# RELATIONSHIP BETWEEN FLUORIDE CONTENTS AND LOSS OF LICHENS NEAR AN ALUMINIUM WORKS

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(Received May 16, 1991; revised August 20, 1991)

**Abstract.** The relationship between F contents and damage to previously unpolluted saxicolous lichens (*Ramalina* sp) was examined in the vicinity of an Al works on the island of Anglesey, North Wales. Damage was greatest $<2$ km from the works, where 41% of *Ramalina* thalli showed $>50\%$ chlorosis and necrosis. Loss of lichens (measured by changes in percent cover in 58 permanent quadrats) decreased with increasing distance from the works. Lichens well-exposed to emissions had the largest F content and 20 to 30% more losses than those less-exposed. Well-exposed lichens had rates of loss of cover of 4.9% $km^{-1}$ $yr^{-1}$, whereas more sheltered thalli had losses of 3.7% $km^{-1}$ $yr^{-1}$. In contrast, relatively uncontaminated lichens increased in % cover. Content of F reflected both distance from the works and exposure to emissions; losses, and F content, were closely related ($r^2 = 0.90$). Lichens containing 300, 100 and 50 $\mu g$ F $g^{-1}$ dry weight lost 46, 15 and 10% of cover $yr^{-1}$, respectively.

## 1. Introduction

Lichens have been used increasingly as indicators of pollution and to monitor environmental change. Their virtual absence from heavily industrialized and urban areas has been known for over 100 yr and, of late, this has been attributed to $SO_2$ pollution (Hawksworth, 1971; Gilbert, 1973). More recently, the effects of acid rain have also been considered (Gilbert, 1986). Expansion of the Al industry in the 1960s drew attention to F emissions as having effects on lichens (Martin and Jacquard, 1968; Barkman, 1969). Since then, studies have observed the presence or absence of species near emission sources, and zones of damage have been mapped (Gilbert, 1971; LeBlanc *et al.*, 1972; Roberts and Thompson, 1980; Perkins and Millar, 1987a, b). While investigations of effects of S pollutants have relied upon ambient $SO_2$ measurements to develop scales of pollution (Hawksworth and Rose, 1970), determinations of the S content of lichens have been few (O'Hare, 1974; Olkkonen and Takala, 1975). Many determinations of F contents, however, have been made (Gilbert, 1971; LeBlanc *et al.*, 1971; Hällgren and Nyman, 1977; Takala *et al.*, 1978; Perkins *et al.*, 1980; Asta and Garrec, 1980; Davies, 1982; Davies and Notcutt, 1988). One study associated damage with F content of lichens which survived around long-established sources (Gilbert, 1971); two others used transplanted material (LeBlanc *et al.*, 1971; Swieboda and Kalemba, 1978). Few investigations, however, have attempted to directly relate F content with damage. The aim of this paper is to examine this relationship, in previously uncontaminated lichens, at different distances from an Al works.

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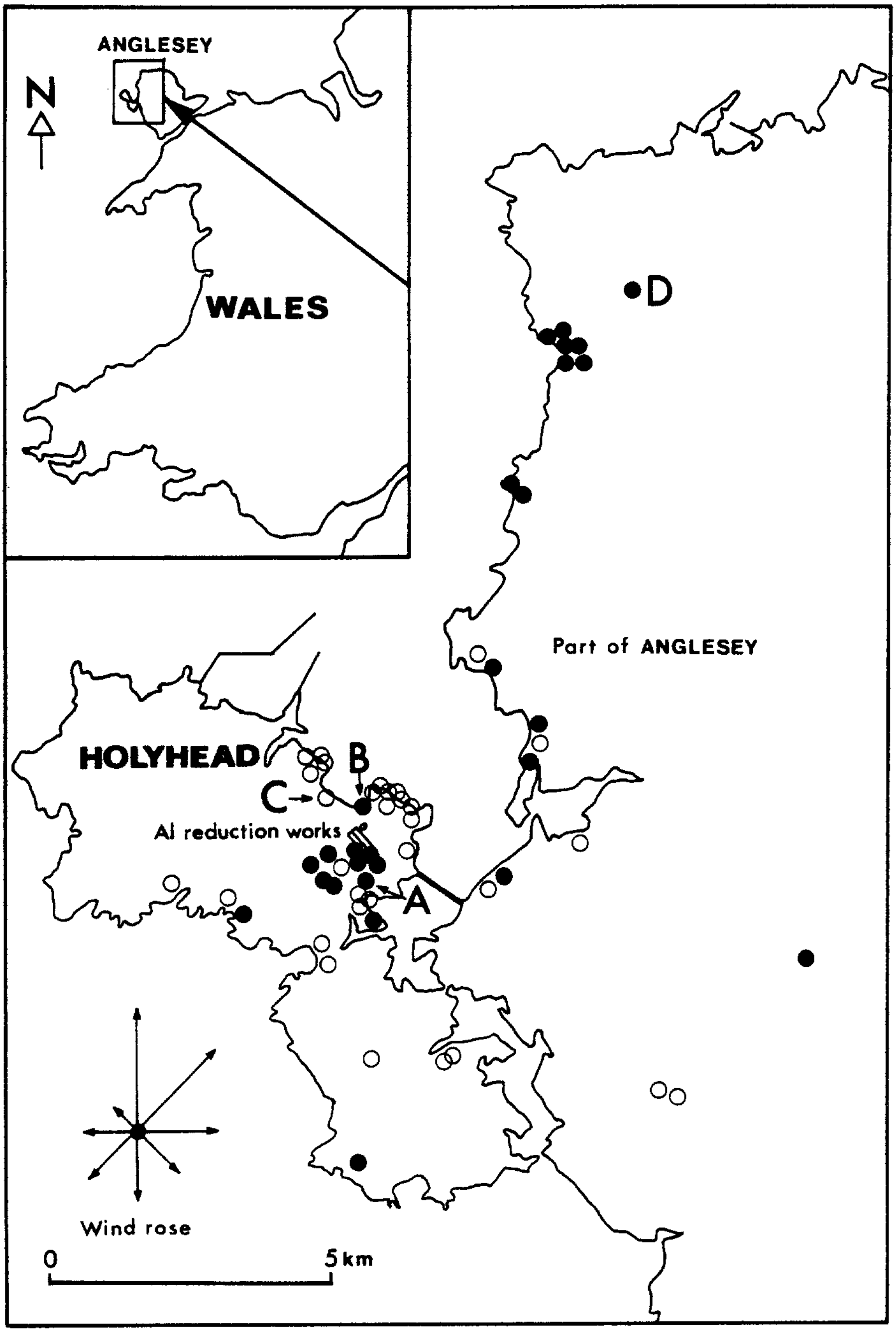


Fig. 1. Map showing the location of lichen quadrats well-exposed (●) and less-exposed (○) to emissions from the Al reduction works in Anglesey, North Wales. Data of quadrats A-D are used in Figure 2.

## 2. Site and Methods

Lichens were studied around a 100 000 t capacity Al reduction works opened in 1970 near Holyhead, Isle of Anglesey, North Wales (53°18′ N 4°36′ W). Saxicolous lichens occur abundantly in the area on rocky outcrops and old stone walls marking field boundaries. Geologically, these rocks are green-mica-schists of the New Harbour group, in the pre-Cambrian Mona Complex (Greenly, 1919). Lichens were photographed annually (35 mm color film), usually in June, at 58 permanent quadrats (20 × 14 cm) using a rigid tripod located in small holes drilled into the rock. After projecting the transparency onto a screen, lichens were counted at the intersections of a 46 × 28 cm grid, and their cover (as % of the original value) determined as previously described (Perkins and Millar, 1987a). The pale-green fruticose (shrubby) *Ramalina siliquosa* and *R. subfarinacea* sometimes forming dense swards covering large patches of rock, occurred in 42 and 16 quadrats, respectively. Quadrats were situated from the shore up to 5.5 km inland, and to a distance of 10.6 km from the works (Figure 1). Quadrats in the open with aspects facing the works were classified as well-exposed; in contrast, those facing away and in the lee of headlands, walls, woodland or scrub, were classified as less-exposed. It was rare to find both well- and less-exposed lichens, suitable for quadrats, at the same location. Samples of *Ramalina* (enough for 2 g dry weight) were collected for determination of F near, but not from, the 59 quadrats. Sampling directly from the quadrats would have precluded further long-term observations of cover. Total F was determined by ion-selective electrode following alkali fusion, using the method described by Allen *et al.* (1974).

## 3. Results

Soon after emissions commenced at the Al works in 1970, corticolous lichens nearby developed typical fluoride-induced injury symptoms (Perkins and Millar, 1987a). Injury to the saxicolous lichen flora was slower, but when assessed in 1974, 60% of thalli were damaged up to 10 km from the works. Damage was greatest <2 km from the works (Table I), where 91% of thalli were damaged and only 9% undamaged. Many *Ramalina* thalli (41%) showed >50% chlorosis and/or necrosis. Laboratory examination revealed plasmolysis of the algal component, loss of photosynthetic ability, and abnormal thickening of fungal hyphae. As distance from the works increased, the number of quadrats showing damage, and the level of injury, decreased.

### 3.1. Effects on growth and loss of lichens

*R. siliquosa*, well exposed on a wall 0.6 km S of the works, contained 20 $\mu g$ F $g^{-1}$, dw 9 mo before emissions commenced (Figure 1, quadrat A). Within 12 mo thalli were chlorotic and soon developed necrotic patches. As F concentrations reached 396 $\mu g\ g^{-1}$, thalli rapidly disintegrated and were lost from the quadrat

TABLE I

Pattern of injury to the thalli of saxicolous lichens (*Ramalina* sp) at different distances from the Al reduction works in Anglesey, North Wales, 4 yr after emissions commenced

| Distance from source of emissions (km) | Thalli (%) showing chlorosis and necrosis | | | |
|---|---|---|---|---|
| | 0 | <25% | 25–50% | >50% |
| <2 | 9 | 22 | 28 | 41 |
| 2–4 | 63 | 21 | 8 | 8 |
| 4–10 | 72 | 22 | 6 | 0 |
| >10 | 100 | 0 | 0 | 0 |

(Figure 2, A). In quadrat B, 0.6 km N, where F reached 369 μg $g^{-1}$ in 1976, cover was reduced to 15% of the pre-emissions value. Only blackened fragments (0.7%) remained in 1985. Lichens in quadrat C, 0.7 km NW, were more sheltered and accumulated F more slowly, reaching 108 μg $g^{-1}$ in 1982. Cover reduced to 25% by 1983, but in response to decreasing emissions (Perkins, unpublished data) new growth had occurred in 1985. In contrast, in well-exposed quadrat D at 10.6 km downwind, F increased from 11 μg $g^{-1}$ in 1970 to 41 μg $g^{-1}$ in 1975, since then concentrations have varied around a 1976–85 mean of 35 μg $g^{-1}$. Although F analyses were done on lichens at this site, a quadrat was not established until 1973. From 1973 to 1985 thalli remained green and cover increased by 108%.

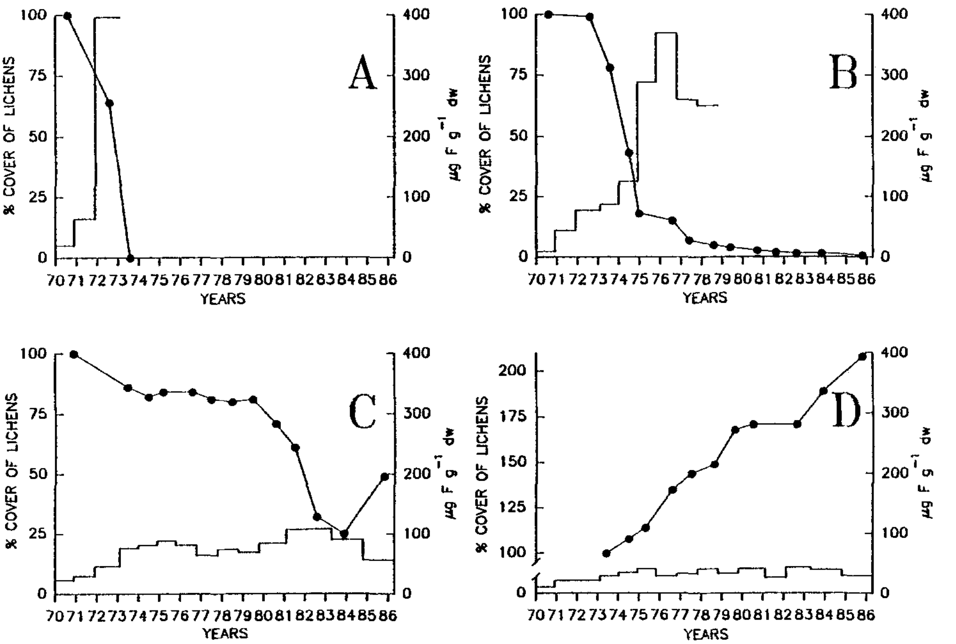


Fig. 2. Contents of F (histograms in μ F $g^{-1}$ dw) and cover (—●— as % of value first recorded) of the saxicolous lichen *Ramalina siliquosa*), at 4 different locations near the Al works in Anglesey, North Wales.

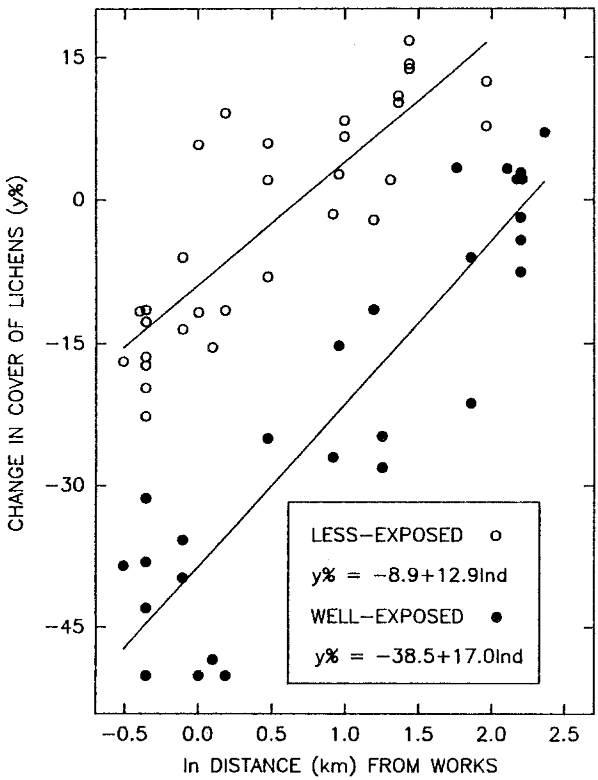


Fig. 3. Relationships between the annual change in cover (as % of value first recorded) of lichens (*Ramalina* sp), and distance (km) from the Al works in Anglesey, North Wales.

### 3.2. Losses in relation to distance from the source of emissions

Change in cover (%) of *Ramalina* at all sites (annual mean of the years 1973–76 in 58 quadrats) was only weakly positively correlated ($r^2$ = 0.35, P<0.01) with distance (natural logarithm transformation) from the works (Figure 3). Well-exposed quadrats treated separately ($n$ = 27) were more closely correlated ($r^2$ = 0.83, P<0.001) and showed greater losses. Less-exposed quadrats (n = 31) were similarly closely correlated with distance ($r^2$ = 0.71, P<0.001) and less damaged. Well-exposed quadrats showed on average 30% more losses at 0.5 km and somewhat less (20%) at 10 km from the works. Loss of cover was 4.9% $km^{-1}$ $yr^{-1}$ in well-exposed and 3.7% $km^{-1}$ $yr^{-1}$ in less-exposed thalli. These losses should be compared with an average 9% $km^{-1}$ $yr^{-1}$ increase of cover in the relatively uncontaminated quadrat D (Figure 2).

### 3.3. Losses in relation to F contents

Change of cover (%) was closely negatively correlated ($r^2$ = 0.90, P<0.001) with F content (natural logarithm transformation), the points (which include well- and

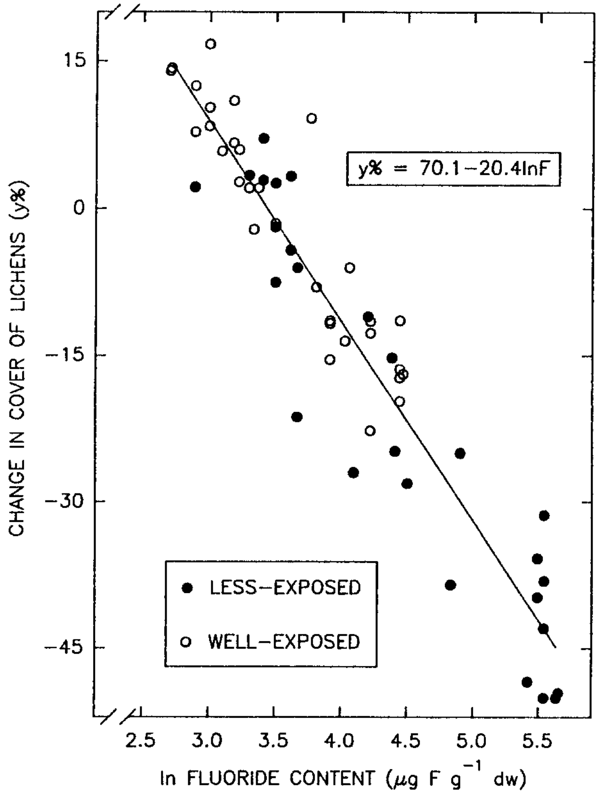


Fig. 4. Relationship between the annual change in cover (as % of value first recorded) of lichens (*Ramalina* sp), and F content (μ F $g^{-1}$ dw), at different distances from the Al works in Anglesey, North Wales.

less-exposed sites) are less scattered (Figure 4) than with the distance relationship (Figure 3). Loss of *Ramalina* was greatest where F contents were largest, and least where smallest.

## 4. Discussion

The study of the introduction of a pollutant to a previously unpolluted area obviates a criticism that absence of lichens, around long-established sources, could be due to lack of suitable habitats. The pre-emissions lichen flora was typical of an unpolluted rural area and it was unlikely that lichens had been affected by S pollutants as found near some other industries e.g. brick (Davies, 1982) and iron-sintering works (Hällgren and Nyman, 1977).

Results indicate that loss of cover of *Ramalina* was closely correlated with total F content of the thalli. Although this relationship has been established it is possible that another pollutant, itself correlated with F, could be responsible for the damage. The observed effects, however, are most likely caused by F accumulations: these may be the result of both wet and dry depositions of gaseous HF and F-containing particles, compounds including Al, Ca and Na, principally emitted by Al works (Barbour *et al.*, 1978). Experimental fumigations with HF (Nash, 1971; Comeau and LeBlanc, 1972) have demonstrated similar signs to those found in this investigation. Microscopic examination of *Ramalina* from the study area, fumigated with HF, showed similar injury to that found near the Al works (M. Galun, personal communication).

Different species of lichen vary in their tolerance of F. While fruticose corticulous (e.g. *Evernia prunastri* or *R. farinacea*) and some foliose species (e.g. *Hypogymnia physodes* or *P. saxatilis*) are killed following introduction of F (or $SO_2$) pollutants, others (e.g. *P. perlata* and *P. caperata*) are intolerant of $SO_2$, but are tolerant of F. That both *P. perlata* and *P. caperata* were surviving close to the works indicated that $SO_2$ had not increased, thereby causing the observed damage (Perkins and Millar, 1987a). Very intolerant, or tolerant but slow growing lichens (particularly crustose) are not very useful for long-term monitoring. Saxicolous *Ramalina* has proved to be useful in this respect because it is moderately tolerant yet relatively quick growing in unpolluted atmospheres.

The loss of *Ramalina* was closely correlated with F content. Using the regression equation of figure 4 as a predictor, lichens containing 300, 200, and 100 $\mu g$ F $g^{-1}$ would be expected to have losses of cover of 46, 38, and 24% $yr^{-1}$. These annual losses show that *Ramalina* containing $>200$ $\mu g$ would disappear in under 5 yr, whereas it would take at least 15 yr for thalli containing 100 $\mu g$ to disappear. *Ramalina* containing 50 $\mu g$ would be reduced to 30% of the original cover. These reductions correspond well with the losses observed over the period 1971–85 (Perkins and Millar, 1987b).

Differential exposure to the emissions resulted in only a weak relationship of loss in % cover with distance from the source. The wide scatter of points was mainly due to the variation in exposure of lichens to the emissions' plume. Well-exposed lichens accumulated more F and had 20 to 30% greater losses at all distances than less-exposed lichens. Concentrations of F $>100$ $\mu$ $g^{-}$ dry weight led to large losses; and in some locations close to the source, lichens completely disappeared. Subsequent surveys, without prior knowledge of the abundant pre-emissions flora, would not have shown the loss of the well-exposed lichens. Some more sheltered, less-affected, lichens still survive in favorable locations, and following reduction in emissions' level, have been regrowing from the remnant damaged thalli.

**Acknowledgments**

The work was partly supported by grants from the Welsh Office; the Department of Environment (Contract No. 481/70); and the Nature Conservancy Council (Contract No. HF 3-03-297). I am grateful to Mr. R. O. Millar for assistance during the work; the Chemical Service at Merlewood Research Station for F analyses; and Anglesey Aluminium Metal Ltd. for their co-operation during the investigations.

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