

Potential of lichens for monitoring iodine-129 and chlorine-36

O. R. Daillant · A. Bernollin · M. Josset ·
K. L. Fifield

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Abstract Chlorine-36 (half life 3.01×10^5 year), a beta emitter, is produced naturally but its presence has been enhanced by atmospheric weapons testing and other nuclear activities. Iodine-129 has a half life of 1.57×10^7 years and is also produced by nuclear activities, in particular fuel reprocessing. Many elements have a long biological half-life in lichens, which were thus investigated so as to assess their suitability for ^{36}Cl and ^{129}I monitoring. Lichens sampled between 1998 and 2008 were analysed for total chlorine, and selected samples were processed for ^{36}Cl measurement using Accelerator Mass Spectrometry (AMS); ^{129}I was analyzed by gamma spectrometry. Different aspects are discussed: long-term storage in lichens versus environmental mobility, levels in samples collected near a reprocessing facility, and potential for spatial and temporal monitoring.

Keywords Biomonitoring · Lichens · Chlorine 36 ·
Iodine 129

Introduction

Lichens are widely used to monitor trace elements; after deposition, these elements are trapped either intracellularly

or extracellularly with quite long residence times. Half lives for lead or caesium for example are in the range of 1–3 years [1]. Lichens have also been used more recently to monitor the presence of tritium and radiocarbon near nuclear facilities [2]: these elements are taken up via photosynthesis of tritiated water and $^{14}\text{CO}_2$. The organically bound (i.e. non exchangeable fraction) then remains in the lichen with long residence times as well.

Some authors have investigated the comparative suitability of tree barks [3] and lichens [4] for biomonitoring of different elements, in particular sea related Cl. Lichens have also recently been used to follow deposition of toxic chlorinated molecules [5]; however, papers on bio-accumulation of the radioactive isotopes of the halogen elements, chlorine and iodine are rare. Research has been done on the presence of these elements in three regions around Chernobyl [6], and results are compared with those of the present study. Difficulties arise from the fact that these elements, being mobile in the environment, may still be mobile once they are present in the lichen thallus. Many lichens have chlorinated lichen substances. Examples can be found in Elix [7], and in a review by Huneck [8]. Lichens actually produce many chlorinated compounds, some 50 to 100 (Elix J.A. personal communication 2008.). These can be metabolized from deposition of salts, and it is not clear to what extent this process is reversible.

Chlorine-36 has a half life of 3×10^5 years. It is produced naturally in the atmosphere by cosmic-ray induced disintegration of argon nuclei and falls out on the earth's surface in rainfall at a rate $\sim 20 \text{ ats/m}^2/\text{s}$. During the nuclear testing era, atmospheric levels of ^{36}Cl peaked in 1958 in the northern hemisphere at a thousand times the natural level [9]. Since sea-spray is the dominant source of chloride in the atmosphere, natural $^{36}\text{Cl}/\text{Cl}$ ratios vary with distance from the coast, and range from 30 to 150×10^{-15} .

O. R. Daillant (✉)
Observatoire Mycologique, Néronde, 71250 Mazille, France
e-mail: olivier.daillant@skynet.be

A. Bernollin · M. Josset
Association pour le Contrôle de la Radioactivité dans l'Ouest,
138, Rue de l'Eglise, 14200 Hérouville Saint Clair, France

K. L. Fifield
Department of Nuclear Physics, School of Physical Sciences,
The Australian National University, Canberra, ACT 0200,
Australia

Between 1951 and 1953, this ratio reached a peak of $16600 \pm 5700 (\times 10^{-15})$.

Iodine-129 has a half life of 1.57×10^7 years. It is produced naturally in the spontaneous fission of ^{238}U , and released into the atmosphere through volcanoes. Natural $^{129}\text{I}/\text{I}$ ratios are $\sim 10^{-12}$. In the past 50 years, anthropogenic production of ^{129}I has introduced much larger amounts of ^{129}I into the environment. Nuclear testing increased the natural inventory of ^{129}I by 43 to 150 kg (0.28 to 0.98 TBq) [10]. The largest contribution to the man-made inventory has come from reprocessing, though. According to the Groupe Radioécologie Nord Cotentin and other authors [10], European reprocessing plants have released 3200 kg (23 TBq), with La Hague accounting for 70% of that value. In contrast, the Chernobyl accident discharged only 2 kg into the environment.

Experimental

Analyses were performed on lichens collected between 1998 and 2008 in two areas in France (Fig. 1a): around the Areva (formerly Cogema) reprocessing plant of La Hague in the Nord Cotentin (detailed map: Fig. 1b), and in the Burgundy region, in the center east of France, so as to have an area of reference far from a main source of emission. Sampling near the La Hague facilities was designed to investigate the influences of the main wind direction (south and west), distance from the source and distance from the seashore. Due to the different environments, species could not be the same in the two areas. In the La Hague area care was taken to sample lichens of the same genus (*Ramalina*) and in most cases of the same species (*Ramalina siliquosa*). In Burgundy, a wider range of species was collected, some growing on soil, some on rocks or bark, so as to investigate possible differences in their behaviour: *Cladonia dubia* (*C. dubia*), *Evernia prunastri*, *Hypogymnia physodes*, *Lasallia pustulata*, *Parmelia caperata* (*P. caperata*), *Parmelia sulcata* (*P. sulcata*) and *Xanthoria parietina*.

Chlorine was analysed by X-ray fluorescence and chlorides with ion chromatography (CSAAB, University of Dijon, France). For ^{36}Cl measurement, samples were prepared by grinding the lichens to a powder, leaching with MQ water, and precipitating chloride as AgCl . After purification to remove sulphur using the prescription of Conard et al. [11], $^{36}\text{Cl}/\text{Cl}$ ratios were measured by accelerator mass spectrometry (AMS) using the 14UD accelerator at the Australian National University, Canberra. Details of the AMS methodology are given in Fifield et al. [12].

Iodine 129 was analysed by gamma spectrometry at the ACRO Laboratory, using an N-type hyper-pure Ge detector with an efficiency of 32%. Although the energy line of ^{129}I

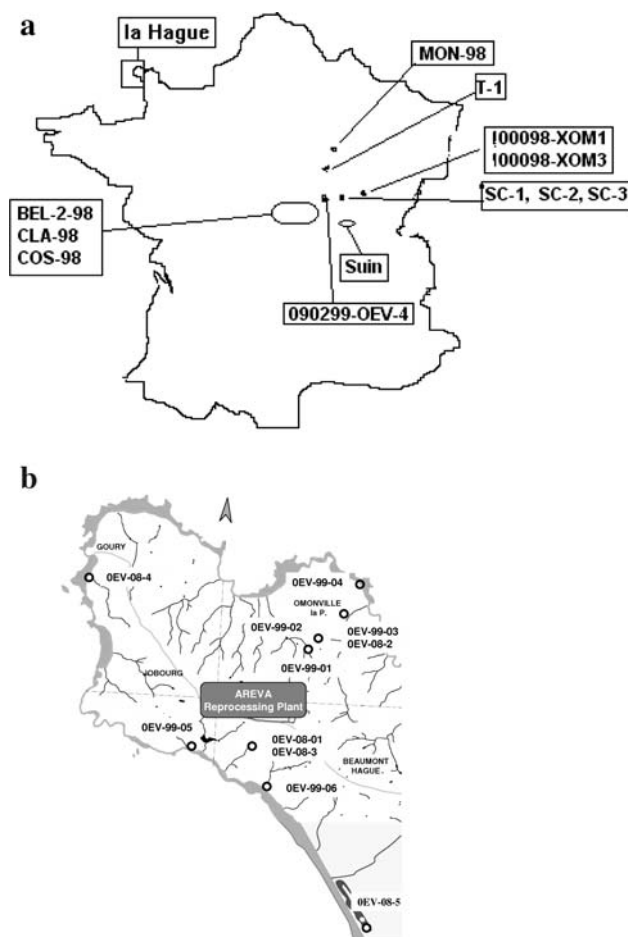


Fig. 1 a Map of France, with the different sampling areas; b detailed map of the La Hague area, with sampling points and emission site

is low, it is possible to detect it in samples around La Hague due to their comparatively high activity; the reliability of the results has been cross checked in intercomparative tests organised by the competent French authority (Institut de Radioprotection et de Sûreté Nucléaire, IRSN). Details with references to the Official Journal can be checked on the site of the laboratory (www.acro.eu.org/labo.html). Results are expressed as Bq/kg dry matter.

Results and discussion

Results are shown in Tables 1, 2, 3, 4, respectively for chlorine-36, total chlorine, chlorides and iodine-129. Total chlorine content in lichens is quite high and varied by one order of magnitude. Differences between species seemed to be more important than the location of sampling. The values are comparable to those reported by Chant et al. [6], for *P. sulcata*, which were in the range of 400–1000 mg/kg. The content of chloride ions varied even more, ranging from a low of 9.8 mg/kg for the terricolous lichen *C. dubia* to a

Table 1 Results for chlorine-36 expressed as ratio to total Cl and in absolute terms

Code	Origin	Sampling date	Lichen	³⁶ Cl/Cl × 10 ⁻¹⁵	Chlorine (mg/g)	10 ⁵ atoms ³⁶ Cl/g lichen
BEL 2-98	Nièvre, Burgundy	1998	<i>P. caperata</i>	96 ± 6	0.55	8.9 ± 0.5
CLA-98	Nièvre, Burgundy	1998	<i>P. sulcata</i>	132 ± 8	0.23	5.2 ± 0.3
COS-98	Nièvre, Burgundy	1998	<i>P. sulcata</i>	159 ± 10	0.23	6.2 ± 0.4
OEV-99-04	La Hague 4 km from source on seashore	1999	<i>R. siliquosa</i>	45 ± 3	1.00	7.7 ± 0.6
OEV-99-02	La Hague 2.5 km from source 2 km from seashore	1999	<i>R. siliquosa</i>	702 ± 27	0.29	34.6 ± 1.3

Table 2 Results for total chlorine in mg/kg dry mass

Code	Origin	Lichen	Total chlorine (mg/kg)
MON-98	Montbard, Burgundy	<i>Xanthoria parietina</i>	871
T-1	Saint Brisson, Morvan, Burgundy	<i>Parmelia sulcata</i>	2486
SC-1	Saint Clément, Burgundy	<i>Hypogymnia physodes</i>	1866
SC-2	Saint Clément, Burgundy	<i>Parmelia caperata</i>	586
SC-3	Saint Clément, Burgundy	<i>Evernia prunastri</i>	1866
BEL 2-98	Belleville, Nièvre, Burgundy	<i>Parmelia caperata</i>	550
CLA-98	Clamecy, Burgundy	<i>Parmelia sulcata</i>	230
COS-98	Cosne sur Loire, Burgundy	<i>Parmelia sulcata</i>	230
OEV-99-04	La Hague on seashore 4 km from source	<i>Ramalina siliquosa</i>	1000
OEV-99-02	La Hague 2.5 km from source 2 km from seashore	<i>Ramalina siliquosa</i>	290

Table 3 Chloride content of lichens sampled from the same spot on the same day; origin: Suin, Burgundy

Species	Growing on	Chloride (mg/kg)
<i>Parmelia caperata</i>	Rock	87.7
<i>Parmelia caperata</i>	Bark	235.0
<i>Parmelia sulcata</i>	Bark	37.7
<i>Evernia prunastri</i>	Bark	210.3
Soil	–	24.9
<i>Cladonia dubia</i>	Soil	9.8
<i>Hypogymnia physodes</i>	Bark	18.9
<i>Lasallia pustulata</i>	Rock	119.9

high of 235 mg/kg for *P. caperata*, although all the samples were collected on the same day at the same locality. The interspecific difference between total chlorine and chlorides may be attributed to the ratio of bound versus free chlorine, which in turn would depend on the metabolism of each species.

It was possible to spot quite clearly the emissions of the La Hague plant in the lichen sample closest to the plant: the

³⁶Cl concentration is a factor of five higher than the average of the other samples. Interestingly, the ³⁶Cl concentration in the second sample from the vicinity of the La Hague plant shows no evidence of a contribution from the plant, since it falls within the range of the Burgundy samples. The ³⁶Cl/Cl ratio, however, is substantially lower, presumably because the sample’s proximity to the coast results in a higher chlorine content. These data can be compared with former results for lichens in 3 areas around Chernobyl [6], for which the ³⁶Cl/Cl ratio ranged from 1.6 to 81.5 × 10⁻¹². The most contaminated lichen from La Hague has a ratio of 0.7 × 10⁻¹².

The situation is different for ¹²⁹I: it is below the detection limit in Burgundy but can clearly be detected around the La Hague reprocessing plant. Values range from 2.8 to 55 Bq/kg (average 17.8). The results for four sampling sites in a transect under the main wind directions (OEV-99-01 to OEV-99-04) show a coherent pattern of decreasing activity. Chant et al. [6]. report activities ranging from 6 to 79.5 mBq/kg with an average of 42 mBq/kg for the areas under investigation near Chernobyl, i.e. nearly 500 times less than in the La Hague area. This can be explained by the different conditions:

Table 4 Results for iodine-129 expressed in Bq/kg (dry matter)

	Origin	Sampling date	Lichen	Distance from source	Bq/kg
<i>La Hague area</i>					
OEV-99-01	Ferme Grand Bel	22-Feb-99	<i>Ramalina siliquosa</i>	1.5 km NE	55.0 ± 9
OEV-99-02	Diguleville	22-Feb-99	<i>Ramalina siliquosa</i>	2.5 km NE	23.0 ± 5
OEV-99-03	Omonville	22-Feb-99	<i>Ramalina siliquosa</i>	3.5 km NE	34.0 ± 8
OEV-99-04	Seashore	22-Feb-99	<i>Ramalina siliquosa</i>	4 km NE	8.4 ± 2.3
OEV-99-05	Lac Moulinets	22-Feb-99	<i>Ramalina siliquosa</i>	1.5 SW	4.8 ± 2.1
OEV-99-06	Herquemoulin	22-Feb-99	<i>Ramalina siliquosa</i>	2 S	3.5 ± 1.6
OEV-08-01	Herqueville	18-Jun-08	<i>Ramalina siliquosa</i>	1 km S	15.1 ± 2.7
OEV-08-2	Omonville	18-Jun-08	<i>Ramalina siliquosa</i>	3.5 km NE	2.8 ± 0.7
OEV-08-3	Herqueville	20-Aug-08	<i>Ramalina siliquosa</i>	1 km S	13.6 ± 2.3
OEV-08-4	Goury	20-Aug-08	<i>Ramalina siliquosa</i>	4.5 NW	<1
<i>Burgundy</i>					
100998-XOM-4	Suin, Burgundy	10-Sept-98	<i>Lasallia pustulata</i>		<3
100998-XOM-1	Chalon sur Saône	10-Sept-98	<i>Xanthoria parietina</i>		<12
100998-XOM-3	Chalon sur Saône	10-Sept-98	<i>Xanthoria parietina</i>		<10
100998-XOM-5	Suin, Burgundy	10-Sept-98	<i>Lasallia pustulata</i>		<4
090299-0EV-4	Gueugnon, Burgundy	02-Feb-99	<i>Parmelia sulcata</i>		<8

accidental release with long range transport in one case and continuous releases of much larger activities with more local deposition in the other. It could also suggest that residence time of iodine in lichens may be shorter than for many other elements: lichens analysed by Chant et al. [6] were gathered in 1990, i.e. 4 years after deposition.

Overall, the ^{129}I activity in lichens of the La Hague area seems to have decreased between 1999 and 2008, except that values in samples South and South West of the plant are higher in 2008 than they were in 1999. This could indicate a recent increase in releases, or a sea-to-land transfer. As increased levels of ^{137}Cs were also detected (not reported here) the first option seems more likely.

Conclusions

These preliminary results are promising as values are quite coherent with emission and deposition patterns. Data shows that contamination around La Hague is lower than in areas around Chernobyl by at least one order of magnitude for ^{36}Cl , and higher by at least two orders of magnitude for ^{129}I . Deposition patterns along a transect are very coherent suggesting the suitability of lichens for monitoring of ^{129}I . Residence time of deposited iodine should yet be investigated more closely so as to make lichens fully reliable. For ^{36}Cl , lichens should be used with additional care, as the distribution between chlorine salts and organic compounds is not yet fully investigated and obviously varies strongly between species. As a consequence species sampled should be the same, so as to allow for meaningful comparisons. As

many species store chlorine in organic molecules, this approach could nevertheless be fruitful. Making broader research on the behaviour of chlorine in lichens, along the lines suggested by Sheppard [13] for vascular plants will be an asset. It is interesting to investigate chlorine and iodine in parallel, as their presence is strongly influenced by the distance from the sea. As an example, chlorine measures would indicate whether ^{129}I activity in lichens originates from a direct release or from a sea to land transfer. A last point worth exploring would be the medium- and long-term follow up of the overall presence of ^{36}Cl and ^{129}I in the biosphere. Lichens are organisms that have low interaction with other compartments of the environment, once elements have been taken up and stored: they would be more reliable than soil or other biological samples for the follow up of global burden of ^{36}Cl and ^{129}I . This includes the very long term monitoring, beyond the horizon bioindication usually aims at.

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