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MARINE GRADIENTS OF HALOGENS IN MOSS STUDIED BY EPITHERMAL NEUTRON ACTIVATION ANALYSIS

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Introduction

It has been known for a long time that the ocean is a source of halogens (Cl, Br, I) to the terrestrial environment.[1] However, gradient studies of the supply of halogens to the terrestrial environment have been unsystematic and incomplete. A main reason for that is probably the lack of appropriate analytical methods by which these elements can be determined with satisfactory sensitivity and accuracy in environmental samples.

To elucidate marine gradients of these elements, a transect study in Northern Norway was undertaken using the feather moss *Hylocomium splendens* and of organic-rich natural humus layer surface soil (transects 1 and 2) collected at distances of 0-300 km from the coastline. The results for soils from the same transects have been discussed elsewhere,[2] and are shown here just for comparison with the moss data. Epithermal neutron activation analysis (ENAA) was chosen for the simultaneous determination of chlorine, bromine and iodine in samples from these transects. This technique has already been widely used for the analysis of moss and soil samples in Russia.[3-5]

Epithermal activation offers an advantage when elements with a high quotient of resonance activation integral to thermal neutron activation cross-section ($Q_0=I_0/\sigma_0$) are to be determined in a matrix where the elements responsible for major interfering activities have isotopes with significantly lower ratios. The Q values for the halogen radioisotopes in question and some interfering nuclides are given in Table 1. It is readily seen that the determination of Br and I can be considerably improved in most environmental samples by (ENAA), as demonstrated in this paper for mosses. The feasibility for Cl determination is about the same in this case as when thermal neutrons are used for activation.[2]

Table 1. Nuclear data relevant to the present paper

Radionuclide	$T_{1/2}$	Q [4]	Major γ-rays, keV
^{38}Cl	37.2 min	0.69	1642, 2167
^{80}Br	17.7	13.2	618
^{82}Br	35.3 h	19.3	554, 776
^{128}I	25.0 min	24.8	443
^{24}Na	15.0 h	0.59	1368, 2754
^{28}Al	2.24 min	0.71	1779
^{56}Mn	2.58 h	1.05	846, 1811, 2113

In order to extend this gradient study for mosses, data from previous nationwide deposition surveys in Norway in 1977[6] and 1985,[7] employing thermal neutron activation of moss samples, were used in the present paper to produce similar marine gradients for Br and I at more southerly latitudes (transects 3–6).

Experimental

Sampling

The network of sampling sites is shown in Fig. 1.

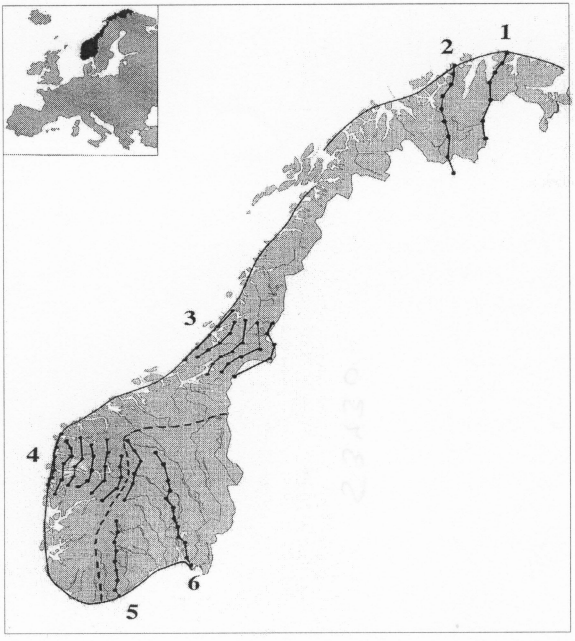

Figure 1. Moss and soil transects in Norway

Samples of moss and natural surface soil were collected in 1995 at forest and heath-land sites along coast-inland transects 1 and 2 perpendicular to the coastline in Finnmark, Northern Norway. Transects 3-6 in the middle and southern part of Norway were based on data from the nationwide moss surveys in 1977 and 1985, using arithmetic means of values from the same sites in the two years. In the case of Transects 3 and 4 lines parallel to the coast were drawn through 4-5 sites, and mean values from all these sites were averaged in order to improve the statistics.

Sampling of the moss in 1995 along transects 1 and 2 was carried out according to a procedure described elsewhere.[8] The length of the transects as the crow flies were respectively 245 km and 305 km. The number of sampling sites along each of the two gradients was 7 and 9, respectively. At each site 5–10 sub-samples were taken within a 50x50 m area and these were combined in the field. The unwashed samples were air-dried at 30 °C and extraneous plant material was removed. The last three years' growth segments of each *Hylocomium* plant were taken for the analysis. No further homogenisation of the samples was performed. Disposal polythene gloves were used during all handling of samples.

Soil samples were collected using a corer with 10 cm internal diameter, and the upper 0–3 cm or 0–4 cm of the humus layer was taken for analysis after cutting surface vegetation and removing loose litter. The sampling sites for moss and soil were selected where the soil was a podzol with a well developed organic surface layer.

Analysis

The 1995 samples were subjected to ENAA in the IBR-2 reactor at Dubna, which is characterised by a high epithermal-to-thermal neutron flux ratio. A cadmium-lined irradiation position in the reactor was used. After a 3 min irradiation and 20 min delay the activities of ^{38}Cl, ^{80}Br, and ^{128}I were recorded by γ-spectrometry using respectively the 2167, 618, and 443-keV lines. Further details on irradiation and counting facilities are given elsewhere.[9]

Quality assurance

The analytical quality was checked against international reference samples.[10] The halogen concentrations in three moss samples from the 1977 Norwegian moss survey[6] analysed in 1978 by conventional NAA are compared in Table 2 with ENAA values from Dubna.

Table 2. Halogen concentration in moss samples from the 1977 survey (μg/g) obtained by conventional NAA in Norway and by ENAA in Russia. Counting error (%) in parentheses

Moss sample No.	Cl (NAA)	Cl (ENAA)	Br (NAA)	Br (ENAA)	I (NAA)	I (ENAA)
454-77	110	145 (15)	4.2	4.3 (15)	1.4	1.7 (12)
456-77	70	104 (15)	3.1	3.6 (15)	2.4	2.0 (10)
476-77	190	172 (15)	6.1	5.8 (15)	2.4	2.7 (12)

An important conclusion from this comparison is that that in spite of over 10 years of storage of the moss samples the halogen contents did not change within error estimations (10–12% for I and 15% for Cl and Br). This means that moss samples stored for a long time at room temperature may still have retained their halogen contents.

Results and discussion

The concentrations of Cl, Br and I in moss samples as a function of a distance from the coastline are shown for all transects in Fig. 2. Parameters of an exponential trendline for Cl, Br, and I concentrations in moss versus distance to the coastline are given in Table 3. The close to exponential shapes of the transects indicate that the marine environment is the only significant source, at least within the first 300 km from the coastline.

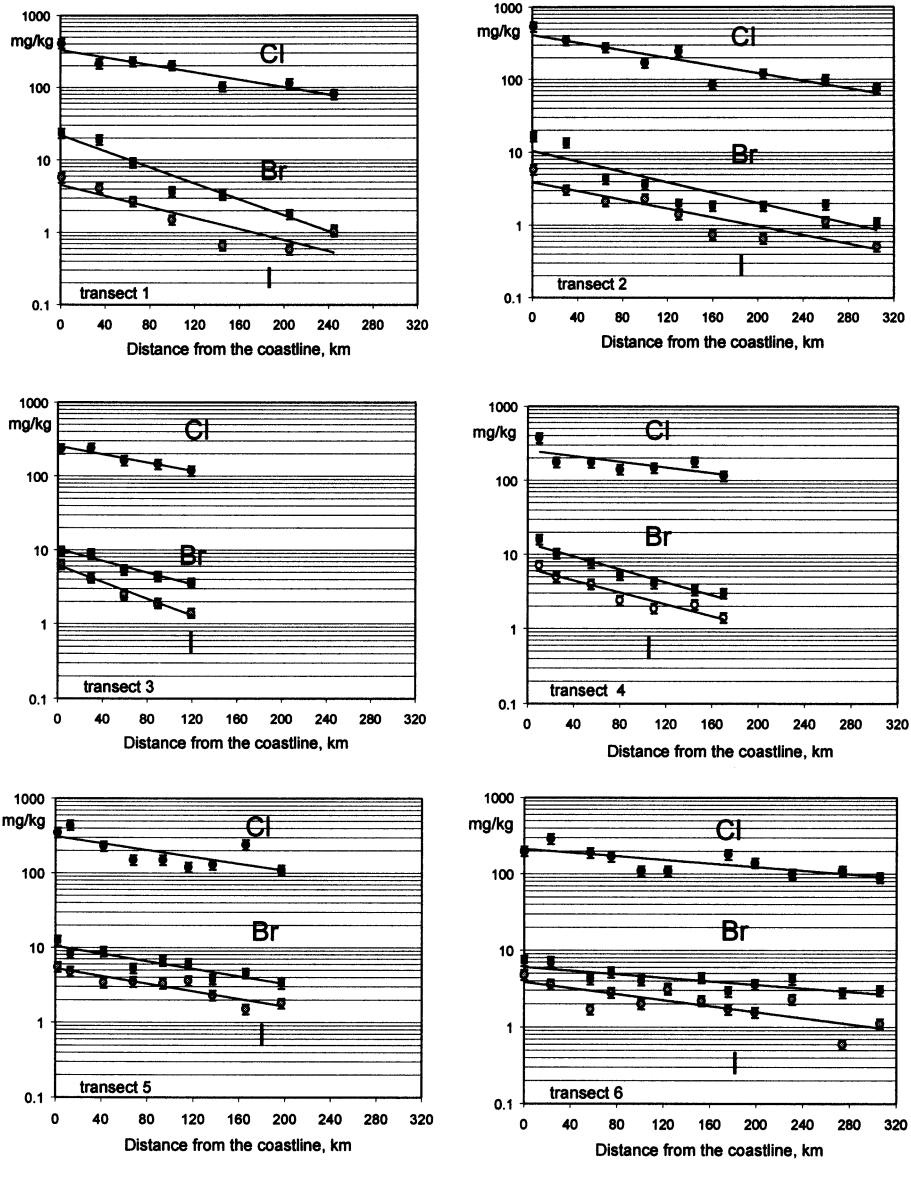

Figure 2. Concentration of Cl, Br, and I in the moss in transects 1-6

Table 3. Parameters of an exponential trendline for Cl, Br, and I concentrations in moss versus distance to the coastline

Intercept			
Transect No.	**Cl**	**Br**	**I**
1	331	21.8	4.5
2	412	10.4	4.0
3	255	10.3	6.2
4	252	14.0	6.4
5	311	10.4	5.3
6	214	6.0	3.8
Slope			
Transect No.	**Cl**	**Br**	**I**
1	-0.0060	-0.0127	-0.0088
2	-0.0061	-0.0081	-0.0069
3	-0.0064	-0.0091	-0.0131
4	-0.0044	-0.0101	-0.0093
5	-0.0053	-0.0058	-0.0059
6	-0.0028	-0.0027	-0.0045

The intercept with the *y*-axis, representing the extrapolated value for moss at the coastline, is relatively similar for all three elements in transects 1–5, about 300 μg/g Cl, 11 μg/g Br, and 5 μg/g I. Exceptions are Br in transect 1 and Cl in transect 2 which are appreciably higher than the general level, the reasons for which are not known. Transect 6, which starts in an area generally less exposed to strong winds than is generally the case along the coast of Norway, shows coastal halogen values of the order of 30% less than the general level.

The slopes of the exponential curve expresses the decline of halogen concentration as a function of distance along the transect. Here the decline of Cl is slower than that of Br and I, which show similar values. The most likely explanation of this difference seems to be that Cl is weaker bound to the moss surface than Br and I. The exact speciation of the halogens in the wet and dry deposition reaching the moss surface is not known. It may be fairly safe however to assume that the Cl deposition is mainly as the chloride anion, either dissolved in precipitation or in seasalt aerosols that will eventually dissolve. If the moss surface acts similar to synthetic anion exchangers the doubly charged sulphate anion, also present in high concentration in sea water, will be significantly stronger bound than the singly charged chloride and hence compete effectively for the positive charges. At distances far from the sea where the total marine deposition is low this exchange of chloride will occur at a much lower rate. It is assumed that Br and I are supplied in forms more strongly bound to the moss than chloride.

It is also noticed from Table 3 that the decline of all three elements with distance from the ocean is slower along the two southern transects than in the west and north. This is particularly the case for Transect 6 where the slopes are less than one half of the average values. This difference may be explained taking into account differences in

topography. In the north and west the increase in altitude with distance from the coastline is much steeper than inn the south-east. The associated orographic precipitation is likely to remove most of the substances derived from the marine environment before they reach far inland. In the south-east, and particularly along Transect 6, the landscape is relatively flat, and the orographic effect presumably less important.

In order to show a true atmospheric deposition gradient the concentration in moss must be calibrated against the bulk deposition, e.g. as measured by an open precipitation collector, and the ratio must be constant over the whole gradient. Such calibrations have been done for a number of other elements,[11] but to the knowledge of the authors not for halogens. The transects shown in this paper therefore do not necessarily reflect the true rate of decreased deposition of the halogens as a function of distance to the ocean.

In Fig. 3 Cl/Br and Br/I ratios as a function of distance from the ocean are shown for mosses and soils from transects 1 and 2 together. In both cases the trends are different.

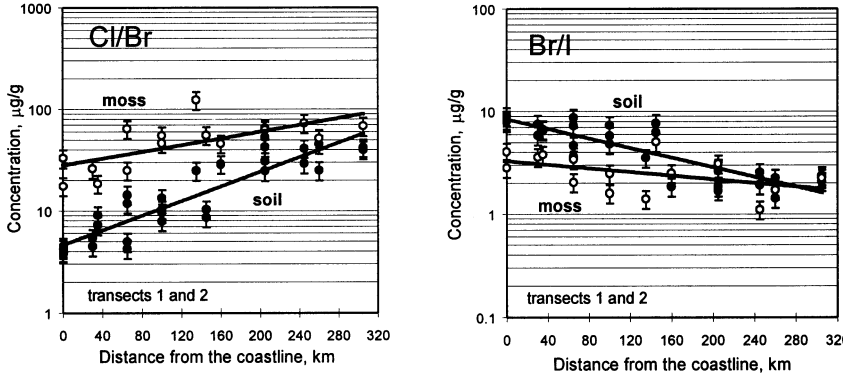

Figure 3. Ratios between halogens in moss and soil along the transects 1 and 2

The Cl/Br ratio is much higher in moss than in soil at the coast, but the curves tend to converge at large distances from the ocean. The time factor is probably important here. The surface soil at the coast is probably nearly saturated with sulphate from marine deposition over a long time, offering very limited binding capacity for chloride, whereas the shorter-lived moss is less saturated. The Br/I ratio is appreciably higher in the soil at the coast, whereas the ratio is similar for soil and moss at distances of 250 km or more. Reasons for this different behaviour in soil and moss are not known. Even in the soil at 250-300 km distance from the ocean most of the Br and I in the organic surface soil is probably of marine origin.[2]

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Изучение морских градиентов галогенов во мхах
с помощью эпитеплового нейтронного активационного анализа

Эпитепловой нейтронный активационный анализ является хорошим аналитическим методом для одновременного определения хлора, брома и йода в объектах окружающей среды. В настоящей работе этот метод применен для изучения градиентов этих элементов морского происхождения на примерах изучения трансектов в северной Норвегии, где образцы мха *Hylocomium splendens* были собраны на расстоянии 0–300 км от побережья. Концентрация всех трех элементов в образцах мха падает экспоненциально, как функция расстояния от океана, явно свидетельствуя о том, что основным источником этих элементов является морская атмосфера. Эти результаты сравниваются с аналогичными данными для образцов поверхностных почв, собранных вдоль тех же градиентов. Также проводится сравнение с данными, полученными ранее с помощью обычного нейтронного активационного анализа мхов, собранных аналогичным образом в других географических районах Норвегии. Было установлено, что наклон экспоненциальных кривых менее выражен для всех трех элементов в юго-восточной части Норвегии, чем в северной и западной, возможно, из-за топографических различий. Дается объяснение изменению отношения Cl/Br и Br/I в образцах мха в зависимости от расстояния от океана для всех трансектов.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ.

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Marine Gradients of Halogens in Moss Studied
by Epithermal Neutron Activation Analysis

Epithermal neutron activation analysis is known to be a powerful technique for the simultaneous study of chlorine, bromine and iodine in environmental samples. In this paper it is shown to be useful to elucidate marine gradients of these elements. Examples are from a transect study in northern Norway where samples of the feather moss *Hylocomium splendens* were collected at distances 0–300 km from the coastline. All three elements decreased exponentially as a function of distance from the ocean in the moss samples, strongly indicating that atmospheric supply from the marine environment is the predominant source of these elements to the terrestrial ecosystem. These results are compared with similar data for surface soils along the same gradients. Comparison is also made with previous data for halogens in moss in Norway obtained by conventional NAA and covering similar transects in other geographical regions. The Cl/Br and Br/I ratios in moss showed a regular change distance from the ocean in all transects, and hypotheses for this behaviour are presented.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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