BOREAL ENVIRONMENT RESEARCH 7: 91–97
Helsinki 19 June 2002
ISSN 1239-6095

Technetium-99 in biota samples collected along the Finnish coast in 1999

Erkki Ilus, Vesa-Pekka Vartti, Tarja K. Ikäheimonen, Jukka Mattila and Seppo Klemola

STUK – Radiation and Nuclear Safety Authority, P.O. Box 14, FIN-00881 Helsinki, Finland

Ilus, E., Vartti, V.-P., Ikäheimonen, T. K., Mattila, J. & Klemola, S. 2002. Technetium-99 in biota samples collected along the Finnish coast in 1999. *Boreal Env. Res.* 7: 91–97. ISSN 1239-6095

The aim of the study was to develop a method for analysing ^{99}Tc at STUK, and to establish whether ^{99}Tc can be detected in Finnish coastal waters. Samples of *Fucus vesiculosus, Myriophyllum* spp., *Macoma baltica, Mytilus edulis, Saduria entomon* and seawater were collected at more than 30 stations along the western and southern coasts of Finland for ^{99}Tc analysis. Small amounts of ^{99}Tc were observed in all the *Fucus* samples collected; the activity concentrations ranged from 1.6 to 11.6 Bq kg^{-1} dry wt. The highest concentrations were found in two samples taken from the northernmost stations in the Quark, probably for biological reasons. Due to the low salinity of the water, *Fucus vesiculosus* is very slow-growing and small in this area, which is at the extreme limit of its permanent distribution range in the Baltic Sea. In seawater and in all the other biota samples, the concentration of ^{99}Tc was below the detection limit, which supports the use of *Fucus* as an indicator organism for ^{99}Tc in the marine environment. Global fallout from atmospheric nuclear weapons tests carried out in the 1950s and 1960s is certainly the most important source of ^{99}Tc detected in *Fucus* on the Finnish coast. In addition, the samples were analysed for gamma-emitting radionuclides.

Introduction

Artificial radioactivity in the Baltic Sea originates from four principal sources: (1) fallout from the Chernobyl nuclear power plant accident in 1986, (2) global fallout from atmospheric nuclear weapons tests carried out in the late 1950s and early 1960s, (3) aquatic discharges from nuclear reprocessing plants in Western Europe (Sellafield, UK and La Hague, France) entering with the inflow of saline waters through the Danish Straits, and (4) aquatic discharges from nuclear facilities operating in the Baltic Sea region. The input of ^{137}Cs and ^{134}Cs from the Chernobyl accident is clearly the most significant of these sources, while discharges from local nuclear facilities have been of minor importance (Ilus and Ilus 2000). Discharges from Western European reprocessing plants have influenced the concentrations of certain radionuclides (^{137}Cs, ^{134}Cs and ^{99}Tc) in the marine environment of the southern Baltic Sea.

Aquatic discharges of ^{99}Tc from Sellafield have been reported since 1952 (Ilus and Ilus 2000). The first discharge peak was reported in 1978 but the discharges from Sellafield were low in 1981–1993 being less than those from La Hague. The next time the aquatic discharges of ^{99}Tc from Sellafield were considerably increased in late 1994 when a new Enhanced Actinide Removal Plant (EARP) began operating. ^{99}Tc is a long-lived, artificial radionuclide formed in significant quantities by fission processes that occur in nuclear reactors. It is a soft β^{-}-emitter (E_{max} = 0.292 MeV) and has a half-life of 213 000 years. Transported by ocean currents, the recent releases from Sellafield had reached the Norwegian coast by 1996 (Brown *et al*. 1998).

In 1998, Nordic Nuclear Safety Research (NKS) initiated a project entitled 'Radioactive tracers in Nordic sea areas'. One of the topics was to study the use of ^{99}Tc as a tracer for transport of contaminated water masses from the Irish Sea to Nordic waters, including the Baltic Sea. The present study is the Finnish contribution to this joint Nordic project. The aim was to establish whether ^{99}Tc can be detected in the coastal waters of the Finnish mainland. Holm *et al*. (1986) had earlier reported the detection of ^{99}Tc in seaweed samples from the east coast of Sweden and the Åland Islands taken in the early 1980s. ^{99}Tc had not previously been analysed at STUK, and so another goal of the study was to develop a method for analysing ^{99}Tc in the laboratory.

Material and methods

Fucus on the Finnish coast

The bladderwrack, *Fucus vesiculosus,* is a marine organism that also tolerates the brackish water conditions of the Baltic Sea. The salinity of the water decreases gradually from the Danish Straits towards the northernmost regions. Off the coast of Finland, the salinity of surface water is at its highest (6‰–7‰) in the southern part of the southwestern Archipelago and the Åland Islands. From there it decreases northwards and eastwards and approaches zero at the end of the Gulf of Finland and the Gulf of Bothnia.

The shape and size of *Fucus* changes as salinity of the water decreases. In the southwestern Archipelago, the *Fucus* fronds are relatively long (40 cm) and broad, and the *Fucus* belts are often uniform, dense and luxuriant. In contrast, at the northernmost sampling station, Norrskär in the Quark (Fig. 1), which lies at the extreme limit of the permanent distribution range of haptophytic *Fucus,* the fronds were very small (10–15 cm), slow-growing, narrow and less ramified. Due to the low salinity of the water the species occurs only sporadically in the area north of the Quark, and is mostly loose-lying.

Sampling and pre-treatment of samples

In June–July 1999, samples of *Fucus vesiculosus* were collected at 30 stations along the western and southern coasts of Finland (Fig. 1). In addition, samples were collected from the areas surrounding the nuclear power plants at Loviisa and Olkiluoto. Most of the sampling stations were the same as those used in STUK's earlier coastal surveys (Ilus *et al*. 1988). The samples were taken mainly from a depth of 1–3 metres by scuba diving. Due to the low salinity of the water and the action of ice in winter, *Fucus* does not exist in the uppermost littoral zone on the Finnish coast.

Two divers collected the algae one by one in net bags. Only well-developed and attached (haptophytic) plants were chosen, and the entire thalli including the basal parts were sampled. Each sample comprised numerous individuals because the *Fucus* was relatively small and the minimum amount needed for a representative sample was 1.5 kg fresh wt. Only a part of the sample was analysed.

Sea water samples were taken simultaneously with the *Fucus* samples at 8 stations. The samples were taken directly from the surface water into plastic kegs. The volume of the samples was 60 litres. Larger water samples would be desirable but the method used in this study was not capable to treat larger water volumes. Using this method the detection limit of ^{99}Tc was 0.16 Bq m^{-3}. Samples of *Myriophyllum* were taken

Fig. 1. Location of the sampling stations.

by scuba diving in the waters off Olkiluoto. To determine the share of atmospheric fallout in the ^{99}Tc values of the biota samples, one *Myriophyllum* sample was taken from an inland lake (Enäjärvi) in southern Finland. This sample was taken by wading in water 1 m deep. The *Myriophyllum* samples were 162–2300 g fresh wt. The samples of *Mytilus edulis* (600–1600 g fresh wt.) were taken by scuba diving, simultaneously with the *Fucus* samples. *Macoma baltica* (220 g fresh wt.) was taken by an Ekman-Birge grab and a sieve, and *Saduria entomon* (174 g fresh wt.) with bait-traps.

The seaweed samples were shaken thoroughly on porous paper immediately after sampling. Then they were preliminarily dried at room temperature in the laboratory. The final drying for all the biota samples was performed at 105 °C overnight. After drying, the dry weight was recorded and the samples were homogenised by milling. About 10 g of dry biota sample was used for analysis.

Developing a method for analysing ^{99}Tc

A new modification of the method for analysing ^{99}Tc in marine samples was developed. The method is based on extraction chromatography using a special reagent (TEVA resin). After pre-treatment, Tc is extracted into the resin, which is then measured with a liquid scintillation analyser. Yield measurements were made using gamma-spectrometry and a short-lived ^{99m}Tc tracer. This method is suitable for various kinds of environmental samples, though the pre-treatments are different. The effectiveness of the measurement of ^{99}Tc is about 80% and the theoretical detection limit is 0.003 Bq per sample. The method was tested in an intercomparison exercise of seaweed samples arranged by the Risø National Laboratory, Denmark. Our result was in good agreement with those reported by the other participating laboratories. The method is summarized in Fig. 2. A more detailed description of determination methods

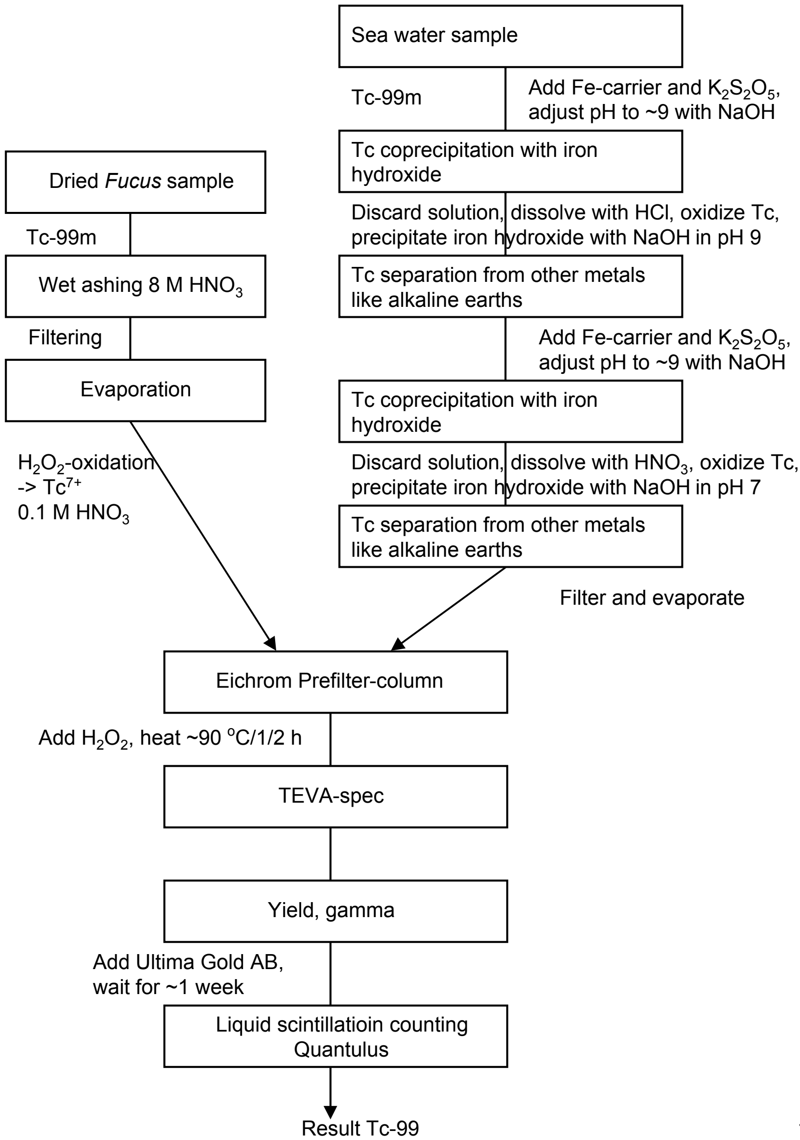

Fig. 2. The analysis method for ^{99}Tc.

for seawater and biota is given in Ikäheimonen *et al*. (2002).

Results and discussion

Small amounts of ^{99}Tc were observed in all the *Fucus* samples and the activity concentrations ranged from 1.6 to 11.6 Bq kg^{-1} dry wt. (Table 1 and Fig. 3). The values were somewhat higher than those published by Holm *et al*. (1986) from the Åland Islands in 1983. In the samples collected from the Gulf of Finland the average concentration was 3.4 (2.1–4.4) Bq kg^{-1} dry wt., and in those collected from the Archipelago Sea and Åland Islands 2.9 (1.6–4.7) Bq kg^{-1} dry wt. In the samples collected from the Bothnian Sea the average concentration was 5.3 (1.9–11.6) Bq kg^{-1} dry wt. In the two seawater samples analysed, the ^{99}Tc concentrations were below the detection limit of 0.16 Bq m^{-3}. Thus, it was not possible to calculate the concentration factor for ^{99}Tc. In 1986, the concentrations of ^{99}Tc were 0.023–0.183 Bq m^{-3} in seawater samples collected from the Gulf of Bothnia and Gulf of Finland (Aarkrog *et al.* 1988). Holm *et al.* (1986) calculated that the activity concentration ratio *Fucus*/water was about 40 000 in the Baltic Sea, whereas in the Irish Sea the concentration factor has been estimated to be about three times higher (Brown *et al.* 1998).

The activity concentrations of ^{99}Tc were clearly highest (11.4 and 11.6 Bq kg^{-1} dry wt.) in the two *Fucus* samples taken from the northernmost stations in the Quark (Fig. 3). This was probably due to the biological factors described earlier in this paper. In the Quark, *Fucus* occurs in extreme conditions due to the low salinity of the water. The *Fucus* thalli are slow-growing and small in this area, and this may increase the uptake of radionuclides from the surroundings to the seaweed. Other biological factors, such as the length of the growing period, the amount of epiphytes, etc., may also affect the uptake of radionuclides.

Global fallout from nuclear weapons tests is certainly the most important source of ^{99}Tc detected in *Fucus* on the Finnish coast. Confir-

Table 1. ^{99}Tc in *Fucus vesiculosus* samples collected in June–July 1999 along the Finnish coast.

Station	Municipality	Area	Location	Bq kg^{-1} dry wt	Uncertainty (1σ) %
A	Mustasaari	Norrskär	Norrberget W	11.4	8
B	Maalahti	Rönnskären	Fälskär W	11.6	7
C	Närpiö	Nämpnäs	Öskata W	4.6	14
D	Kristiinankaupunki	Skaftung	Idsgrunds grynnan W	4.6	9
E	Merikarvia	Truutinkari	Manunkallio W	6.9	8
G1	Eurajoki	Olkiluoto	Susikari NE	1.9	9
G2	Eurajoki	Olkiluoto	Valkiakari W	4.2	10
G3	Eurajoki	Olkiluoto	Kaalonpuhdin matala S	2.6	9
G4	Rauma	Olkiluoto	Kalliopöllä NE	2.2	18
H	Uusikaupunki	Pyhämaa	Letto NW	3.2	6
I	Kustavi	Isokari	Hamskeri N	4.8	11
J	Vårdö	Västra Simskäla	Norrgård S	2.8	7
K	Geta	Långö	Dånö bron N	3.3	10
L	Eckerö	Storby	Berghamn S	4.7	11
M	Lemland	Järsö	Järsö SW	1.6	27
N	Lumparland	Svinö	Svinö SE	2.3	17
O	Föglö	Sommarö	Havsklippan N	3.0	14
P	Kökar	Karlbylandet	Vervan W	3.0	20
Q	Houtskari	Fiskö	Fiskö W	2.6	13
R	Nauvo	Seili	Högholmen SE	2.5	14
S	Korppoo	Jurmo	Killingharu S	3.1	9
T	Dragsfjärd	Långholmen	Södra Bärskärsgrund S	3.5	8
Ü	Hanko	Tvärminne	Långskär SE	4.1	9
U	Inkoo	Grundsö	Djävulsgrundet S	3.5	10
V	Kirkkonummi	Stora Mickelskären	Salgrunden E	3.2	9
W	Helsinki	Katajaluoto	Trutkobben SE	3.8	8
X	Porvoo	Onas	Rönnskär E	3.3	7
Y	Porvoo	Pellinki	Lökskär SE	4.4	7
Z1	Loviisa	Hästholmsfjärden W	Halkokari E (19.5.1999)	4.0	8
Z1	Loviisa	Hästholmsfjärden W	Halkokari E (10.8.1999)	2.7	8
Z2	Loviisa	Hästholmsfjärden W	Åmusholmen SE	2.1	13
Z3	Ruotsinpyhtää	Hästholmsfjärden E	Bölsviken W	2.1	16
Z4	Pernaja	Storskarven	Storskarven E	3.3	6
Z5	Pernaja	Orrengrund	Östergrund S	3.6	16
Å	Pyhtää	Kaunissaari	Pienkari E	3.5	20
Ä	Kotka	Haapasaari	Veitkari S	4.1	9
Ö	Vehkalahti	Ulko-Tammio	Ulko-Tammio E	3.8	7

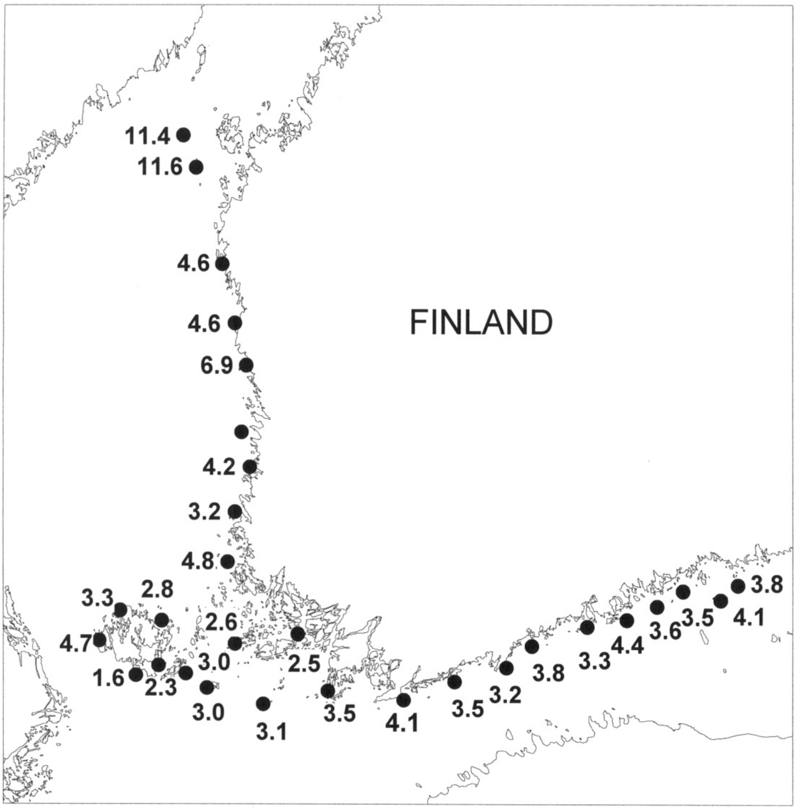

Fig. 3. Activity concentrations of ^{99}Tc in *Fucus vesiculosus* (Bq kg^{-1} dry wt.) along the Finnish coast in 1999.

mation of this was sought by analysing a few samples of another aquatic plant, *Myriophyllum* spp., collected from an inland lake in southern Finland and from the sea area off Olkiluoto. However, the ^{99}Tc concentrations were below the detection limit in these samples and it was not possible to draw any conclusion on this basis.

Fucus samples collected from the discharge areas of the Finnish nuclear power plants at Loviisa and Olkiluoto did not indicate any traces of local ^{99}Tc releases. The concentrations of ^{99}Tc in the samples collected from the immediate vicinities of the power plants (*see* Table 1: Stations G1-4 and Z1-3) did not differ from the general level in the surrounding area.

The activity concentrations of ^{99}Tc in *Fucus* sampled from the Åland Islands in 1983, as reported by Holm *et al.* (1986), varied between 1.9 and 3.3 Bq kg^{-1} dry wt. In the samples collected along the east coast of Sweden the concentrations varied between 1.8 and 5.8 Bq kg^{-1} dry wt., and in those from the west coast of Sweden between 22 and 380 Bq kg^{-1} dry wt. Despite the marked increase in the ^{99}Tc results between 1982 and 1983, Holm *et al.* (op. cit.) concluded that the most important source of ^{99}Tc on the east coast of Sweden was fallout from nuclear detonation tests. The rise in ^{99}Tc values in the Danish Straits in 1982 and 1983 correlated with the preceding peak of ^{99}Tc discharges from Sellafield (1978) and the estimated transit time of 4 years from the Irish Sea to the Danish Straits (Aarkrog *et al.* 1986).

In 1996–1998, the highest levels of ^{99}Tc in the Norwegian coastal areas of the Norwegian Sea, the Outer Oslo Fjord and the North Sea were recorded in lobster and seaweed samples (Brown *et al.* 1998). Shrimps and mussels seem to accumulate ^{99}Tc to a much lower degree. The contents of ^{99}Tc in *Fucus vesiculosus* and *Fucus serratus* were generally in the range of 79–170 Bq kg^{-1} dry wt., in lobsters 56–270 Bq kg^{-1} dry wt. and in mussels 2.4–7.6 Bq kg^{-1} dry wt. Our

Table 2. Analyses of ^{99}Tc in other biota samples.

Species	Sampling site	Bq kg^{-1} dry wt. (below the detection limit)
Vascular plants		
Myriophyllum sp.	Sammatti, Enäjärvi (inland lake)	< 1.2
Myriophyllum spicatum (1)	Eurajoki, Olkiluoto, Kaalonpuhdin matala S (G3)	< 0.7
Myriophyllum spicatum (2)	Eurajoki, Olkiluoto, Kaalonpuhdin matala S (G3)	< 0.6
Mussels		
Macoma baltica	Eurajoki, Olkiluoto, Kaalonpuhti W	< 0.8
Mytilus edulis	Eurajoki, Olkiluoto, Kaalonpuhdin matala S (G3)	< 0.7
Mytilus edulis	Houtskari, Fiskö W (Q)	< 0.6
Mytilus edulis (1)	Korppoo, Jurmo, Killingharu S (S)	< 0.6
Mytilus edulis (2)	Korppoo, Jurmo, Killingharu S (S)	< 0.6
Crustaceans		
Saduria entomon	Ruotsinpyhtää, Hästholmsfjärden E (near Loviisa)	< 0.9

results from the Finnish coast support the use of *Fucus* as an indicator organism for ^{99}Tc and many other radionuclides in the marine environment. This is confirmed in the results of our ^{99}Tc analyses of the other biota samples (Table 2). The contents of ^{99}Tc were below the detection limit in all the *Myriophyllum, Macoma baltica, Mytilus edulis* and *Saduria entomon* samples analysed, although the *Fucus* samples from the same sampling points showed detectable amounts of ^{99}Tc.

In addition to ^{99}Tc, the samples were analysed for gamma-emitting radionuclides. The activity concentrations of ^{137}Cs in the *Fucus* samples ranged from 32 to 88 Bq kg^{-1} dry wt. Both the maximum and minimum values occurred in the Southwestern Archipelago. In general, the ^{137}Cs concentrations have become more uniform since our previous survey in 1995, except in the Åland Islands, where the average activity concentration (62 Bq kg^{-1} dry wt.) was still higher than elsewhere. The decrease in ^{137}Cs concentrations in *Fucus* has slowed down in the 1990s. Small amounts of ^{60}Co originating from the Olkiluoto nuclear power plant were observed at 4 stations on the west coast of Finland, and traces of ^{60}Co originating from the Forsmark nuclear power plant in Sweden were observed at 1 station in the Åland Islands. In addition, small amounts of hospital-derived ^{131}I were detected at 2 stations near by the city of Helsinki.

Acknowledgements: This work was financially supported by Nordic Nuclear Safety Research (NKS).

References

Aarkrog A., Dahlgaard H., Hallstadius L., Holm E., Mattsson S. & Rioseco J. 1986. Time trend of ^{99}Tc in Seaweed from Greenland Waters. In: Desmet G. & Myttenaere C. (ed.), *Technetium in the environment*. Elsevier Appl. Sci. Publ., pp. 69–78.

Aarkrog A., Carlsson L., Chen Q.J., Dahlgaard H., Holm E., Huynh-Ngoc L., Jensen L.H., Nielsen S.P. & Nies H. 1988. Origin of technetium-99 and its use as a marine tracer. *Nature* 335: 338–340.

Brown J., Kolstad A.K., Lind B., Rudjord A.L. & Strand P. 1998. Technetium-99 Contamination in the North Sea and in Norwegian Coastal Areas 1996 and 1997. *Strålevern Rapport* 1998(3): 1–17.

Holm E., Rioseco J., Mattsson S. 1986. Technetium-99 in the Baltic Sea. In: Desmet G. & Myttenaere C. (ed.), *Technetium in the environment*. Elsevier Appl. Sci. Publ., pp. 61–68.

Ikäheimonen T.K., Vartti V-P., Ilus E. & Mattila J. 2002. Technetium-99 in *Fucus* and seawater samples in the Finnish coastal area of the Baltic Sea, 1999. *Journal of Radioanalytical and Nuclear Chemistry* 252: 309–313.

Ilus E. & Ilus T. 2000. Sources of radioactivity. In: Nielsen S.P. (ed.), *The radiological exposure of the population of the European Community to radioactivity in the Baltic Sea, Marina-Balt project*. Radiation Protection 110, EUR 19200 EN, European Communities, Luxembourg, pp. 9–76.

Ilus E., Klemola S., Sjöblom K.-L. & Ikäheimonen T.K. 1988. Radioactivity of *Fucus vesiculosus* along the Finnish coast in 1987. *Report STUK-A*83: 1–36.

Received 16 January 2001, accepted 10 May 2002