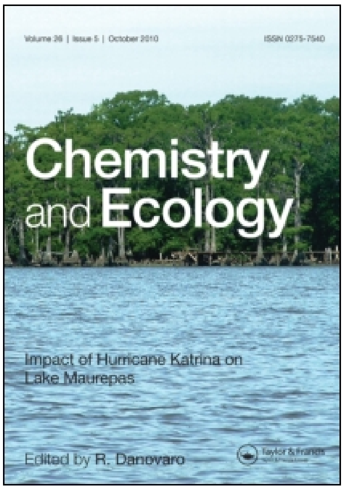

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

The Existence and Removal of Evaporable ^{137}Cs-Containing Compound(S) From the Extract of Lichen *Cetraria Islandica*

O. Nedič[a]; A. Stankovič[a]; S. Stankovič[a]
[a] INEP - Institute for the Application of Nuclear Energy, Zemun, Yugoslavia

To cite this Article Nedič, O. , Stankovič, A. and Stankovič, S.(1998) 'The Existence and Removal of Evaporable ^{137}Cs-Containing Compound(S) From the Extract of Lichen *Cetraria Islandica*', Chemistry and Ecology, 14: 2, 143 — 149
To link to this Article: DOI: 10.1080/02757549808035549
URL: http://dx.doi.org/10.1080/02757549808035549

Chemistry and Ecology, 1998, Vol. 14, pp. 143–149
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published under license
under the Gordon and Breach Science
Publishers imprint.
Printed in India.

THE EXISTENCE AND REMOVAL OF EVAPORABLE ^{137}CS-CONTAINING COMPOUND(S) FROM THE EXTRACT OF LICHEN *CETRARIA ISLANDICA*

O. NEDIĆ*, A. STANKOVIĆ and S. STANKOVIĆ

INEP – Institute for the Application of Nuclear Energy,
Banatska 31b, 11080 Zemun, Yugoslavia

(Received 11 August 1997; In final form 10 December 1997)

The aim of the work described here was to investigate the existence of evaporable ^{137}Cs-containing compound(s) in lichen and to suggest a possible way of dealing with a phenomenon during lichen exploitation. A sample of lichen, *Cetraria islandica*, was submitted to aqueous extraction and the extract was monitored to be ^{137}Cs-radioactive. It was heated according to the experimental schedule and the resulting vapour passed over a layer of activated charcoal. By measuring the decrease in the radioactivity content of the lichen extract after heating and the radioactivity of the adsorbent it was found that a significant amount of the extracted ^{137}Cs could be evaporated and bound to the charcoal adsorbent (40.6%). If not captured, this radiocaesium may lead to air pollution, especially of immediate breathing space.

Keywords: ^{137}Caesium; lichen; evaporation; adsorption; activated charcoal

INTRODUCTION

Lichens are known to be natural collectors of artificially produced pollutants (Grass *et al.*, 1994; Coppins and van den Boom, 1995; Ford *et al.*, 1995), and as such are recognized as reliable monitors of the extent of environmental pollution (Caniglia *et al.*, 1994; Brakenhielm and Qinghong, 1995; Sloof, 1995). They are used as a source of natural products in nutritional and pharmaceutical industry and the presence of hazardous compounds could present human health concerns to

---

*Corresponding author.

those processing or using the product. *Cladonia*, *Usnea* and *Cetraria* lichens are recognized to have antibiotic and laxative features. Usnic acid (from *Usnea barbata*) is incorporated into pharmaceutical products used for the treatment of external inflammatory processes and surface injuries. Aqueous extract of *Cetraria islandica*, due to its high content of mucous substances, established itself as an expectorant in treating cough, bronchitis and asthma. Aromatic compounds of *Evernia prunastri* and *Pseudoevernia furfuracea* are incorporated in soaps, perfumes and after-shave lotions. *C. islandica* is a source of special bread flour as well as initial material in alcohol fermentation. *Umbilicaria muhlenbergii* is used in soup and salad preparations (Tucakov, 1990; Richardson, 1991). The application of lichens in foods and medicines is very wide. According to their chemical nature, lichen substances are isolated in aqueous or organic solvents employing various physicochemical procedures, some of which include heating (Gorshkova *et al.*, 1997). Depending on the structure of compounds and technological process (type of solvent or method) certain pollutants could be avoided in specific preparations.

Lichens have a very high efficiency for the retention of fallout ^{137}caesium. Both ^{137}Cs and ^{134}Cs, gamma-emitting radionuclides originating from the Chernobyl accident in 1986, accumulated to a very high degree in lichens (Strandberg, 1994; Nifontonova, 1995). Due to its relatively short half-life of 2.1 years, ^{134}Cs is no longer present in a significant quantity in contrast to ^{137}Cs, which has a half-life of 30.2 years (Commissariat a l'Energie Atomique, 1988). ^{137}Cs content in *Cladonia-Cetraria* lichens from Finland, the United States and the Soviet Union collected during 1960–1970, ranged between 407 and 2368 $\mathrm{Bq kg^{-1}}$ dry weight (Tuominen and Jaakkola, 1973). In our laboratory, on the other hand, it was found that mean ^{137}Cs-radioactivity value for twenty samples of the same lichen species collected in different parts of Yugoslavia in 1987 was 10392 $\mathrm{Bq kg^{-1}}$ dry weight for *C. islandica* and 13610 $\mathrm{Bq kg^{-1}}$ for *E. prunastri* (Stanković *et al.*, 1991).

Our previous work has demonstrated that lichen extracts prepared in organic solvents are much less ^{137}Cs-contaminated than aqueous extracts (Nedić *et al.*, 1995) and it is to be expected that lichen compounds that are isolated in organic solvents are, in general, weakly contaminated with ^{137}Cs, if they are contaminated at all (to incorporate caesium specific functional groups are needed). Radioactivities of aqueous extracts were considerable. It was noticed that ^{137}Cs-radioactivity of aqueous solutions decreased upon heating; i.e., the initial activity of starting material was always greater than the total sum of all isolated products. The aim of this work was to investigate the extent to which the existence of evaporable ^{137}Cs in the extract could explain this discrepancy, and whether activated charcoal could be used as an adsorber to reduce the release of this contaminant to the local atmosphere. The lichen, *C. islandica*, served as a model system.

MATERIALS AND METHODS

Radioactivity measurements were carried out on a gamma-spectrometer Canberra-Ortec (8192 channels). The resolution was 6.8% and the energy used for determining ^{137}Cs was 661.6 keV. The window width was 0.05 cm and the efficiency of counting was 8.7%. Measuring period was one hour and the error of the method was at most 10%. Radioactivity changes were traced by ^{137}Cs measurements on the lichen, extract (before and after each heating step), activated charcoal, filter paper and beaker.

A sample of the lichen *C. islandica* (50.0 g) was thoroughly ground and soaked in distilled water (1000 ml) in a glass beaker. The mixture was stirred with a magnet for 2 h at room temperature and then for 48 h at 4°C. After the extraction phase, the lichen was separated from the solution; first by filtration and then by centrifugation. The remaining lichen material was allowed to dry in the air.

In the first experiment the adsorptive capacity of activated charcoal was determined. The extract (850 ml) in a beaker was put in a water bath at 70°C and tightly covered with a specially constructed sponge made of activated charcoal (10.0 g; Sigma Chemical Company) in filter paper (adsorbent fitted on a beaker like a lid). The temperature of 70°C was chosen as to avoid boiling and direct contact between liquid and adsorbent. The extract was allowed to evaporate for 2 h after which the activated charcoal was removed and air-dried. The same procedure was carried out with a new extract for the evaporation periods of 4 h and 6 h.

In a second experiment the total amount of ^{137}Cs-containing compound(s) that could evaporate was determined. While heating the fresh extract (850 ml), several charcoal sponges (10.0 g each) were changed successively. Each adsorbent was allowed to collect ^{137}Cs-substances until saturation. New adsorbent portions were used as many times as it was needed to exhaust evaporable ^{137}Cs from the extract.

RESULTS

Measurements demonstrated that ^{137}Cs-containing compound(s) originating from the *C. islandica* extract were adsorbed by the activated charcoal. The radioactivities of the glass beaker and filter paper before and after the experiment were practically the same (at background level, the difference could not be estimated accurately).

A heating period of 4 h was necessary and sufficient to saturate the adsorbent, under the described conditions (see Tab. I). The radioactivity gained by activated charcoal after 6 h heating was only 4.5% greater than after 4 h heating. For the second experiment time interval of 4 h was used to collect ^{137}Cs-containing substances with each charcoal portion. The results monitoring changes in the radioactivity of the lichen *C. islandica* after extraction as well as the changes exhibited by the extract and activated charcoal upon evaporation are presented in Table II.

The radioactivity of the lichen decreased by 26.3% upon extraction and the radioactivity of the extract decreased by 40.6% upon evaporation. The sum of the radioactivities of five charcoal portions was 106.3% of the radioactivity lost from the aqueous lichen extract

TABLE I Adsorption of ^{137}Cs-containing compounds from the extract of lichen *C. islandica* on to activated charcoal upon evaporation

	Initial radioactivity (*Bq*)	*Final radioactivity* (*Bq*)	*Radioactivity change* (*Bq*)
Activated charcoal 1 (2 h evaporation)	88	111	23
Activated charcoal 2 (4 h evaporation)	88	154	66
Activated charcoal 3 (6 h evaporation)	88	157	69

TABLE II Radioactivity changes in the lichen *C. islandica*, aqueous extract and charcoal adsorbent upon evaporation

	Initial radioactivity (Bq)	*Final radioactivity (Bq)*	*Radioactivity change (Bq)*
Lichen	2056	1515	541
Extract	547	325	222
Activated charcoal 1	88	155	67
Activated charcoal 2	88	153	65
Activated charcoal 3	88	154	66
Activated charcoal 4	88	120	32
Activated charcoal 5	88	94	6

indicating that, within measurement error, the whole "evaporable" ^{137}Cs-radioactivity was captured by the activated charcoal.

The adsorption capacities of the first three sponges could be interpreted as 66 Bq on average (6.6 $\mathrm{Bqg^{-1}}$ activated charcoal). The fourth sponge adsorbed less ^{137}Cs, displaying only 32 Bq (3.2 $\mathrm{Bqg^{-1}}$). The adsorption on the last sponge was 6 Bq and as such within error limits (9.1% of the maximum adsorption capacity). The evaporation of caesium seems to be a function of its concentration in the extract.

DISCUSSION

Caesium is usually determined in a soluble form in liquid systems employing ion exchangers that selectively bind caesium ions (Gaur, 1996). Most of the caesium compounds that have been studied up-to-date evaporate at very high temperatures (above 400°C) due to their inorganic nature (Žilkina *et al.*, 1973). The results obtained in this work showed that the lichen *C. islandica* contains one or more compounds that incorporate caesium and are evaporable upon heating at 70°C. The conditions chosen for this experiment were such as to imitate the conditions usually employed in sample concentration (vacuum evaporation in a water bath). By measuring the radioactivity of the glassware and filter paper it was possible to exclude any other adsorption proceses during the experiment.

The lichen *C. islandica* was used as a demonstration example, but many of the lichen species that we have examined after the Chernobyl accident were and still are considerably radioactive: *Cladonia fimbriata*

(L.) Fr., *Usnea barbata*, *Evernia prunastri*, *Lobaria pulmonaria*, *Hypogimnia physodes* (Stanković and Stanković, 1995). As they are continually used in food and pharmaceutical industry, it is important to determine a degree of ^{137}Cs-contamination and to choose appropriate technological procedure for the exploitation. When an open system is used workers are directly exposed to contamination by inhalation and skin deposition. Closed systems like laboratory plants working under vacuum conditions shelter laboratory workers to a certain extent but overall contamination is not avoided. The results presented here suggest that if lichens are ^{137}Cs-contaminated, aqueous extracts should not be consumed directly, and if they are used for isolation of specific compounds (some of which may not be radioactive) heating should be avoided or at least secured with an appropriate vapour adsorbent.

References

Brakenhielm, S. and Qinghong, L. (1995) Spatial and temporal variability of algal and lichen epiphytes on trees in relation to pollutant deposition in Sweden. *Water, Air and Soil Pollution*, **79**, 61–74.

Caniglia, G., Calliari, I., Celin, I. and Tollardo, A. M. (1994) Metal determination by EDXRF in lichens – a contribution to pollutants monitoring. *Biological Trace Element Research*, **43–45**, 213–221.

Commissariat a l'Energie Atomique (1988) *Etalons de Radioactivité*. Oris, Damri. Catalogue, pp. 53–81.

Coppins, B. J. and van den Boom, P. P. G. (1995) *Micarea confusa:* a new species from zinc-and cadmium-contaminated sites in Belgium and the Netherlands. *Lichenologist*, **27**, 81–90.

Ford, J., Landers, D., Kugler, D., Lasorsa, B., Allen-Gil, S., Crecelius, E. and Martinson, J. (1995) Inorganic contaminants in Arctic Alaskan ecosystems: long-range atmospheric transport or local point sources? *The Science of the Total Environement*, **160–161**, 323–335.

Gaur, S. (1996) Determination of Cs-137 in environmental water by ion-exchange chromatography. *Journal of Chromatography A*, **733**, 57–71.

Gorshkova, R. P., Nazarenko, E. L., Zubkov, V. A., Stepanenko, L. S. and Isakov, V. V. (1997) Structural study of polysaccharides from *Cetraria cucullata* and *Cetraria islandica* lichens. *Bioorganic Chemistry* (*Russia*), **23**, 134–138.

Grass, F., Bichler, M., Dorner, J., Holzner, H., Ritschel, A., Ramadan, A., Westphal, G. P. and Gwozdz, R. (1994) Application of short-lived radionuclides in neutron activation analysis of biological and environmental samples. *Biological Trace Element Research*, **43–45**, 33–46.

Nedić, O., Stanković, A., Stanković, S. and Krainčanić, M. (1995) Chemical localization of ^{137}Cs in the lichen *Cetraria islandica*. *Archives of Environmental Contamination and Toxicology*, **29**, 380–383.

Nifontonova, M. (1995) Radionuclides in the moss lichen cover of tundra communities in the Yamal Peninsula. *The Science of the Total Environment*, **161**, 749–752.

Richardson, D. H. S. (1991) Lichens and man. In *Frontiers in Mycology*. Ed. by D. L. Hawksworth, C. A. B. International, Regensburg, pp. 187–210.

Sloof, J. E. (1995) Lichens as quantitative biomonitors for atmospheric trace-element deposition, using transplants. *Atmospheric Environment*, **29**, 11–20.

Stanković, S., Krainčanić, M. and Stanković, A. (1991) Radioactive caesium 134 and 137 in lichen samples inside the period 1986–1990. *Proceedings of the XVI Yugoslavian Symposium on Radiation Protection*, Neum, pp. 119–123.

Stanković, S. and Stanković, A. (1995) Contamination of unimproved ecosystems by caesium-137, 134. *Ecologica*, **2**, 16–19.

Strandberg, M. (1994) Radiocaesium in a Danish pine forest ecosystem. *The Science of the Total Environment*, **157**, 125–132.

Tucakov, J. (1990) *Treatment with Plants*, Rad, Belgrade, pp. 357–358.

Tuominen, Y. and Jaakkala, T. (1973) Absorption and accumulation of mineral elements and radioactive nuclides. In *The Lichens*. Eds. by V. Ahmadjian and M. E. Hale, Academic Press, New York, pp. 185–223.

Žilkina, M. I., Gedeonov, L. I., Gritchenko, Z. G. and Flegontov, V. M. (1973) The most frequent forms of ^{90}Sr and ^{137}Cs found in atmospheric deposits and global radioactive fallout. *Radiochemistry (Russia)*, **15**, 576–58.