ACCUMULATION OF FLUORIDE BY LICHENS IN THE VICINITY OF ETNA VOLCANO

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Abstract. Volcanoes are known to discharge gaseous fluorides to the atmosphere, but measurement of these is difficult, and the dispersion characteristics have not previously been studied in detail. Samples of lichens were collected from the slopes of Etna Volcano in 1985 and 1987, in order to monitor these gases. Subsequent analysis for fluoride showed levels ranging from 2 to 141 $\mu g\ g^{-1}$, compared with control values of $< 2\ \mu g\ g^{-1}$. The fluoride accumulation patterns clearly show that there is a major input from the volcano's plume, with the highest levels on the downwind side; these are attributed to the prevailing winds and to the local topographic influences. The fluoride levels in the lichens are compared with those resulting from industrial pollution.

1. Introduction

The release of fluorides into the atmosphere is commonly associated with industrial processes such as aluminium smelting and brick firing, which may locally lead to toxic concentrations of fluoride in plants or animals. A natural process which can lead to fluoride being expelled into the atmosphere is volcanicity, and the magnitude of some volcanic eruptions and the nature of the emissions are such that these can result in much more widespread and harmful fluoride poisoning than may be caused by man. Incidences of fluorosis in Iceland caused by volcanic eruptions are well documented, and Fridriksson (1983) gives a summary of these.

Fluorides may be emitted from a volcano either as particulate matter, in the form of microscopic salt particles compounds adsorbed on to tephra (volcanic ash), or as a gas phase. During an eruption, both gases and particulate matter are released in large volumes over a short period of time, whereas during a quiescent phase the principal activity is the slow release of a gas plume.

There are no intrinsic problems in sampling the particulate matter and measuring the fluoride content of this; for example, Oskarsson (1980) determined the fluoride concentration of ashes following an eruption in Iceland, and used the data to plot isofluors. However, study of the release of gaseous fluoride has proved to be more difficult. Samples have to be collected either from a fumarole or directly from the plume, which usually involves inserting a collector tube into the discharging gases, or flying aircraft fitted with gas sampling equipment through the plume.

Both techniques carry with them the risk of sample contamination by the atmosphere. In addition, the fluoride levels measured may not be representative of the gases as a whole, and will only be a record of the discharges over a very short period of time. It has been shown that fluoride levels in volcanic gases vary according to plume temperature (Hirabayashi *et al.*, 1986), and to phase of activity (Naughton *et al.*, 1975; Rose *et al.*, 1986). Single measurements are, therefore, not a reliable indicator of the long term gaseous fluoride emissions, and will not indicate the area affected by such emissions.

The use of lichens to monitor atmospheric industrial pollution, particularly fluorides, is a well established technique. Although lichens do not give an absolute measure of the content of any gases being discharged to the atmosphere, they can be used to detect the long term output, and to determine the dispersion characteristics of these gases. This technique of measurement therefore offers considerable potential in the study of volcanic gases, and would facilitate a comparison of volcanic discharges and industrial pollution. This paper presents the results of surveys carried out on Mt. Etna, using lichens to study the emissions of gaseous fluoride from this volcano.

2. Etna Volcano

Etna is one of the world's most active volcanoes, with frequent eruptions of lava (e.g., in 1981, 1984, 1985, 1987), and a plume which is continuously discharged from the summit. It is also Europe's largest volcano (Figure 1), rising from sea level to over 3000 m. On the eastern side is a 5 km wide, steep sided, flat floored valley, the Valle del Bove, which extends eastwards for about 8 km from the summit area, forming a marked topographic feature.

An effect of the height of the mountain is that precipitation increases from 600 mm on the lower slopes to the west and south, to over 1200 mm at the summit and on the higher ground of the eastern side. Most of this precipitation falls during the winter months, frequently as snow on the upper slopes. The prevailing winds are from the west and north-west; these drive the plume predominantly over the eastern slopes, where it tends to be funnelled down into the Valle del Bove.

Attempts have been made to analyze this plume, and although sampling is recognized to be difficult (Chester *et al.*, 1985) some analyses of the fluoride content of the plume have been made. Faivre Pierret *et al.* (1977) tried to calculate HF discharges from Etna, based on the total SO_2 flux (measured by correlation spectrometer) and the HF/SO_2 ratio in plume samples. They estimated that approximately 30 t day^{-1} of fluoride was emitted from the volcano, principally as HF, and although this figure may not be very accurate it is of a sufficient magnitude to suggest that vegetation on the volcano may be affected by fluoride. Garrec *et al.* (1977), working on Etna examined 10 samples of clover from above 2000 m, and showed that the levels of fluoride in these increased from 113 to 295 μg F g^{-1} dry matter with increasing proximity to the crater. Two samples from the lower slopes contained fluoride levels of 8 and 14 μg g^{-1}. However, since higher plants were used it is not clear to what extent the different levels of fluoride were due to plume emissions, or fluoride variations in the soils derived from the volcanic rocks.

This emphasizes an advantage of using lichens as monitors, since they only absorb materials from the atmosphere (rather than the substrate), and therefore only atmospheric inputs of fluoride will be recorded.

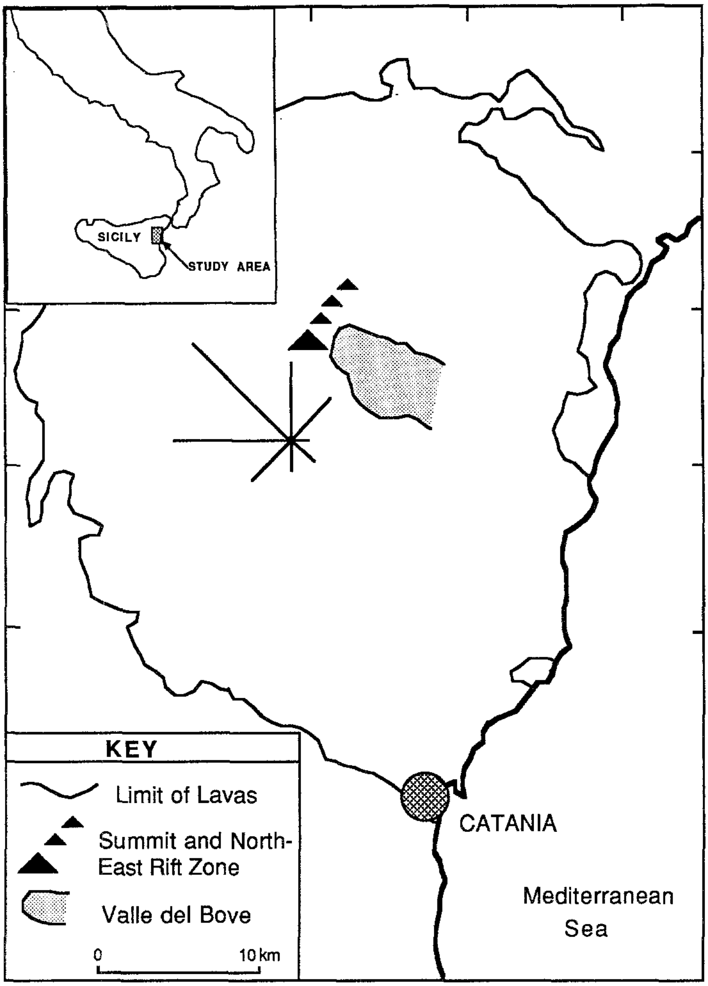

Fig. 1. Mt. Etna – location and principal features; wind rose at Serra la Nave Observatory.

3. Materials and Methods

In 1985 a preliminary survey of Mt. Etna was carried out, with the aim of determining the levels of fluoride which may occur in the lichens. Lichens were sampled from 77 sites around the volcano; these sites were selected to give a good spread of data points. Owing to the altitudinal range, it was not possible to restrict sampling to one species. Two species were chosen for study, *Xanthoria parietina* and *Stereocaulon vesuvianum*, which were found from sea level to 1250 m and 165 to 1830 m, respectively. These gave a sufficient altitude range for this study; in the zone of overlap, samples of both species from the same site showed no marked interspecific variation in fluoride content, and the data are therefore combined in the results.

As a result of the preliminary 1985 survey, a further sampling program was carried out in 1987, with the same two species of lichen selected for study; 56 sites were sampled.

For both surveys, a greater number of sites were sampled on the eastern side of the volcano, since the plume is usually blown across this area. The absence of sites around the summit is due to the lack of specimens in this area of very young lavas. All the sites are within 25 km of the summit, with the exception of two control sites located in the central region of Sicily approximately 90 km from the volcano.

The specimens were washed, dried, and ashed following the procedure of Hall (1963), and analyzed for fluoride by selective ion electrode.

4. Results and Discussion

The results of the 1985 survey are shown on Figure 2, expressed as $\mu g\ g^{-1}$ dry weight and displayed as four ranges of concentrations. The values vary from 2 to 125 $\mu g\ F\ g^{-1}$, with the highest levels on the upper eastern and north-eastern slopes.

The 1987 results are presented on Figure 3, using the same four categories of concentration as for the 1985 data. For this later survey, a greater proportion of the sites sampled were from the northern and eastern slopes; the suburban area of Catania was avoided due to the risk of industrial contamination, which was detected at one site in 1985. Similar values to 1985 were recorded, ranging from 2 to 141 $\mu g\ F\ g^{-1}$, with the highest concentrations found in samples taken from within the Valle del Bove. The control values were 1 and 2 $\mu g\ F\ g^{-1}$, respectively.

The distribution pattern of the 1987 data and the values of the controls confirm the conclusion drawn from the preliminary 1985 survey (Notcutt and Davies, 1988), that there is a marked discharge of volcanogenic fluoride which can be accumulated by the lichens in considerable quantities.

A comparison of the 1985 and 1987 data shows a remarkably similar pattern, both in terms of concentrations and areal distributions. The 1985 samples were collected after an extensive period of plume activity, and this similarity between the two sets of data confirms that the lichens are reflecting long term influences.

The levels of fluoride are noticeably higher on the north-east and east slopes, with the highest values occurring in and around the Valle del Bove, and reaching a maximum of 141 $\mu g\ g^{-1}$ in a sample taken from within this depression, at a distance of 5 km from the plume source. Although fluoride levels generally decrease with distance from the summit the pattern of dispersal away from this area is not uniform.

The principal factor controlling fluoride distribution is the prevailing wind. In an upland area such as this extrapolation from meteorological data is uncertain, but the evidence from the observatory at Serra la Nave (Figure 1) shows that the dominant wind directions are from the west and north-west. This would cause emanations from the summit to be driven mainly towards the east, which would account for the regionally higher levels of fluoride on this side. However, this pattern is considerably influenced by the topography, in particular the Valle del Bove and the North-East Rift Zone. The

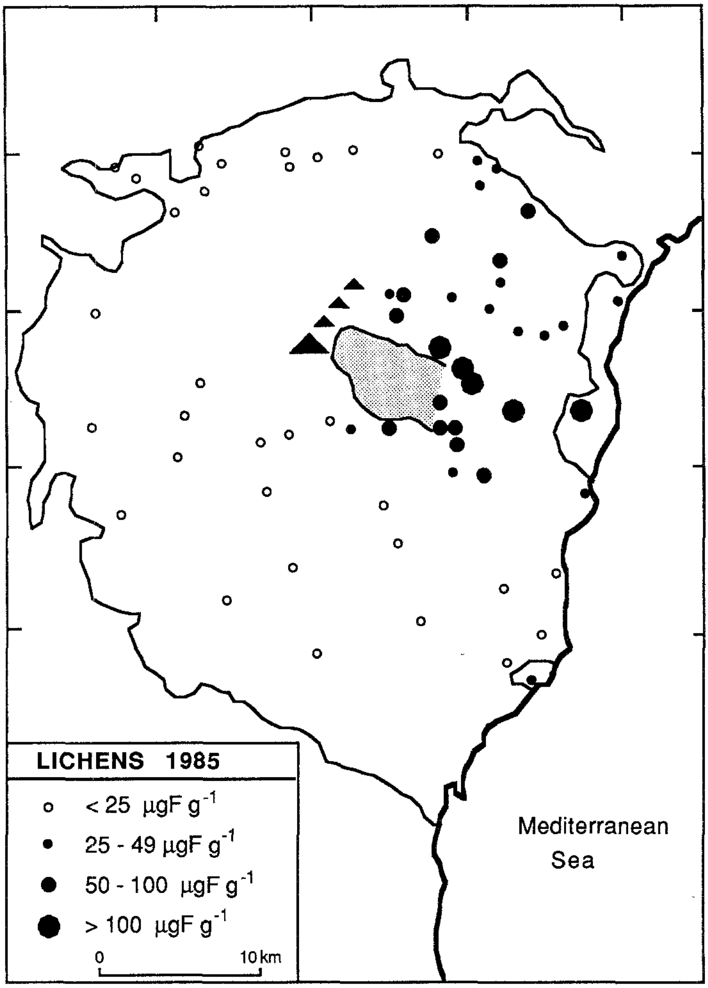

Fig. 2. Fluoride concentrations in lichens, 1985 (as proportion dry weight).

size and shape of the Valle del Bove is such that winds tend to be funnelled down into it, subsequently fanning out over the lower slopes, resulting in the higher concentrations found within the valley and in the vicinity of its mouth. The plume also spreads over the sides of the valley, particularly the northern rim, and is the cause of the increased levels of fluoride on these flanks.

The North-East Rift Zone forms a high ridge, which acts as a barrier and diverts the plume over the north-east slope. This results in the higher fluoride levels over this area, with some lower values caused by local topographic features.

Five of the sites sampled showed a lichen fluoride level in excess of 100 $\mu g\, g^{-1}$; no morphological damage was observed in any of the specimens. Such concentrations are similar to those resulting from certain types of industrial pollution. For example, Perkins

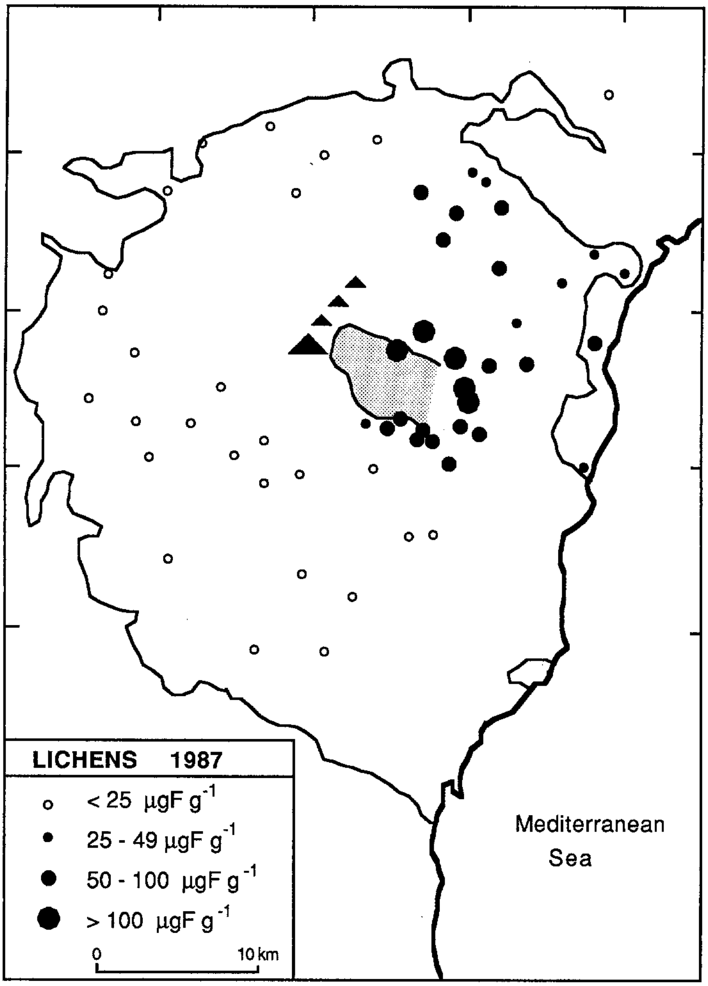

Fig. 3. Fluoride concentrations in lichens, 1987 (as proportion dry weight).

and Millar (1987) monitored the effects on lichens of fluoride emissions from the aluminium works in Anglesey, North Wales. Before emissions commenced in 1970, lichens contained a mean of 16 $\mu g\ g^{-1}$; after commissioning, the levels of fluoride in some lichens were in excess of 200 $\mu g\ g^{-1}$ within 1 km of the works, with concentrations decreasing with distance from the works. Increased levels of fluoride in herbage (Perkins *et al.*, 1979) and small mammal bones (Walton, 1985) in this area have also been recorded.

This comparison indicates that gaseous fluorides emitted by volcanoes could have effects higher up the food chain, and demonstrates that lichens are not only effective as monitors of the dispersal of volcanic gases, but can also be used to identify a potential environmental hazard.

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