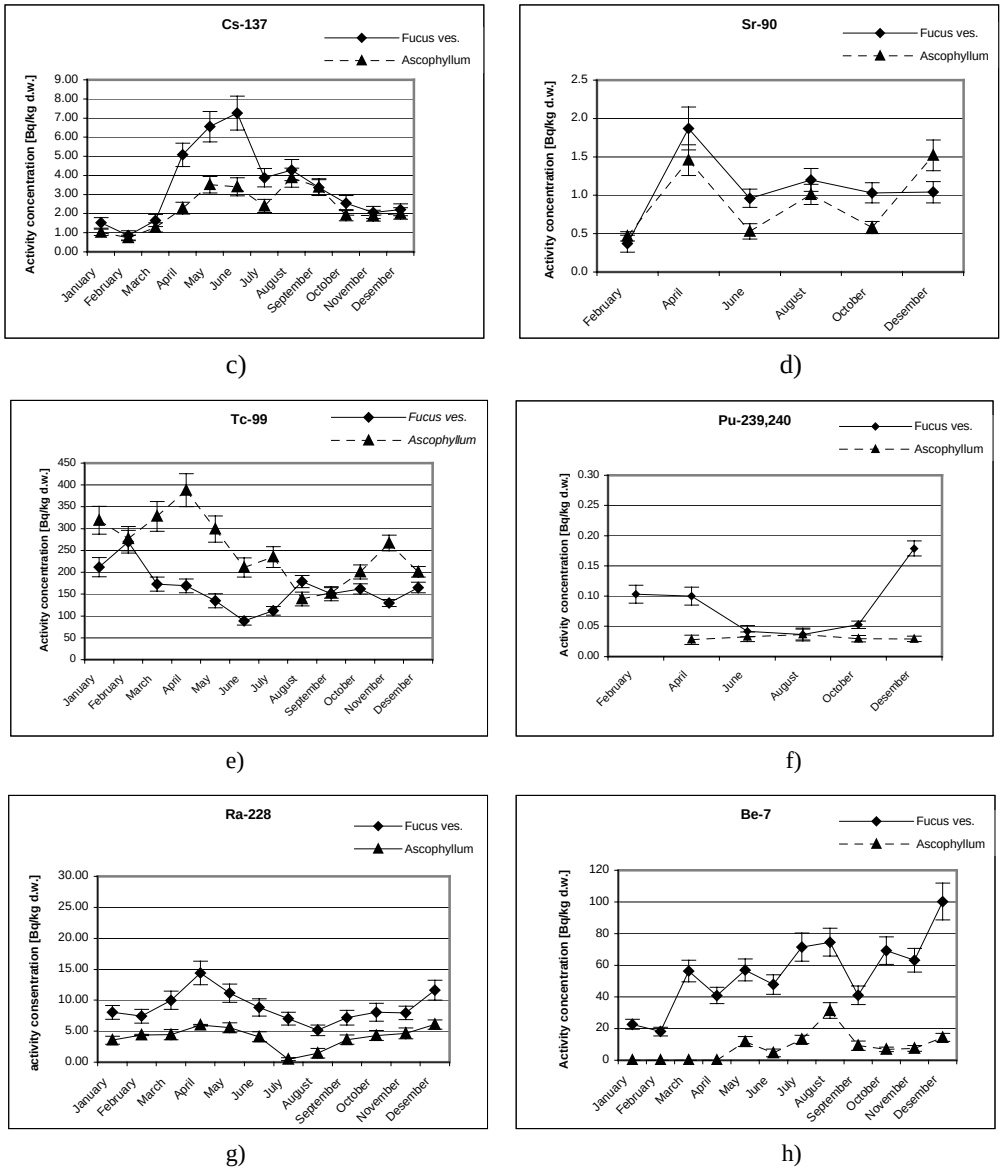
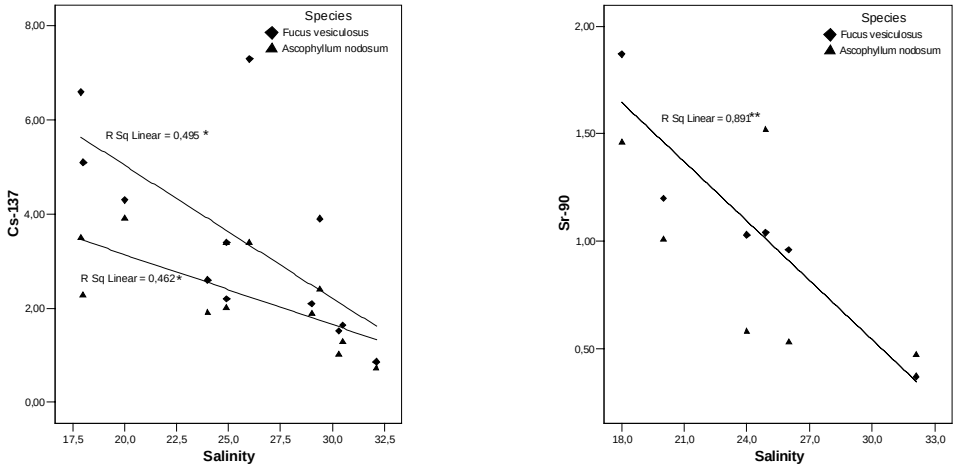


Figure 1. Measured salinity and activity concentrations. Error bars represent two standard deviations in measurement uncertainties.

The accumulation of ^{137}Cs and ^{40}K has been shown to be highest in the receptacles and the new vegetative tissue of *Fucus vesiculosus* [9]. Because *Fucus vesiculosus* grows more rapidly and lives for a shorter time than *Ascophyllum nodosum* the ratio of the biomass of new vegetative tissue to the biomass of the whole plant is greater for *Fucus vesiculosus* than for *Ascophyllum nodosum.* This may explain why the concentrations of ^{40}K and ^{137}Cs are higher in *Fucus vesiculosus* than in *Ascophyllum nodosum.* The ^{90}Sr-concentrations varied from 0.3-1.9 Bq/kg d. w. in *Fucus vesiculosus* and from 0.5-1.5 Bq/kg d. w. in *Ascophyllum nodosum*. The highest concentrations were measured in the samples from April. There was a significant negative correlation between ^{90}Sr concentration in *Fucus vesiculosus* and salinity (Pearson correlations significant at a 0.01 level). For Ascophyllum our data did not give a significant correlation, maybe because of too few data. The correlation is shown in figure 2b.

The ^{99}Tc-concentrations varied from 90-270 Bq/kg d. w. in *Fucus vesiculosus*, and from 140-390 Bq/kg d. w. in *Ascophyllum nodosum.* The concentrations were in average 60 % higher for *Ascophyllum* than for *Fucus* ($p = 0.0023$), which indicates that ^{99}Tc is more effectively taken up in *Ascophyllum* than in *Fucus*. The higher concentrations of ^{99}Tc in *Ascophyllum nodosum* compared to *Fucus vesiculosus* found in this study are in agreement with earlier measurements of seaweed from the Norwegian coast [3]. There were no correlations between salinity and ^{99}Tc concentration for either of the two species. This may indicate that there is a slower dynamic in the mechanisms of uptake and loss of technetium than for caesium and strontium. The difference in temporal pattern for the two species indicates different dynamic processes for uptake and retention of technetium in the two species. Because *Ascophyllum nodosum* grows more slowly and lives longer than *Fucus vesiculosus*, the ^{99}Tc might be integrated over a longer time span in *Ascophyllum nodosum* than in *Fucus vesiculosus*, and also the effect of growth dilution should be less pronounced in *Ascophyllum nodosum* than in *Fucus vesiculosus*. This could give a greater memory effect in *Ascophyllum nodosum* than in *Fucus vesiculosus* when pooled samples of individual plants of different age are measured.



a) b)

Figure 2. Correlation between activity concentration and salinity for ^{137}Cs (a) and ^{90}Sr (b).

The ^{239,240}Pu-concentrations were very low in both species, ranging from 0.03-0.18 Bq/kg d. w. For *Ascophyllum nodosum* there were apparently no seasonal variations, and for *Fucus vesiculosus* the concentrations were highest during winter and early spring.

The concentrations of ^{228}Ra varied from 5.1-14.4 Bq/kg d. w. in *Fucus vesiculosus*, and from below the detection limit (0.5 Bq/kg) to 6.1 Bq/kg d. w. in *Ascophyllum nodosum.* The concentrations in *Fucus vesiculosus* were in average twice as high as in Ascophyllum nodosum. The difference is statistical significant ($p < 0.00$). This is in agreement with previous results reported in a literature study covering naturally occurring radionuclides in the marine environments [17], showing higher concentration factors for radium in *Fucus vesiculosus* than in *Ascophyllum nodosum*.

The ^{7}Be-concentrations were significant higher in *Fucus vesiculosus* than in *Ascophyllum nodosum*, varying from 18-100 Bq/kg d. w. for *Fucus vesiculosus*, and from below the detection limit of about 1 Bq/kg to 30 Bq/kg in *Ascophyllum nodosum.* ^{7}Be is formed in the atmosphere, and is mainly released to ground level by precipitation. The observed variations might be due to variations in precipitation and other atmospheric condition, although at the moment we haven not any weather data to support this.

4. CONCLUSIONS

The results show that ^{40}K, ^{137}Cs, ^{90}Sr, ^{7}Be and ^{228}Ra are more efficiently taken up in *Fucus vesiculosus* than in *Ascophyllum nodosum*, while the opposite is the case for ^{99}Tc. The accumulation of ^{137}Cs and ^{40}K has been shown to be highest in the receptacles and the new vegetative tissue of *Fucus vesiculosus* [9]. Because *Fucus vesiculosus* grows more rapidly and lives for a shorter time than *Ascophyllum nodosum* the ratio of the biomass of new vegetative tissue to the total biomass is greater for *Fucus vesiculosus* than for *Ascophyllum nodosum* in samples consisting of several individual plants, with a mixture of young and old plants. This may explain why the concentrations of ^{40}K and ^{137}Cs, and probably the other cations, are higher in *Fucus vesiculosus* than in *Ascophyllum nodosum*.

The two species showed similar temporal patterns in activity concentrations of ^{137}Cs, ^{90}Sr, ^{228}Ra and ^{7}Be, which indicate that the mechanisms for uptake and secretion of these nuclides are the same for the two species. The temporal variations in activity concentrations of ^{137}Cs may be explained from several factors giving the same type of effect. Firstly, a negative correlation between salinity and measured concentrations in the seaweed (related to salinity data) indicates a relatively fast response to variations in seawater concentrations. Secondly, the salinity itself has been shown to influence the uptake of ^{137}Cs, low salinity giving the highest uptake [10]. Thirdly, temperature and light controls the initial rate of uptake of ^{137}Cs [11], and increasing water temperatures and improving light conditions in spring and early summer therefore also explain the increased concentrations in this period. Finally part of the decrease in ^{137}Cs concentrations in July and August may be explained by growth dilution because of rapid growth in this period. A negative correlation between salinity and ^{90}Sr concentration in *Fucus vesiculosus* was also found, indicating a relatively fast response to variations in seawater concentrations also for strontium. A lack of correlation between salinity and ^{99}Tc concentrations in the algae indicates a slower dynamic in uptake and secretion for technetium than for caesium and strontium (e.g. longer biological half life). The difference in growth rate and life length of the two species may also explain the difference in temporal pattern between the two species for ^{99}Tc. These factors are more important for elements/compounds with long biological half life, and will give a greater memory effect in the slow growing, long living *Ascophyllum nodosum* than in the faster growing and shorter living *Fucus vesiculosus*.

This study confirms that *Fucus vesiculosus* is a very good indicator organism for radioactivity in marine environments. *Ascophyllum nodosum* is also a good indicator organism, but have slightly lower concentration factors for all the radionuclides in this study except technetium. *Ascophyllum nodosum* seems to have a slower response to change in seawater concentrations of technetium than *Fucus vesiculosus*, which gives a lower time resolution for *Ascophyllum nodosum*. This might be an advantage when sampling is less frequent.

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References

[1] Lindahl, P., Ellmark, C., Gäfvert, T., Mattson, S., Roos, P., Holm, E. and Erlandson, B., *J. Environ. Radioactivity* **67** (2003) 145-156
[2] Carlson, L. and Holm, E., *J. Environ. Radioactivity* **15** (1992) 231-248
[3] Holm, E., Rioseco, J. and Christensen, G. C., "^{99}Tc in Fucus from Norwegian waters", International symposium on the behaviour of long-lived radionuclides in the marine environment, A. Cigna and M. Myttenaere Eds. (CEC, Luxemburg, 1994) pp. 357-367.

[4] Duniec, S., Carlson, L., Hallstudius, L. and Holm, E., "Fucus vesiculosus (L.) as a bio-indicator for ^{137}Cs in the Baltic Sea and Kattegat", Seminar on the behaviour of radionuclides in estuaries. Renesse, 17.-19. Sept. 1984, (CEC, Luxemburg, 1985) pp 229-239.
[5] Yiou, F., Raisbeck, G. M., Christensen, G. C. and Holm, E. ^{129}I/^{127}I, ^{129}I/^{137}Cs and ^{129}I/^{99}Tc in the Norwegian coastal current from 1980 to 1998, *J. Environ. Radioactivity* **60** (2002) 61-71
[6] Christensen, G. C. and Selnaes, T.D., "Study of marine radioactivity along the Norwegian coast, 1980-1994", in Environmental impact of radioactive releases, IAEA proceedings, (IAEA, Vienna, 1995) pp. 618-622
[7] Christensen, G. C. and Strålberg, The radiological exposure of the population of the European Community to radioactivity in the Baltic Sea, S. P. Nielsen Ed., EUR 19200, *Rad. Protection* **110** (2000) pp. 433-438
[8] Dahlgaard, H., Bergan, T. D. S. and Christensen, G. C., *Radiopro.* **32(C2)** (1997) 353-358
[9] Carlson, L. and Erlandsson, B., *Environ. Pollut.* **73** (1991) 53-70
[10] Carlson, L. and Erlandsson, B., *J. Environ. Radioactivity* **13** (1991) 309-322
[11] Dahlgaard, H. and Boelskifte, S., *J. Environ. Radioactivity* **16** (1992) 49-63
[12] IAEA Technical report series No. 310, The environmental behaviour of radium, Vol. I-II, (IAEA, Vienna, 1990)
[13] Erickson, M. D., The procedures manual of the environmental measurement laboratory, Vol II, 28th edition (U.S. Department of energy, New York, 1997) p 4.5.4
[14] Varskog, P., Bjerk, T. O. and Ruud, A. B., "pH-controlled EDTA titration as an alternative method for determination of the chemical yield of yttrium in ^{90}Sr-analyses", Conference on Rapid Radioactivity Measurments in Emergency and Routine Situations, Teddington, U.K., 1997, S. Jerome and K. Inn Eds. (NPL, Teddington, 1997) pp 237-242
[15] Chen, Q., Aarkrog, A., Nielsen, S.P., Dahlgaard, H., Nies, N., Yu, Y. and Mandrup, K., Determination of plutonium in environmental samples by controlled anion exchange, RISØ-M-2856 (1991) 17 p
[16] Holm, E., Rioseco, J. and Garcia-Leon, M., *Nucl. Instr. Meth. Res.* **223** (1984), 204
[17] Strålberg, E., Varskog, A.T.S., Raaum, A and Varskog, P. Naturally occurring radionuclides in the marine environment – an overview of current knowledge with emphasis on the North Sea area, Norse Decom, ND/E-19/03 (2003)