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ENVIRONMENTAL IMPACT OF MAGMATIC FLUORINE EMISSION IN THE MT. ETNA AREA

PhD Thesis by
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1. Introduction

Fluorine is the most reactive and the most electronegative of all elements, meaning that it has a powerful attraction for electrons and that it is able to attack all other elements, with the exception of oxygen and nitrogen, so it is not found in the free elemental state in nature. Fluorine is widely distributed throughout the earth's crust as the fluoride ion. Fluorine is reported to be the 13th most abundant element in the earth's crust (Smith and Hodge, 1979), with an average concentration of 0.032% by weight.

Fluorides are released into the environment naturally through the weathering and dissolution of minerals, the emissions from volcanoes and from marine aerosols (WHO, 2002). Fluorides are also released into the environment via coal combustion and process waters and waste from various industrial processes, including steel manufacture, primary aluminium, copper and nickel production, phosphate ore processing, phosphate fertilizer production and use, petroleum refining, glass, brick and ceramic manufacturing, and glue and adhesive production (WHO, 2002). Based on available data, phosphate ore production and use as well as aluminium manufacture are the major industrial sources of fluoride release into the environment.

According to Wellburn (1997), fluorine (in the form of HF) occupies - after O_3, SO_2 and nitrogen-containing air pollutants - the fourth place with regard to its detrimental effects on harvest, at least in the US. Relative to its weight fluorine even has the highest level of phytotoxicity of all air pollutants. Wellburn (1997) reports that F-related damages at sensitive plants can develop at concentration levels 10 to 10.000 times lower than other pollutants.

There is no doubt that inorganic fluoride was one of the major air pollutants of the 20th century damaging crops, forests and natural vegetation, and causing fluorosis in factory workers, livestock and wild mammals. However there have been enormous improvements during the last 40 years in the containment and scrubbing of emissions, so that modern fluoride emitting industries generally have little or no environmental impact outside the factory fence at the present time (Weinstein and

Davison, 2003). On the other hand, fluoride emissions from volcanoes and the natural occurrence of excessive amounts of fluoride in drinking water have affected the health of humans and livestock for centuries, if not millennia. For example some historical report tells that Pliny the Elder was dispatched by fluoride-containing fumes from a Vesuvian eruption, although other state that the cause of its death had actually no relation to volcanic activity. Whether the story is true or not, fluoride was certainly the agent responsible for the death of sheep after the volcanic eruption described in the Icelandic sagas, and fluoride emissions from volcanoes continue to affect the health of humans and livestock today (Georgsson and Petursson, 1972; Fridriksson, 1983; Araya et al., 1990; Cronin et al., 2002).

Fluorine is emitted by volcanoes mostly as HF, but emissions from Vesuvius and Vulcano in Italy have been shown to contain also NH_4F, SiF_4, $(NH_4)_2SiF_6$, $NaSiF_6$, K_2SiF_6 and KBF_4 (Weinstein and Davison, 2003). Volcanoes are also an important source of organo-fluorides, including some CFCs (Schwandner et al., 2004).

Estimations of the global release of fluorine to the atmosphere by volcanic activity ranges from 50 to 8600 Gg/a (Cadle, 1980; Symonds et al., 1988; Halmer et al., 2002) with the lowest figures being probably an underestimate. Average HF emission rates from Mt. Etna can be estimated to about 75 Gg/a (Aiuppa et al., 2004a). This makes Mt. Etna the largest known point atmospheric source of fluorine (Francis et al., 1998), even stronger than todays estimated anthropogenic release over whole Europe (Preunkert et al., 2001).

The environmental impact of anthropogenic fluorine emissions have long been studied considering all main type of activity, for example coal burning (Ando et al., 2001), aluminium smelters (Egli et al., 2004) or phosphate fertiliser production (Klumpp et al, 1996) and all types of receptors (air – Liu, 1995; glaciers - Preunkert et al., 2001; surface waters – Skjelkvale, 1994; vegetation – Weinstein, 1977; Weinstein and Davison, 2003; soils – Polomski et al., 1982; wildlife – Kierdorf and Kierdorf, 2000; etc.). Considerably fewer studies have been devoted to the consequences of volcanic fluorine emissions and most of them were focussed on the impact of fluorine released

through explosive volcanic eruptions (Georgsson and Petursson, 1972; Oskarsson, 1980; Thorarinsson, 1979; Cronin et al., 2002). Recent researches have highlighted that passive degassing – quietly but persistently releasing volcanogenic pollutants - may also have profound impact on the ecosystems downwind, sometimes disrupting the social and economic activities of populations (Delmelle et. al., 2002; Delmelle, 2003). In this context, the impact of volcanogenic fluorine has been assessed on vegetation growing along the flanks of volcanoes (Guadeloupe – Garrec et al., 1977; Masaya – Garrec et al., 1984; Etna – Garrec et al., 1984; Notcutt and Davies, 1989; La Palma – Davies and Nottcut, 1989; Hawaii - Notcutt and Davies, 1993; Furnas - Notcutt and Davies, 1999) on rainwater chemistry (Hawaii - Harding & Miller, 1982; Vulcano Island – Capasso et al., 1993; Etna – Aiuppa et al., 2001; Stromboli Island – Bellomo et al., 2003) and on soils (Delmelle et al., 2003).

The aim of the present PhD thesis is to provide original data on the geochemical cycling of fluorine of an active volcanic system like Mt. Etna. An assessment of the impact of volcanic fluorine on the local environment is also attempted by analysing different media (atmospheric air, rainwater, volcanic ashes, vegetation and soil).

2. Study area and methods

2.1. Study area description

The study area is located on the eastern coast of Sicily (latitude 37°30'-37°55' N and longitude 14°47' – 15°15' E) and covers an area of about 1200 km^2 (Fig. 1). Mt. Etna is a large stratovolcano that has built upon tensional faults cutting a $\approx$20 km thick continental crust (Chester et al., 1985). Etnean volcanism, related to the break-up of the African plate margin during its collision with the European continental block since the Upper Miocene (Barberi et al., 1974), began at 0.5 Ma. The

edifice consists of a lower shield unit overlain by a stratovolcano (Chester et al., 1985). The shield complex formed over Miocene flysch sediments (rising to ca. 1300 m elevation) to the NW and clayey Pleistocene formations to the SE.

The volcanic products range from alkali-basalts to trachites although most lavas have hawaiitic composition (Tanguy et al. 1997). The present-day activity of Mt. Etna is characterised by frequent summit and lateral eruptions (Tanguy et al., 1997) and huge emissions of magmatic volatiles from the summit craters and the upper flanks, the latter as diffuse soil emanations (Allard et al., 1991). These emissions result from open-conduit degassing of alkali basalt-hawaiite magma which rises from a shallow mantle diapir (D'Alessandro et al., 1997a; Hirn et al., 1997).

The surface of Etna's edifice lacks of a real hydrographic network and waters mostly tend to seep and feed the underground circulation, the run-off coefficient being only 5%, and evapo-transpiration about 20% (Ferrara, 1975). The importance of the effective infiltration is highlighted by high outflows at the springs along the perimeter of the volcano, at the contact with the underlying impermeable sedimentary rocks especially along the coastline, where considerable amounts of water are discharged into the sea (Ogniben, 1966; Ferrara, 1975).

2.2. Recent volcanic activity

In the period from 1997 to 2003, quiet degassing was interrupted by several paroxysmal episodes. The most important episodes are the following: (i) 23 lava fountain episodes (Sep. 98-Feb. 99) followed by a subterminal eruption (Feb. 99-Nov. 99) from the SE crater; (ii) a violent effusive and explosive terminal eruption at the Bocca Nuova crater (17 October-4 November 1999); (iii) 64 lava fountain episodes quite regularly spaced in time at the SE crater (26 January-24 June 2000); (iv) a short but intense flank eruption (17 July-9 August 2001) that emitted an unusually high proportion of pyroclastic material (Behncke and Neri, 2003) and was preceded by 15 strong strombolian to lava fountain episodes at the SE crater. Besides abundant lava effusive activity from a S-trending

10-km long eruptive fracture, intense ash emission were produced from a newly opened vent at 2550 m a.s.l., with a thin ash veil covering the entire south-eastern sector of the volcano. After about one year of quiescence, characterised by unusually low SO_2 emission rates from the summit craters a new lateral eruption started suddenly on October 27, 2002, preceded by very few geophysical precursor signals (Andronico et al., 2004). This eruption, which lasted until the end of January 2003 was also characterized by intense ash emission in the first two months leading to a even higher proportion of pyroclastic material with respect to the previous eruption (Andronico et al., 2004).

2.3. Summit crater gas emissions

Mt. Etna's recent activity is characterized by permanent open-conduit passive degassing, interrupted by paroxysmal activity (effusive to moderately explosive) at the summit craters and/or newly formed flank craters (Acocella and Neri, 2003). At present, Etna's central conduit feeds four summit craters (called Voragine, Bocca Nuova, South-East and North-East), whose vents cover an area of about 0.5 km^2 and range in altitude from about 3200 to more than 3300 m a.s.l.. Degassing at the summit craters has continued without interruption in the last few decades, although only rarely have all the craters been degassing contemporaneously. In most atmospheric conditions, Etna's summit plume is dispersed by winds at about the same altitude as the emission point. Lofting of the plume is a very rare phenomenon, limited to less than a few hundred meters when wind speed is very low. Instead, very strong westerly winds often funnel the plume down into the Valle del Bove depression (Fig. 1), leading to fumigation of the rims of the Valle del Bove and the upper eastern flanks of the volcano sometimes reaching lower altitudes (1500 m a.s.l.).

Sulphur dioxide fluxes from the summit crater have been measured with COSPEC methodologies at intervals since the middle of the 1970's and on regular basis since 1987, giving a long-term average emission rate of 5500 Mg/d for the 1987-2000 period (Caltabiano et al., 2004). Fluxes of many

other compounds released in gaseous and/or particulate form have been estimated cross-correlating SO_2 fluxes with SO_2/compound ratios measured in the plume (Allard et al., 1991; Bùat-Menard and Arnold, 1978; Andres et al., 1993; Gauthier and Le Cloarec, 1998; Aiuppa, 1999).

Average HF emission rates from Mt. Etna can be estimated in about 200 Mg/d considering an average SO_2/HF plume mass ratio of about 27 (Francis et al., 1998; Pennisi and Le Cloarec, 1998; Aiuppa et al., 2002, 2004b; Burton et al., 2003).

2.4. Climate and vegetation cover

The area of the volcano displays peculiar climatic conditions with respect to the Mediterranean climate of the surrounding areas, due to its altitude and geographical position. In fact, an upward variation of climatic conditions, from subtropical to cold, through temperate, is observed. Precipitation is strongly influenced by elevation and exposure of the flanks to the dominant winds, the most important wet air masses coming from the eastern sector (Ionian sea). Most of the rainfall is concentrated on the eastern flank of the volcano, as the volcano itself induces the condensation. Thirty-year averaged data (1965-1994) indicate that rainfall ranges from 400 mm on the lower SW flank up to 1200 mm at 600-700 m elevation on the E flank, with a mean value of about 800 mm for the entire area. All sectors display maximum precipitation in the autumn-winter season (mostly in October) while the minimum is always in July (generally absence of precipitation) (Fig. 1d). At higher elevation (> 2000 m), snow represents a significant part of the precipitation for most of the year (October-April).

A reliable record of meteorological data for Etna's summit area is not available. It has been shown, however, that meteorological soundings made at the Italian Air Force station of Birgi, about 200 km west of the volcano, are a proxy for wind speed on Etna's summit crater area (Caltabiano et al., 1994). The wind rose in Figure 1b, based on Birgi station's 1997-2003 dataset, highlights the prevalence (47%) of westerly to north-westerly winds at 700 hPa (corresponding to a mean altitude

of about 3100 m). Anfossi and Sacchetti (1994) obtained similar indications from trajectory calculations made using data from the European Center for Medium-Range Weather Forecasts. During 1989, in fact, more than 50% of the trajectories starting from the top of the volcano pointed to western sectors. Basing on the wind rose we divided the study area in downwind from 22°50' to 200°50' (East) and upwind from 200°50' to 22°50' (West) with respect to summit crater emissions (black line in Fig. 1b). It must be stated that it is not true that areas in the upwind direction are never reached by summit crater emission but the probability to be reached is very low. The lowest probability will be in the 282°50' direction while the highest in the 102°50'.

Mean wind velocity at 700 hPa during 2001-2003 was 11 m/s. Figure 1c shows that the highest wind velocities are reached by wind coming from the western sectors.

Parallel to the climatic conditions, vegetation displays variations with altitude and three zones can be recognised (Chester et al., 1985). The first one (*regione pedemontana*), which extends from sea level to 1000 m, is the most intensively exploited for agricultural use and has almost entirely lost its original vegetative cover. The second region (*regione boschiva*), extending approximately from 1000 to 2200 m a.s.l., is still covered by large forest areas. Agriculture is limited to the lower margin (mainly pasture land) and most of the original species were replaced by replantation (pines) and by commercial forestry (chestnuts). The last region (*regione deserta*), which is found above the tree limit (> 2200 m a.s.l.), is characterised for most of its extension by the volcanic desert and displays only alpine vegetation.

2.5. Sample collection and analysis

Collection sites of the different media are reported in fig. 2. Sites were chosen to obtain a good coverage of the study area both up- and downwind with respect to the summit craters. For atmospheric air, vegetation and soils sampling were made in areas least affected by anthropogenic activities. Some of the sites were selected for multimedia sampling.

2.5.1 Atmospheric gases

Atmospheric concentrations of HF were determined through passive (diffusive) sampling devices that are based on molecular diffusion and a specific and efficient sorbent (Ferm and Svarnberg, 1998; Aiuppa et al. 2004a). These devices are widely used in the study of atmospheric pollution, the detected species depending on the specific used sorbent, and in the present work NaOH was used for determination of acidic gases (SO_2, HCl and HF). The samplers are made of a cylinder of inert material 1.5 cm long and 1 cm in diameter with the open end protected by a screen and an impregnated filter on its closed bottom. The samplers, placed 1-2.5 m above the ground sheltered from rainwater, give a time-integrated value of gas concentrations and detection limits are inversely proportional to the sampling time and length of the cylinder and directly proportional to its diameter. Analysis was made by IC at the IVL laboratories (Sweden). The lower detection limits for one-month sampling are for HF, HCl and SO_2 about 0.1, 0.5 and 0.4 $\mu g \cdot m^{-3}$ respectively. Samplers were set in the field at distances between 1.5 and 11.2 km from the Etnean summit craters (Fig. 2) providing time-integrated mean gas concentrations in air during the one-month exposure period from end of May to end of June 2002.

2.5.2 Rainwater

About 700 rainwater samples were collected in the period Oct. 1997 – Oct. 2003 with an approximately monthly frequency using a network of 15 rain gauges located at various altitudes along the flanks of Mt. Etna (Fig. 2). Rain gauges were bulk collectors, permanently open to the atmosphere, collecting both the wet and dry deposition. They were made of a low-density polyethylene (LDPE) funnel of 30 cm diameter and a LDPE container of about 30 litres, protected from direct sunlight. 250 ml of paraffin oil were added to the container to prevent evaporation. Purity of the oil was tested analysing deionised water equilibrated for 1 month with the oil. Concentrations of the analysed compounds in the test samples were always below the detection

limit. The uptake of ionic solute by the oil was also tested equilibrating standard solutions with the oil for 1 month. Differences from the calibration standards were always within the analytical error. IC analysis was performed on filtered aliquots (0.2 µm).

Fluoride content (together with Cl, NO_3 and SO_4) was determined with a Dionex ion chromatograph with an AS14 column, suppresser and conductivity detector, using a 1 mM sodium bicarbonate 3.5 mM sodium carbonate solution as eluent (1.1 ml/min). Fresh working eluent was prepared daily, filtered through a 0.2 mm pore size membrane filter and degassed prior to use.

To minimise the "water dip" and its interference with the fluoride peak, sample were mixed with a proper amount of concentrated eluent solution to match the eluent matrix. With a 25 µl introduction system, the detection limit for fluorine was 0.005 mg/l, with precision $\leq 3\%$.

2.5.3 Volcanic ashes

Ash samples (not exposed to rain) produced by explosive activity during the July-August 2001 and October 2002 – January 2003 flank eruptions were investigated in this study. During the 2001 eruption, samples were collected at 35 sites on the 24th of July, representing the integrated deposition of 5 days during the main deposition period. Twenty-five samples were sieved through standard sieves to measure the grain size distribution. For these samples, leaching was performed also on each grain size class. The grain size classes are expressed in Φ units corresponding to $-\log_2 x$ were x is the highest size of the grains of that class expressed in mm.

For the 2002-2003 eruption 46 ash samples, representative of deposition periods ranging from some hours to a couple of days, were collected at different sites along the flanks of the volcano.

All samples were leached following the method proposed by Armienta et al. (1998). For the leachate analysis, 1 g of ash was eluted in 25 ml of deionised water for 2 hours with constant agitation. The supernatant was subsequently centrifuged at 3500 rpm for 15 min. and filtered through 0.45 µm filters. More than 200 leachate samples were analysed by IC.

2.5.4 Vegetation

The analysis of fluorine content in Etnean vegetation focused on two of the most widespread tree species in the area: Chestnut (*Castanea Sativa*) and Pine (*Pinus Nigra*). Pine were generally of the subspecies *Laricius* (Corsican Pine), the subspecies *Austriaca* (Austrian Pine) was sometimes used (where *Laricius* was absent). Samples were taken all around Mt. Etna, at distances from the central craters ranging from 4.2 to 15.6 km (Fig. 2). Chestnut samples were collected in November 2001, October 2002 and in September 2003, while pine samples were collected in September 2003. Branches were collected generally from lower half of the tree crown, at heights between 2 and 4 m. At each sampling site a composite sample was obtained putting together branches from different sides of the tree and from at least three plants growing in an area of about 100 m^2. Samples were not washed in the laboratory but samplings were generally made during or immediately after heavy rainfalls so that contribution of particulate adhering on the surface is probably negligible. Branches were air-dried; leaves and needles were subsequently hand-picked and further dried in the oven at 40°C for about two days. Pine needles were separated into years of growth.

Analysis of total fluorine content was performed by alkali fusion – selective electrode technique on ground aliquots and the results are expressed as µg/g on dry weight basis. Detection limit is 1 µg/g and precision ≤ 10%.

2.5.5 Soils

Fifty-seven soil-sampling sites were selected on Mt Etna (Fig. 2). Areas with minimum anthropogenic disturbance on the soil were chosen, being at distances from the summit craters between 3.7 and 16 km. Samples were collected between June and July 2002. At each sampling

site, a composite sample of the first 5 cm of the soil profile was collected – composed of at least 4 points within an area of about 100 m^2.

Moreover, five soil profiles of different depth (50-130 cm) were collected both downwind and upwind the summit craters (Fig. 2). All profiles were divided in sub-samples, corresponding prevailingly to different pyroclastic levels rather than to true pedogenic horizons.

Soils were air dried, sieved through a 2 mm sieve and thoroughly mixed. An aliquot of each sample was used to characterize its grain-size distribution. Soil samples were analysed for total fluorine content (F_{TOT}), for fluorine extractable with acid oxalate (F_{OX}), which represents the F aliquot bonded to amorphous phases like allophane and imogolite, and water soluble fluorine (F_{H2O}) the least bounded form. F_{OX} comprises F_{H2O}, while F_{TOT} comprises both F_{OX} and F_{H2O}.

For the analysis of soluble fluorine content, aliquots of the soil were leached with a water/sample ratio of 50 for 18 hours with continuously shaking. The suspension was then centrifuged for 15 min. at 5000 rpm and the supernatant was filtered (0.2 µm) and analysed by IC.

Fluorine adsorption experiments were made on the sub-samples of two profiles (Etna3 and Etna5). An aliquot of 2g of each sub-sample was equilibrated, at room temperature and under constant shaking, with 50 ml of rainwater with a F content of 3.82 mg/l. About 1ml of the surnatant was sampled after centrifugation and analyzed by IC after 2, 4, 8, 24. 192 hours.

Oxalate extractable fluoride (F_{OX}) was determined at a soil/solution ratio of 1/50 in an extraction solution of 0.2 M ammonium oxalate and 0.2 M oxalic acid at pH 3 (Blakemore et al., 1987). The samples were shaken for 4 hours in the dark, centrifuged, filtered, and the concentration of F determined with a combination fluoride electrode (Orion), after adding total ionic strength buffer (TISAB 3 Fluka) for decomplexation of fluoride.

Analysis of total fluorine content was performed by alkali fusion – selective electrode technique. Detection limit is 1 µg/g and precision ≤ 10%.

2.5.6 Total fluoride determination by Alkali Fusion-Selective Electrode technique

Approximately 0.50 g of samples (soil or vegetation), were weighted to the nearest 0.0001 g directly into nickel crucibles and moistened slightly with distilled water. This was followed by the addition of 6.0 ml of a 16 M sodium hydroxide solution, placed in an oven (150 °C) for 1h and then removed. After sodium hydroxide had solidified, the crucible was placed in a muffle furnace at 300° C. The temperature was then raised to 600°C and the sample fused at this temperature for 30 min. After cooling, 10 ml of distilled water was added to the sample and slightly heated to facilitate the dissolution of the fusion cake. About 8 ml of concentrated hydrochloric acid was added drop-wise decreasing the pH from 12.0-13.0 to 8.0 - 8.5 under the control of a pHmeter. Subsequently the samples were transferred to a 50 ml volumetric flask, diluted to volume, and then filtered (0.45 μm). This step eliminates most of the Al and Fe, both interfering in F determinations by the ion-selective electrode (McQuaker and Gurney, 1977). Analysis was performed on 20 ml aliquots to which 2 ml of ionic strength buffer (TISAB 3 - Fluka) was added and whose pH was adjusted to obtain a value of 5.2 – 5.4. Reagent blanks were always prepared together with the samples and were brought through the whole procedure and were used for blank determination as well as preparing the standard solution with fluoride concentrations of 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5 and 10 mg/l. The standard solution and sample solution were analysed using a Orion fluoride ion-selective electrode.

3. Results

3.1. Air concentrations

Concentrations measured with the passive samplers (Table 1) are in the ranges <0.1-3 $\mu g/m^3$ (HF), <0.5-74 $\mu g/m^3$ (HCl) and 2.7-720 $\mu g/m^3$ (SO_2). HF was detected in only 7 of the 19 sites and, more importantly, only in those closest to the summit craters (sites TDF, PLU, PDN, VBN, SAS, CIT and PRO; Fig. 2). This range of volatile air concentrations measured in the diffusive tubes was 20 to 10,000 times lower than the respective abundances in the undiluted plume, sampled close to the emission vents by active methods (Fig. 3a, triangles; one-hour active plume air pumping on soda-treated cellulose filters, following the procedure described in Aiuppa et al., (2002)). However, it exceeds the respective concentrations commonly reported for rural sites by a factor of up to 100 (Fig. 4 - WHO, 2002).

Decisive support to the hypothesis of the mainly volcanogenic origin of SO_2, HCl and HF measured by diffusive tubes is given by Figure 3b, where time-averaged volatile concentrations at the various sites are plotted versus the corresponding distance from the summit craters. As a general feature, the plots clearly show a steep, monotonic decrease in volatile air concentrations with distance from the craters, suggesting a dominant (or, as regards HF, even exclusive) volcanic contribution to the air burden of acidic gases. This trend (declining with distance) is particularly evident in the diffusive tubes installed on the eastern flanks, where the volcanic plume is generally blown by the prevailing westerly winds, in areas which are known to be those mostly affected by plume fumigation.

Figure 3a highlights that the SO_2/HF volatile ratios measured by passive methods in the sites closest to the crater are consistent both with those measured by active methods on the crater rim and with FTIR methods (Aiuppa et al., 2004b; M. Burton, pers. comm.). The SO_2/HF ratios in diffusive tubes tend to increase with distance from the summit craters, but we must note the possible inaccuracy of

our SO_2/HF ratios determined over ~3 km from the source, as HF concentrations were only slightly above the detection limit of the diffusive tubes.

3.2. Rainwater

The analysed rainwater samples display a wide range of fluorine contents (Table 2) from less then 0.005 mg/l up to 227 mg/l (TDF Feb. 1999 – Aiuppa et al., 2001). Values higher than 10 mg/l, which are very unusual in rainwater, were measured only in samples collected close to the craters. The only comparable values (39.4 ± 40.1 mg/l) found in literature were measured in rainwater samples collected on the active crater of Poás volcano in Costa Rica (Rowe et al. 1995).

Chlorine also displays a wide range of concentration values from 0.78 mg/l to 1408 mg/l. The Cl/F ratio ranges from 0.81 up to more then 8600. Figure 5 shows that in the Etnean area samples collected at high altitudes, close to the summit craters, have Cl/F ratios closely matching those typical of the volcanic plume. Samples collected at low altitude were subdivided on the basis of the sector they belong. Samples collected on the western sector (upwind the summit craters) generally display the lowest concentrations, and have Cl/F ratios often very different from plume signature. Samples from the eastern sector show the widest range of Cl/F ratios and generally higher F and Cl contents, which can respectively be ascribed to more extensive contribution from the plume (due to the prevailing winds) and from sea spray (due to the lower distance to the coast).

A noticeable feature of the acquired data is that samples collected during the rainy autumn-winter period commonly display higher Cl/F ratios. This feature possibly reflects the fact that the fluorine has a local source and its concentration in rainwater decreases with increasing rainfall amount through washout processes. Chlorine, on the contrary, has non-negligible additional sources in the (regional) background atmosphere (mostly sea spray), which become prevailing at high precipitation values through rainout processes (Aiuppa et al., 2003a; Bellomo et al., 2003).

Daily fluorine bulk flux to the soil ranges from 0.046 mg/m^2 to 69.8 mg/m^2. Although each sampling site displays a wide range of flux values, generally spanning through 2 orders of magnitude, the highest values were always detected close to the active craters (Fig. 6). For the Etna area, a square power function most properly fit the concentration (median values) versus distance trend of Figure 6, reflecting the increasing dilution of the plume emitted at the summit vents. The rain gauge sited in the highly urbanised and industrialised area of Catania (CAT) also lies on this main pattern, confirming that anthropogenic fluorine sources are negligible in the study area.

3.3. Volcanic ashes

Data acquired from ash leaching are reported in Table 3. Considering the analyses of all grain sizes, ashes of the 2001 eruption reveal leachable fluorine concentrations in the range 15 - 476 μg/g of ash. Values increase with decreasing grain size (Fig. 8), the finest portions ($\Phi = 5$) showing values over an order of magnitude higher than the coarser ones ($\Phi = -2$). This is a common feature, recognized in previous studies (Oskarsson, 1980), due to the higher surface/volume ratio of the finer portions that favours soluble salt condensation. For the same reason distal sites (richer in finer classes) display higher values of soluble fluorine than proximal ones (Fig. 9a). Total soluble fluorine deposition range from 24 to 917 mg/m^2 with the highest values measured in proximal sampling sites (Fig. 9b).

Fluorine deposition with ashes was estimated from the deposition map (Fig. 7) obtaining a value of about 30 Mg. Considering that further ash emission in the period 25 July – 5 August nearly doubled the ash deposition probably F deposition with ashes reached a value of 60 Mg for the whole 2002 eruption.

For the 2002-2003 eruption, leachable fluorine displays values in the range 3 – 213 μg/g (median value 74 μg/g).

3.4. Vegetation

Fluorine contents in chestnut leaves and pine needles, reported in Table 4, range from 1.8 to 35 µg/g DW and from 2.1 to 74 µg/g DW respectively. Although the highest values are generally measured in samples collected downwind the vents, no clear dependence of F content with distance from the summit craters is recognizable, neither in chestnut leaves nor in pine needles (Fig. 10). Chestnut leaves display significantly higher values in the 2002 samples (Fig. 10), while needles of the third year, corresponding to 2001 growing season, display generally the highest values (Fig. 11). Anomalously high values were measured in pine needles at three sites (Figs. 10 - 11). These sites are located downwind the summit Etna's area, and they also are close to lateral eruptive fractures opened during the recent 2001 (SAS) and 2002-2003 (PRO and CIT) eruptions.

3.5. Soils

Results of fluorine content in soils are reported in table 5. Total fluorine content (F_{TOT}) of the 57 topsoil samples range from 112 to 341 µg/g, while fluorine extracted with oxalate (F_{OX}) range from 40 to 196 µg/g (representing from 23 to 93 % of F_{TOT}) and fluorine extracted with distilled water (F_{H2O}) range from 5.1 to 61 µg/g (2-40 % of F_{TOT}). Figure 12 displays the geographical distribution of F_{TOT}, F_{OX} and F_{H2O}, while Figure 13 shows their relation with distance from the summit craters. Samples of the downwind sector generally display higher values. A decreasing trend with distance from the summit craters can be recognized, at least for F_{H2O} values.

Figure 14 plots of F_{TOT}, F_{OX} and F_{H2O} values for the different grain sizes of three topsoil samples. One of these samples was collected on the upwind flank of the volcano (48) while the remaining two were collected on the downwind flank (31 and 35). The three profiles display increasing F_{TOT}, F_{OX} and F_{H2O} contents with decreasing grain size, indicating the greater affinity of fluorine for mineralogical phase(s) enriched in the finer fraction of the soil like clay minerals and amorphous phases of Al and Fe (Perrott et al., 1976). F_{TOT} display no significant differences between upwind

and downwind sample while F_{OX} and F_{H2O} show both higher absolute values and steeper concentration versus grain size relations in the two downwind samples.

Figure 15 investigates the dependence of F_{TOT}, F_{OX} and F_{H2O} on soil profile. F_{TOT} displays a greater range with respect to topsoils (149-490 µg/g – Table 5) with an increasing trend with depth. F_{OX} displays a range of values similar to topsoils (43-153 µg/g – Table 5) and increasing trends in the upwind profiles (Faggio, Leccio and Roverella) and a decreasing trend in the downwind profiles (Etna3 and Etna 5). F_{H2O} shows a decreasing trend in all the profiles (Fig. 15).

4. Discussion

4.1. Total fluorine deposition

The rain-gauges used in this study, being permanently open to the atmosphere, collect in addition to wet deposition also part of the dry deposition. Literature data state that deposition measured with such rain-gauges, known as bulk collectors, could be used as a proxy for total deposition for major ions (Erisman et al., 2003). Although these collectors catch also part of the dry deposition, their collection efficiency is very variable depending on chemical and physical properties of the considered species. Collection efficiency, for example, is very low for gases and increases with increasing particle size. Furthermore hygroscopic particles increase their deposition velocity with increasing atmospheric humidity.

Literature data on fluorine deposition fluxes show that the lowest values typically characterise areas poorly affected by anthropogenic sources like the ice-sheets on the Alps and in Greenland (0.09 – 6.6 mg/m^2/a; De Angelis & Legrand, 1994; Eichler et al., 2000; Preunkert et al., 2001). These deposition fluxes are significantly below the Etna range, provided in this study. In fact, we point out that the lowest deposition fluxes on the volcano are comparable with background values in

industrialised areas (10 – 100 mg/m^2/a; Elias et al., 1995; Saether et al., 1995; Chandrawanshi & Patel, 1999; Matschullat et al., 2000). The highest values, on the other hand, measured near to the summit vents, exceed the typical range measured in heavily polluted sites (200 – 2500 mg/m^2/a; Kauranen, 1978; Saether et al., 1995; Mayer et al., 2000) or near other active volcanoes (570 mg/m^2/a at Kilauea, Hawaii - Harding & Miller, 1982; 44 mg/m^2/a at Vulcano Island, Italy – Capasso et al., 1993). The only comparable deposition values are from a sampling site very close (200 m) to the summit craters of Stromboli (up to 25,500 mg/m^2/a – Bellomo et al., 2003). For comparison, fluorine gas output at Kilauea was estimated at about 0.9 Gg/a (1956-83 period; Gerlach & Graeber, 1985), at about 0.2 Gg/a Vulcano Island (1989-92 period; Italiano et al., 1994) and at Stromboli Island at about 1.8 Gg/a in 1998 (Allard et al., 2000).

Deposition rates determined during 2000-2003, coupled with previous measurements from 1997 to 2000 (Aiuppa et al., 2001), provide a quantitative basis for an assessment of total depositional fluxes of volcanogenic fluorine in the Etnean area throughout six years. In order to compute fluorine deposition fluxes (e.g., total amounts of fluorine deposited over an area of 20 km radius around the summit crater, time-weighted over each exposure period of bulk collectors), we interpolated daily deposition rates (in mg/m^2/d) measured at the 15 sites. Interpolation was performed by the use of simple power functions obtained – for each exposure period – by best fit of deposition rates versus distance trends (in all respect similar to the average trend drawn in Fig. 6) and integrating it over 360°. The so-derived fluorine depositional fluxes, drawn in Figure 16, range 0.2-17.1 Mg/d and average out 1.6±2.7 Mg/d over the 1997-2003 period. These fluxes are assumed to be of sole volcanogenic derivation, in the reasonable hypothesis that other contributions (either geogenic or anthropogenic) in the study area are negligible. They thus can be straightforwardly compared with average HF emission rates from the volcano, averaging ~ 200 Mg/d – based on a long-term average SO$_2$ emission rate of 5,560 Mg/d for the 1987-2000 period (Caltabiano et al., 2004) and a SO$_2$/HF plume mass ratio of ~ 27 (Francis et al., 1998; Pennisi and Le Cloarec, 1998; Aiuppa et al., 2002, 2004b; Burton et al., 2003). Despite inevitable uncertainty in the computation,

it can be estimated that less then about 1 % of total fluorine emissions from the volcano are deposited on the Etna region as wet (and dry) deposition.

Figure 16 compares the calculated F deposition fluxes with the above calculated and time-averaged F emission rates from the summit craters (Bruno et al., 2003; Caltabiano et al., 2004). Although deposition fluxes are characterised by a smooth seasonal trend, with highs during winter (wet) periods, and emission rates are only indicative, because variations in the SO_2/HF plume ratio are not taken into account, a fair correlation with F deposition fluxes can be recognized.

The anomalous phase of magmatic degassing (Bruno et al., 2003) during the October 2002-January 2003 eruptive phase is clearly reflected by exceptional bulk deposition fluxes (Fig. 16), by far the highest ever measured in the area during the six years of observation. This fits earlier findings at other volcanoes (Durand and Grattan, 1999, Thordarson and Self, 2003) that basaltic eruptions may potentially contribute to enhanced deposition of plume-derived volatiles. We estimate that about 1 Gg of volcanogenic fluorine were deposited over the Etnean area throughout the ~90 days of the 2002-2003 eruption (at an average rate of 11.4 Mg/d), which corresponds to about the amount of fluorine deposited during four years of quiescent degassing from the volcano (at an average rate of 0.8 Mg/d). The enhanced total deposition depends not only from higher summit crater emission but also from higher deposition percent (> 3 %) due to higher dry deposition through volcanic ash.

Dry deposition has sometimes been derived from gas and particulate concentration values measured in the atmosphere multiplied by the estimated deposition velocities (V_d). Calculation of fluorine dry deposition along the Etnean flanks could therefore tentatively be estimated from gas concentrations determined with passive samplers, the F particulate emission trough the summit craters being minor (<5%; Aiuppa et al., 2003c) during periods of low ash emission. Deposition velocities for gaseous fluorine (HF) are in the order of 1 cm/s for grass-covered soils (De Temmerman et al., 1985; 1986). For bare soils, they are probably a little lower (V_d=0.5), while for wooded areas typically much higher (V_d 2-5). For the present estimation, we used the intermediate value of 1 cm/s considering the high proportion of bare land in the area close to the summit craters. The so-calculated dry

deposition values are - at the corresponding distance from the crater - lower than bulk deposition values, although in some case only slightly (Fig. 17). Total calculated dry deposition rate for the Etnean area for the period May-June 2002 is 0.06 Mg/d, which represents some 20% of bulk deposition. Considering that May-June 2002 is a dry period in Sicily, it should be argued that dry deposition is - on a yearly basis - a secondary fluorine deposition mechanism, at least on Etnean area. On the contrary, dry deposition is likely the prevailing F-scavenging mechanism during periods of intense ash emission, when soluble fluorine salts are adsorbed on ash particles, later deposited on the ground. Particulate fluorine has, in fact, much shorter residence time in the atmosphere with respect to gaseous fluorine (WHO, 2002). This is reflected by the very high bulk depositions measured during the last two eruptions, accounting for a larger fraction of plume-derived volatile emission rates (3-5 % - Fig. 16). The obtained total deposition value for the 2001 eruption of about 71 Mg compared with the estimated deposition through ash (see par. 3.3) of about 60 Mg gives a percent of dry deposition of at least 85%, much higher than in May-June 2002.

4.2. Impact on vegetation

The predominant route through which gaseous fluoride enters plants is diffusion through the stomata on the leaf. When diffusion into the aqueous phase of the mesophyll from the substomatal space is the rate-limiting process, HF will be absorbed at a greater rate than other gaseous pollutants owing to its lower molecular weight and greater solubility in water (Davison, 1986). Particulate F is deposited to the surface of the leaf, and its subsequent penetration into the leaf is slow and depends upon the solubility of the material, particle size, relative humidity, and the presence of dew or other tree water on the foliar surface. The superficial deposits, which can include gaseous F sorbed to the waxy cuticle of the leaf or materials residing upon it as well as F from the interior of the leaf, can be eluted from the foliar surface by precipitation (McCune and Weinstein, 2002). The amount of F normally accumulated from the soil through the roots is small and there is little relationship

between concentrations in plants and total content in soils (Weinstein, 1977). Some closer relationship is known to exist between concentrations in plants and F_{H2O} in soils, especially in polluted sites where F_{H2O} represents a high percentage of F_{TOT} (Egli et al., 2004). Biological factors, such as species, cultivar, and stage of development, can determine the uptake of F and its concentration in the foliage by affecting stomatal conductance, surface to volume ratios of the leaf, and leaf area index of the plant (Horntvedt, 1997).

Background concentration of F in plants is usually <10 µg/g, while in plants exposed to anthropogenic pollution it can reach values as high as 1000 µg/g (WHO, 2002 – Fig. 18). Chestnut leaves and pine needles collected on the flanks of Mt. Etna display values in the lower range of the plants living in polluted area, although most of the sample also fall within the upper limit of natural vegetation (Fig. 18). This is probably because most studies on harmful effects of anthropogenic fluorine on plants are based on samples collected very close to the pollution source (< 2 km), while samples collected on Etna grow much farther away (> 4.2 and > 6.7 km from summit craters for pines and chestnuts respectively). Present data are comparable with previous data obtained on grass and lichens collected on Etna in 1987 (Nottcut and Davies, 1989 – Fig. 18). Lichens display slightly higher F concentrations probably due to additional direct F uptake from rainwater not mediated by F adsorbing soils. A few data reported by Garrec et al. (1984) display a higher range (113-295 µg/g) for non-specified plant samples collected in 1976 on the north-eastern high flank of the volcano and along the 1971 eruptive fissure. These higher values could be explained by at least one of the following reasons: (i) the samples were collected in the area most affected by plume fumigation; (ii) sample could have been collected from very tolerant and accumulating species such as birch or juniper; (iii) the proximity of the 1971 eruptive fissure could have still affected the surrounding vegetation through F release. The latter hypothesis should be consistent with data reported by Davies and Nottcut (1989), showing enhanced F levels in lichens growing close to an eruptive fissure that had been active tens of years before sample collection.

Many compilations are available in the literature of the relative sensitivities of crops and native species, usually with reference to three classes - 'sensitive', 'intermediate', and 'tolerant' - and the difference between a sensitive and tolerant species may be equivalent to a 20-fold difference in concentration in HF (Arndt et al., 1995; Weinstein, 1977). No data have been found on sensitivities of the two species collected for the present study, although many data have been published on other pine species, which are generally considered sensitive or in few cases intermediate. Fluorine sensitive species have also lower accumulation capacities with respect to tolerant species (Horntvedt, 1997). At sites where both the two species were simultaneously collected (Fig. 19), we point out higher values in chestnut leaves than in pine needles, suggesting a possible higher tolerance of the former.

Chestnut leaves collected in 2002 display the highest value (Fig. 10). This finding, which is not confirmed in pine needles grown in the same period (2nd year), cannot be explained by higher F emission rates from the summit craters. Plume emissions were, in fact, anomalous low in that period (Fig. 16). Previous studies on the effects of contemporaneous presence of SO_2 and HF in atmosphere on plants assessed a lower F accumulation in vegetation due to reduced stomatal conductance in response to the presence of SO_2 (Weinstein, 1977). We may speculate that the reduced SO_2 emission, and consequently lower concentrations in atmosphere, during 2002 could possibly have induced a higher F accumulation through higher stomatal conductance despite lower F emission from the crater. As an alternative explanation, it is interesting to note that - before the 2002 sampling survey - rainfall was less intense and farther back in time (up to one week) than during the 2001 and 2003 surveys, thus increasing the eventuality of some contribution from the particulate fraction deposited on the surface of the leaves. Another possibility is that in the period preceding the sampling the anomalous sites were more frequently subjected to fumigation: this hypothesis is reinforced by the location of theses sites, being comprised in a narrow 40 degrees stripe downwind the summit vents. Pine needles of three sites (PRO, CIT and SAS) display a strong increase of fluorine contents with needle age (Fig. 11), up to values usually associated with visible

symptoms (> 30 µg/g for sensible species). Tip of the needles of the sites PRO and CIT actually appear slightly chlorotic. Needles at the site SAS display much stronger symptoms (strong chlorotic or even necrotic tips), also increasing with needle age. Third year needles (corresponding to growth year 2001) are nearly totally necrotic and fourth year needles totally lacking. The side of the trees facing to the west (pointing toward the direction of the 2100 m vent of the 2001 eruption) appears like burned with the branches totally devoid of needles (Fig. 20). The highly fluorine enriched gases (Aiuppa et al, 2002) released by the lower vent during the 2001 eruption (distance about 1.5 km downwind) were possibly responsible of the damage to vegetation in this site. Similarly, the chestnut leaves collected at VZA (2.5 km downwind) are up to 5 times F-enriched with respect to leaves collected farther away (Fig. 10).

Sites PRO and CIT are located in proximity of the 2002-2003 eruptive fissure (about 2 and 4 km downwind, respectively); there, the milder symptoms detected during sampling survey can be possibly ascribed to greater distance and/or to the different season in which the eruption took place, this latter influencing both vegetative status and fluorine deposition (prevailingly wet). It is to be noted that the above sites (SAS, VZA, PRO and CIT) are characterised by much lower values in 2003 than in previous years (slightly above or even within the range of the other sites are observed in 2003), matching the hypothesised close link between anomalous F-contents and occurrence of volcanic eruptions.

Apart from the above described peculiar cases, vegetation does not display any evident symptom that can be related to the impact of HF or other phytotoxic gases released by the volcano. Indeed, the HF concentrations we measured in air during June 2002 are systematically below phytotoxic values in areas covered by vegetation. Nevertheless, generalisations are not straightforward, as plume emission rates at that time were one order of magnitude lower than long-term averages. If we accept that plume dispersion pattern are substantially constant with time, it is realistic that concentrations harmful to vegetation can be reached, particularly during high HF emission periods and in the downwind area. However, even in high fluorine emission periods, no visible symptom

has ever been noted up to date. This evidence could be tentatively ascribed to the neutralising action played by the high Ca deposition rates in the Etnean area (Aiuppa et al., 2003a), a common feature of the Mediterranean area. Many studies have in fact pointed out the detoxification capacity of Ca with respect to F (Garrec et al., 1978; 1982). Furthermore, as hypothesised by Le Guern et al., (1988), Etnean long-living plants could have developed some kind of resistance to volcanic gas exposure. The same authors reported an example of probable development of such kind of resistance also for pines imported for reforestation from Austria. Only about 20% of these trees, planted at the beginning of the twentieth century, reached maturity, but since 1970's the progeny of these plants showed no symptoms related to volcanic gas exposure, while there is no evidence of diminution of volcanic gas emission.

Annual crops, on the contrary, sometimes display visible necrotic areas on the foliage that farmers relate to volcanic activity. This is particularly true for vegetables with large leaves: probably because leaves provide the main pathway for uptake and accumulation of phytotoxic compounds deposited from the atmosphere. Damage to cultivated plants occurs mainly on the eastern slopes of Mt. Etna up to distances of 20 km from the summit craters. These plants, whose seeds generally come from outside the Etnean area, possibly fail to develop resistance; there is however no direct evidence that fluorine, either in gaseous or ionic form, is actually responsible of the reported damages. Furthermore, even in very high emission periods, it is unlikely that phytotoxic gas level are attained at distances higher than 10 km. More likely, damages could be attributed to acid rains, whose acidity is sometimes derived from dissolution of acid volcanic gases (mainly SO_2 and HCl - Aiuppa et al., 2003a).

4.3. Effects on soils

Total fluorine content in the Etnean soil fall within the range typical of undisturbed soils (i.e., not affected by anomalous fluorine deposition; WHO, 2002 – Fig, 21). However, total soil F is thought

to be a poor indicator of soil pollution status, due to great natural variation in content, in sorption strength and sorption capacity of different soils (Arnesen et al., 1995; Brewer, 1966). Soluble F (F_{H2O}) is probably a better indicator of the pollution situation and the F availability for plants (Arnesen, 1997). Compared with literature data on natural soil samples (WHO, 2002), Etnean soils are anomalous as concern their F_{H2O} values (Fig. 21). The volcanogenic origin of this anomalous F_{H2O} content from atmospheric deposition of plume emissions is suggested by: (i) the inverse relation with the distance from the summit craters for the topsoil samples (Fig. 13) and (ii) the inverse relation with depth in the soil profiles (Fig. 15). F_{OX} and F_{TOT} display less clear relations, probably because they are much more influenced by F inherited from rock weathering. Etnean volcanites have F contents in the 240 - 985 µg/g range (average 550 µg/g – Metrich, 1990). Furthermore, F derived from atmospheric deposition shows a great affinity to soil forming phases, such as clay minerals and amorphous phases (allophane, imogolite, etc), which are enriched in finer portions of the soils (Fig. 14). In fact, while F_{TOT} display no significant differences, F_{OX} and especially F_{H2O} show much higher values and a much steeper increase with decreasing grain-size in samples collected downwind the summit craters (Fig. 14).

4.4. Role of Etnean soils in groundwater protection

Many volcanic areas often display fluorine contents in groundwaters higher than the safe drinking water limit (1.5 mg/l – WHO, 2002). Given the huge average fluorine wet deposition (0.58 Gg/a – Fig. 16), high fluorine concentrations in Etnean groundwater should be expected. Despite volume weighted average value of fluorine concentration in meteoric recharge is about 2 mg/l, F contents in groundwater are typically below the limit for drinking water, ranging from 0.02 to 1.0 mg/l, with an average value of 0.43 mg/l (Aiuppa et al., 2002). The estimated fluorine groundwater discharge in the volcanic aquifer is 0.3 Gg/a (Aiuppa et al., 2002), with a main contribution from rock weathering (0.13 Gg/a – Aiuppa et al., 2000). Thus, an important fluorine sink must be invoked.

Recent studies have demonstrated the great fluorine adsorbing capacity of andosoils typical of active volcanic areas (Zevenberger et al., 1996; Delmelle et al., 2003) and related it to chemisorption on "active" Al-bearing phases, mainly in the form of allophane. Experiments performed on samples of the soil profiles Etna3 and Etna5 highlighted high fluorine adsorption capacities also for the Etnean soils. After 192 hours, the adsorbed F fractions ranged from 0.44 to 0.91, and some samples also showed very high adsorbed fractions (up to 0.54) after only 2 hours (Fig. 22).

Fluorine adsorption capacity of volcanic soils has been proposed as an economical and efficient defluorination method for drinking waters in rural areas in Africa (Zevenbergen et al., 1996). In the Etnean area, volcanic soils exert its defluorination action naturally, retaining about 0.3 Gg of fluorine each year and protecting the very important water resources of the area from excessive fluorine contents.

4.5. Influence on human health

Concern about effects of volcanic gases and ashes on human health has long been expressed (Baxter et al., 1982; Thorarinsson, 1979; Allen et al., 2000), and paroxysmal volcanic activity is suggested as having produced in the past severe effects on air quality and hence on human health in Europe, even at distances of more than 1000 km (Camuffo and Enzi, 1995; Durand and Grattan, 1999; Grattan et al., 2003). Despite many reported cases of negative effects on human health, no one should be directly related with fluorine gases or fluorine on volcanic ashes. This is due to the higher threshold of humans with respect to effect of fluorine gases, as compared to vegetation. The National Institute for Occupational Safety and Health (NIOSH, 2003) indicate an 8-hr time weighted average recommended exposure limit of 3 ppm (2.45 mg/m^3), a 15-min ceiling limit of 6 ppm (4.9 mg/m^3) and an immediately dangerous to life and health level of 30 ppm (24.5 mg/m^3). Transitory symptoms for upper airways and eyes have been ascertained for healthy volunteers

exposed to HF concentrations in the range 0.2-0.6 mg/m^3 (Lund et al., 1997). Such concentrations could easily be reached at Etna on the crater rim (values higher than 2 mg/m^3 have been measured – Aiuppa et al., 2002). Although fluorine values of the same magnitude have been reported close to the vents of many volcanoes, other gases with higher concentration and/or toxicity are of greater concern for human health (e.g. SO$_2$, HCl, As, Hg etc. – Baxter et al., 1990; Durand et al., 2004). The same holds true for Etna.

As we have seen above, fluorine concentrations in groundwater is always within safe drinking water limits (Aiuppa et al., 2003b); thus, the sole effects on human health that might be ascribed to volcanogenic fluorine is the unusually high incidence of malignant pleural mesothelioma in the town of Biancavilla (lower south-western flank of Etna) related to Fluoro-Edenite (Paoletti et al., 2000; Comba et al., 2003). The latter is a newly identified fibrous amphibole (Gianfagna and Oberti, 2001), in which oxidrile groups have been almost completely substituted by fluorine. It is still not clear if fluorine enrichment can be ascribed to processes that acted in the magmatic chamber or after emplacement of the "Biancavilla ignimbrite", which is the only known volcanic formation that contains this dangerous mineral. But this natural health risk factor has been much increased by human activities. The "Biancavilla ignimbrite" has been, in fact, intensively quarried in recent year and used in, often not regulated, building activities of the town of Biancavilla. Effects are probably enhanced by the fact that the rock is often used as loose material for street pavement, exposing population to high concentrations of airborne fibres (Paoletti et al., 2000).

5. Summary

Mt. Etna releases through open conduit degassing on average about 200 Mg hydrogen fluoride each day. Release is highly variable ranging from about 20 to 1000 Mg/d (Francis et al., 1998; Pennisi and Le Cloarec, 1998; Aiuppa et al., 2002, 2004b; Burton et al., 2003). Only about 1% of the

emitted fluorine is deposited on average along the Etnean area, wet deposition being generally the main deposition mechanism. Dry deposition generally accounts for less than 20% of total deposition, but during periods of high ash emission it becomes the principal fluorine deposition process. Condensation and reaction of HF on the surface of ash particles, in fact, is a very effective scavenging mechanism (Oskarsson, 1980).

The imprint of plume-released fluorine on rainwater chemistry and on water extractable fluorine in soils is clearly detectable up distances of more than 20 km from the summit craters in the downwind direction. Volcanogenic HF was detected in air only up to distances of about 6 km in the downwind direction, but this have to be considered a minimum distance because measurements were made in a period of very low emission from the crater (June 2002).

Vegetation displays generally no strong fluorine accumulation except for a few sites, which are either in areas interested by plume fumigation or close to active degassing eruptive fractures of the most recent eruptions (July-August 2001 and October 2002 – January 2003).

Finally, soils, absorbing about 60% of the fluorine deposited from the atmosphere, exert an important protective action of the volcanic aquifers, maintaining the fluorine concentration in groundwater always within the safe drinking water limit (1.5 mg/l – WHO, 2002).

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Table 1 – Gas concentrations in air measured with passive samplers

Site	distance	altitude	HF	HCl	SO$_2$
	km	m.a.s.l.	µg/m^3	µg/m^3	µg/m^3
TDF	1.2	3000	3.0	74	720
PLU	1.7	2920	0.1	5.0	46
PDN	2.5	2850	1.3	40	273
VBN	4.3	2300	0.3	14	107
GAL	4.4	1750	<0.1	0.8	12
SAS	5.5	2050	0.1	5.1	34
CIT	5.9	1750	0.3	7.4	68
PRO	6.3	1800	0.2	4.8	51
SLN	6.7	1725	<0.1	0.6	8.3
ZOC	6.8	1730	<0.1	1.5	11
CUB	7.7	1175	<0.1	1.1	13
SMR	7.9	1630	<0.1	2.6	24
MCL	8.8	1150	<0.1	<0.5	8.1
PCA	9.3	975	<0.1	<0.5	7.6
INT	9.6	1525	<0.1	0.7	6.8
BRO	11.2	1050	<0.1	0.8	6.4

Table 2 – Fluorine content in rainwater and bulk deposition data of the Etnean area

	ARO		CAT		FON		INT		LIN		MAL		NIC		PDN		POZ		PRO		SDO		SLN		TDF		VER		ZAF	
Month	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.	mg/l	dep.
Nov-00	0.07	0.16	0.14	0.16	0.27	0.19	0.12	0.22	1.43	2.48	0.05	0.08	0.14	0.26	b	b	0.31	0.24	14.5	9.51	a	a	0.85	1.52	b	b	b	b	0.20	0.97
Dec-00	b	b	0.08	0.09	0.18	0.19	0.11	0.21	0.25	0.29	0.02	0.02	0.09	0.14	b	b	0.07	0.09	5.49	4.78	a	a	0.34	0.89	33.3	17.6	b	b	0.54	0.90
Jan-01	0.05	0.12	0.04	0.13	0.06	0.23	0.06	0.43	b	b	0.02	0.06	0.05	0.29	b	b	0.05	0.21	0.82	4.20	a	a	0.09	0.63	b	b	0.18	0.47	0.07	0.91
Feb-01	0.13	0.14	0.13	0.05	0.39	0.48	0.38	0.71	0.26	0.43	0.06	0.06	0.24	0.23	10.0	21.3	0.12	0.21	0.61	1.51	a	a	0.75	1.20	b	b	0.19	0.31	1.01	1.73
Mar-01	0.09	0.08	0.27	0.15	0.54	0.19	0.02	0.03	1.26	0.96	0.02	0.02	0.15	0.17	b	b	0.48	0.23	4.70	3.70	0.09	0.05	3.04	2.48	23.4	31.0	0.14	0.10	0.53	0.60
Apr-01	0.18	0.18	0.20	0.12	0.49	0.35	0.07	0.16	0.49	0.75	0.02	0.03	0.60	0.58	b	b	0.28	0.26	0.95	1.62	0.06	0.04	3.19	8.13	21.0	8.46	b	b	a	a
May-01	0.08	0.08	0.09	0.08	0.37	0.13	0.13	0.19	0.23	0.23	0.04	0.04	0.07	0.07	6.59	16.1	0.15	0.11	1.14	1.14	0.03	0.06	0.11	0.16	27.7	13.2	0.12	0.15	0.28	0.47
Jun-01	0.20	0.04	0.27	0.04	0.52	0.05	a	a	0.07	0.04	0.13	0.10	0.62	0.07	1.65	1.23	0.42	0.12	0.33	0.29	0.16	0.04	0.30	0.14	28.7	6.83	0.15	0.03	1.31	0.42
Sep-01	1.17	1.81	0.95	1.17	0.49	0.62	a	a	0.21	0.79	0.04	0.12	1.94	3.12	2.03	3.65	1.35	1.60	1.06	3.36	0.25	0.48	3.35	10.2	6.29	12.1	0.06	0.11	2.45	5.38
Oct-01	c	c	c	c	c	c	0.03	0.01	0.51	0.14	c	c	c	c	4.64	1.35	c	c	0.55	0.29	c	c	0.38	0.09	9.17	1.23	c	c	0.32	0.06
Nov-01	0.10	0.10	0.20	0.10	0.64	0.19	a	a	0.16	0.13	0.55	0.38	0.74	1.07	b	b	0.15	0.12	1.44	1.10	0.08	0.06	0.17	0.31	b	b	3.21	3.95	0.13	0.37
Dec-01	0.08	0.05	b	b	0.07	0.14	a	a	b	b	b	b	0.05	0.08	b	b	0.05	0.10	0.10	0.35	0.03	0.01	0.23	0.41	18.6	5.72	0.04	0.12	0.06	0.30
Jan-02	0.11	0.21	0.09	0.07	0.08	0.08	a	a	0.03	0.07	0.01	0.02	0.42	0.91	6.19	5.99	0.43	0.46	0.49	0.63	0.41	0.62	0.48	0.90	33.3	5.67	0.09	0.15	0.15	0.36
Feb-02	0.42	0.82	0.01	0.02	0.42	1.13	0.22	0.27	0.11	0.46	0.14	0.06	0.42	0.88	b	b	0.42	1.00	0.23	0.39	0.43	0.38	0.47	0.98	20.9	6.26	0.43	0.84	0.42	1.66
Mar-02	0.05	0.05	0.04	0.02	0.07	0.09	0.02	0.04	0.08	0.20	0.06	0.05	0.04	0.04	b	b	0.04	0.06	0.59	1.25	0.02	0.02	0.12	0.14	15.0	7.89	0.08	0.10	0.04	0.11
Apr-02	0.19	0.20	0.15	0.11	0.13	0.22	0.09	0.16	0.12	0.26	0.05	0.10	0.25	0.36	b	b	0.20	0.37	0.20	0.45	0.10	0.13	0.35	0.84	30.8	31.0	0.12	0.24	0.53	1.41
May-02	0.06	0.08	0.03	0.08	0.07	0.10	0.05	0.11	0.02	0.09	0.03	0.06	0.04	0.11	1.88	3.49	0.04	0.08	0.07	0.20	0.04	0.08	0.05	0.11	4.69	4.72	0.02	0.05	0.04	0.13
Jun-02	0.08	0.04	0.09	0.03	0.12	0.04	a	a	0.14	0.14	0.03	0.03	b	b	0.82	3.67	0.11	0.07	0.26	0.39	0.11	0.06	0.21	0.22	a	a	0.04	0.04	0.27	0.14
Aug-02	0.33	0.09	0.37	0.06	0.24	0.10	a	a	0.11	0.08	0.04	0.03	0.16	0.10	2.79	1.34	0.21	0.10	0.24	0.27	0.17	0.11	0.41	0.50	a	a	0.06	0.04	0.36	0.61
Sep-02	0.18	0.06	0.16	0.05	0.16	0.16	a	a	0.12	0.21	0.03	0.04	0.15	0.12	2.76	4.65	0.25	0.37	0.33	0.97	0.03	0.06	0.13	0.24	a	a	0.08	0.17	0.56	1.02
Oct-02	0.04	0.02	0.07	0.02	0.17	0.13	a	a	0.28	0.33	0.01	0.01	0.09	0.05	2.49	9.25	0.17	0.05	2.40	2.37	0.01	0.02	0.09	0.15	a	a	0.05	0.07	0.15	0.18
Nov-02	1.53	3.15	3.75	7.93	5.39	8.32	1.46	4.45	2.98	14.3	4.99	6.34	7.64	18.8	b	b	9.93	21.2	a	a	0.27	0.59	6.65	21.3	a	a	3.53	6.18	9.34	37.8
Dec-02	1.53	4.00	1.39	2.86	4.52	10.3	4.23	23.4	4.76	33.8	0.69	1.87	1.48	6.14	b	b	2.81	9.02	8.42	61.5	1.34	2.67	4.90	33.5	a	a	1.80	7.64	8.35	24.8
Jan-03	0.17	0.24	0.17	0.37	0.63	1.47	0.06	0.26	0.31	1.81	0.04	0.11	0.42	0.89	b	b	0.78	2.18	0.72	3.87	0.04	0.06	0.47	2.27	a	a	0.09	0.39	2.90	11.9
Feb-03	0.05	0.11	0.06	0.14	0.16	0.25	b	b	0.03	0.13	0.02	0.05	0.08	0.31	b	b	0.06	0.17	a	a	0.02	0.04	0.12	0.31	a	a	0.03	0.10	0.23	0.93
Mar-03	0.03	0.05	0.04	0.11	0.07	0.16	0.01	0.03	0.01	0.03	0.01	0.01	0.03	0.10	10.5	13.1	0.07	0.16	a	a	0.02	0.03	0.07	0.13	a	a	0.02	0.05	0.11	0.70
Apr-03	0.05	0.16	0.07	0.16	0.07	0.22	0.02	0.13	0.04	0.28	0.06	0.12	0.06	0.33	b	b	0.06	0.15	a	a	0.05	0.15	0.11	0.84	a	a	0.05	0.17	0.11	0.61
May-03	0.09	0.02	0.04	0.01	0.18	0.07	0.15	0.09	a	a	0.14	0.05	0.03	0.02	b	b	0.06	0.03	a	a	0.10	0.02	0.13	0.08	a	a	0.02	0.01	0.11	0.09
Jun-03	0.18	0.11	0.27	0.04	c	c	0.21	0.27	0.12	0.07	0.16	0.09	0.14	0.06	b	b	c	c	0.11	0.27	b	b	0.34	0.19	a	a	0.04	0.03	0.34	0.13
Jul-03	0.14	0.04	0.10	0.00	0.22	0.06	0.08	0.05	0.05	0.05	0.08	0.06	b	b	1.32	1.91	0.59	0.08	0.07	0.08	0.12	0.12	0.18	0.13	a	a	0.21	0.02	0.63	0.28
Aug-03	0.38	0.04	b	b	b	b	0.05	0.11	0.21	0.12	0.05	0.02	b	b	1.76	0.97	b	b	0.51	0.50	b	b	0.19	0.21	1.33	1.81	0.08	0.05	0.10	0.19
Sep-03	0.04	0.11	0.07	0.12	0.13	0.16	0.04	0.03	0.03	0.10	0.20	0.26	0.05	0.10	0.26	1.35	0.06	0.12	0.04	0.51	0.19	0.06	0.11	0.71	0.27	2.96	0.06	0.08	0.07	0.80
Oct-03	0.03	0.07	0.04	0.12	0.09	0.47	0.06	0.19	0.14	0.91	0.13	0.25	0.02	0.05	8.60	8.79	0.06	0.20	0.65	1.76	0.03	0.07	0.05	0.11	0.41	1.00	0.10	0.14	0.07	0.29

Dep. = deposition in mg/m^2/day; a = collector not exposed; b = cumulated in the following sample; c = no rainfall.

Table 3 – Fluorine concentrations in ash leachates and deposition data

Site			ash dep.	total F dep.	Φ = -2	Φ = -1	Φ = 0	Φ = 1	Φ = 2	Φ = 3	Φ = 4	Φ = 5
	km	F μg/g	g/m^2	g/m^2					F μg/g			
E 1	15.3	54.9	435	0.024	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
E 2	13.7	86.7	390	0.034	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
E 3	10.5	58.2	1210	0.070	n.s.	n.s.	n.s.	92.0	47.4	46.2	85.4	222
E 4	9.3	49.6	1960	0.097	n.s.	n.s.	40.6	53.3	42.8	49.5	76.0	184
E 5	8.3	39.2	2710	0.106	n.s.	n.s.	45.8	37.9	33.0	43.5	60.7	140
E 6	5.8	46.7	2550	0.119	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
E 7	10.7	74.7	730	0.055	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
E 8	10.0	55.4	340	0.019	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
E 9	11.5	56.6	1820	0.103	n.s.	n.s.	39.0	44.6	58.6	53.7	99.2	249
E 10	15.0	52.8	3090	0.163	n.s.	n.s.	n.s.	53.5	50.1	48.4	79.0	280
E 13	17.8	98.0	650	0.064	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
E 17	13.0	51.8	300	0.016	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
E 19	24.5	62.0	390	0.024	n.s.	n.s.	n.s.	n.s.	58.2	59.2	62.0	306
E 20	23.0	67.4	900	0.061	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
E 22	16.3	75.5	2730	0.206	n.s.	n.s.	63.3	69.6	71.8	68.4	100	235
E 23	16.0	95.9	520	0.050	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
E 25	14.0	71.9	2400	0.173	n.s.	n.s.	52.0	56.6	71.2	84.0	112	295
E 26	15.8	65.5	1410	0.092	n.s.	n.s.	n.s.	53.7	50.3	65.5	85.9	239
E 28	20.2	60.4	1510	0.091	n.s.	n.s.	n.s.	61.2	59.2	52.1	84.4	476
E 29	12.7	40.8	2025	0.083	n.s.	n.s.	n.s.	33.4	35.2	47.7	86.2	413
E 32	13.0	65.0	3330	0.217	n.s.	n.s.	n.s.	38.6	57.1	66.8	114	275
E 33	16.7	63.3	3450	0.218	n.s.	n.s.	n.s.	40.6	58.0	65.2	164	326
E 34	22.5	67.4	550	0.037	n.s.	n.s.	n.s.	52.6	59.8	65.0	127	306
E 36	7.2	39.3	4190	0.165	n.s.	n.s.	25.0	29.7	34.6	68.0	206	n.s.
E 37	2.7	40.6	11490	0.466	17.7	28.6	31.9	36.8	53.5	109	295	n.s.
E 38	3.3	37.9	21830	0.828	31.1	34.0	36.4	33.5	46.3	96.9	222	n.s.
E 39	4.3	51.0	18000	0.917	26.5	33.3	38.7	48.0	61.7	109	187	n.s.
E 40	5.0	62.6	5750	0.360	n.s.	37.0	46.7	53.7	61.2	86.7	160	267
E 41	6.2	61.8	5570	0.344	n.s.	36.5	41.4	54.0	60.5	73.4	121	235
E 42	6.8	69.6	3980	0.277	n.s.	n.s.	54.2	54.1	61.4	82.8	151	259
E 43	4.0	37.5	9550	0.358	19.5	24.5	26.6	33.5	49.7	95.8	269	n.s.
E 44	4.7	29.0	23800	0.691	15.0	21.4	24.2	26.7	30.7	83.3	229	n.s.
E 45	6.0	34.4	12170	0.418	n.s.	22.9	28.5	28.1	34.3	65.6	231	n.s.
E 46	6.5	61.1	2330	0.142	n.s.	n.s.	n.s.	49.5	56.9	100	n.s.	n.s.

km = distance from the 2550 m vent of the July-August 2001 lateral eruption; ash dep. = total ash deposition; total F dep. = total leachable fluorine deposition (bulk sample); leachable fluorine analysis performed on separate grain-size classes (Φ) are also reported. n.s. = no sample.

Table 4 – Fluorine contents in chestnut leaves and in pine needles collected in the Etnean area.

CHESTNUT LEAVES				
Year	2001	2002	2003	
SITE		µg/g		km
SLI			7.4	12.9
LIN	6.1		5.7	11.5
CAZ			5.7	14.8
CUB		29	5.0	7.8
SFO	10			8.5
MCL		23	7.5	8.9
SGI	9.6	19	8.4	10.2
PCA	1.8		10	9.8
ZOC		35		7.3
ZOB			17	7.6
PDV	7.8	22	11	7.6
VZA	25	16		7.3
TAR			5.2	13.1
SNI	11			10.5
SLN			7.5	6.7
RAG			6.3	8.1
FIL	5.8			6.9
INT	7.1	7.3	4.9	7.8
BRO	11		6.7	11
SML			6.1	10.5
RAN			7.6	13.2
VER			4.2	15.6
TLR			6.1	11.9

PINE NEEDLES					
Year	4th	3rd	2nd	1st	
SITE		µg/g			km
PRO		26	36	5.5	5.9
SLI	3.9	7.3	4.7	2.4	12.9
LIN		5.4	3.9	3.6	11.5
CAZ	2.3	5.1	4.2	3.2	14.8
CIT	64	49	26	6.0	5.8
CUB	13	9.3	11	2.1	7.8
TAR	2.9	5.5	3.4		13.1
SAS		74	64	16	5.9
NIC		4.2	3.7	2.4	14.3
SLN	6.5	9.1	6.0	3.0	6.7
RAG	5.5	8.6	4.8	4.0	8.1
GAL		5.7	8.2	5.0	4.3
INT	2.9	5.9	4.1	2.9	7.8
BRO	4.4	6.3	4.6	3.7	11.0
MAL		7.8	6.2	6.3	14.2
SMT	10	7.7	7.2	7.4	4.2
SML	4.0	6.3	3.6	4.0	10.5
RAN		2.7	3.8	2.8	13.2
TLR	5.3	8.2	4.4	3.8	11.9
VER	2.2	7.2	5.0	4.1	15.6

Concentration are expressed as µg/g of dry weight; km = distance from the summit craters; sites upwind the summit crater are in italics. Pine samples collected in 2003 are subdivided in years of growth.

Table 5 – Fluorine contents in the Etnean soils

			TOPSOILS				
SITE	km	pH	F $_{H2O}$ µg/g	F $_{OX}$ µg/g	F $_{TOT}$ µg/g	F $_{H2O}$ %	F $_{OX}$ %
ETS01	11.6	6.66	7.9	115	208	4	56
ETS02	10.4	6.43	19.2	134	225	9	59
ETS03	9.4	6.05	16.4	106	183	9	58
ETS04	9.4	6.74	24.5	137	285	9	48
ETS05	8.0	6.62	35.3	175	255	14	69
ETS06	7.6	6.29	18.7	136	198	9	69
ETS07	6.0	6.12	11.0	84	265	4	32
ETS08	7.7	6.67	33.9	149	170	20	88
ETS09	8.8	6.63	15.9	110	257	6	43
ETS10	6.6	6.70	19.6	117	256	8	46
ETS11	5.6	6.48	22.2	165	231	10	71
ETS12	4.7	6.67	31.7	106	210	15	50
ETS13	4.3	6.32	17.0	129	202	8	64
ETS14	5.7	6.79	20.8	97	177	12	55
ETS15	3.7	6.08	8.8	104	183	5	57
ETS16	3.7	6.26	17.6	110	265	7	41
ETS17	4.3	6.16	20.5	174	251	8	69
ETS18	4.4	6.40	61.2	143	154	40	93
ETS19	6.1	6.43	15.0	104	142	11	73
ETS20	7.5	6.85	11.3	65	172	7	38
ETS21	5.0	6.45	18.0	132	214	8	62
ETS22	7.9	6.93	15.5	70	160	10	43
ETS23	8.7	7.03	22.8	78	202	11	39
ETS24	8.7	6.96	18.9	67	206	9	33
ETS25	8.4	6.13	21.3	112	208	10	54
ETS26	7.9	5.77	16.8	124	214	8	58
ETS27	8.0	6.60	23.9	117	227	11	51
ETS28	8.7	6.39	17.1	96	325	5	29
ETS29	10.4	6.87	11.0	79	141	8	56
ETS30	5.8	6.10	27.1	187	313	9	60
ETS31	5.5	6.02	13.8	112	163	8	69
ETS32	6.5	6.16	38.4	132	324	12	41
ETS33	7.3	6.45	22.4	121	295	8	41
ETS34	6.7	6.44	20.8	125	341	6	37
ETS35	5.7	6.25	44.5	134	273	16	49
ETS36	5.7	6.19	28.3	80	150	19	53
ETS37	9.0	6.63	22.6	125	285	8	44
ETS38	7.0	6.67	29.9	154	310	10	50
ETS39	7.6	6.53	30.6	196	215	14	91
ETS40	4.3	5.59	16.0	139	155	10	90
ETS41	4.8	5.67	8.2	113	202	4	56
ETS42	5.4	5.61	10.1	147	295	3	50
ETS43	6.8	6.01	21.9	133	322	7	41
ETS44	7.7	6.70	37.5	154	178	21	87
ETS45	9.3	6.73	24.2	120	306	8	39
ETS46	9.6	6.68	27.9	123	275	10	45
ETS47	7.4	n.d	9.9	65	138	7	47
ETS48	9.3	6.57	7.0	71	214	3	33
ETS49	10.6	6.62	12.2	40	124	10	33
ETS50	11.7	6.58	11.4	138	246	5	56
ETS51	4.8	5.86	20.7	158	331	6	48
ETS52	7.0	6.79	31.3	104	285	11	37
ETS53	8.4	6.66	5.1	70	308	2	23
ETS54	10.5	6.62	14.6	91	158	9	58
ETS55	11.6	6.96	11.8	94	120	10	78
ETS56	14.3	6.63	10.5	80	112	9	72
ETS57	16.0	6.77	8.5	66	154	6	43

SOIL PROFILES					
depth cm	pH	F $_{H2O}$ µg/g	F $_{OX}$ µg/g	F $_{TOT}$ µg/g	Horizon
ROVERELLA					
0-18	7.05	13.0	78.8	228	02A
10-18	7.06	17.4	48.0	171	Ah
18-30	7.07	18.3	60.8	223	A
30-55	7.05	12.5	81.8	228	Bw
55-120	6.70	5.53	153	481	2Bw
FAGGIO					
0-6	6.96	14.1	92.8	240	0v A
6-10	6.81	18.3	78.7	240	Ah
10-15	6.91	19.0	105	228	E
15-50	6.72	11.5	73.9	330	Bw
LECCIO					
0-2	7.13	12.4	50.4	233	02A
2-6	7.02	14.1	70.7	220	Ah
6-20	5.50	11.9	70.0	273	A
20-60	6.69	10.6	136	275	Bw
60-100	6.60	10.6	147	490	2Bw
ETNA 3					
0-0.5	6.50	19.1	112	270	0eC
0.5-3	6.60	13.0	73.8	195	2C
3-35	6.65	14.9	92.6	149	3A
35-75	6.51	7.65	80.6	201	3B
75-80	6.61	9.97	80.2	162	4Ab
80-90	6.36	8.51	64.6	303	5C
90-92	6.46	10.2	73.5	306	6C sm
92-130	6.59	5.00	50.9	313	7C
ETNA 5					
0-15	6.34	27.1	112	252	A
15-32	6.77	27.4	90.6	247	B
32-35	6.69	24.3	53.8	195	Cm
35-38	6.35	6.03	43.1	183	2C
38-60	6.57	28.7	66.0	332	3Bb

GRAIN SIZES				
Φ	pH	F $_{H2O}$ µg/g	F $_{OX}$ µg/g	F $_{TOT}$ µg/g
ETS 31				
-1	6.34	6.75	90	117
0	6.11	7.44	102	159
1	6.41	11.5	86	179
2	6.20	17.0	96	277
3	6.12	21.0	143	287
4	6.14	26.8	129	220
ETS 35				
-1	6.43	17.5	149	211
0	6.45	22.4	123	211
1	6.18	35.7	130	277
2	6.16	39.4	154	303
3	6.22	47.2	186	349
4	6.26	43.9	199	290
ETS 48				
-1	6.65	5.48	70	152
0	6.66	6.01	64	230
1	6.58	5.57	70	252
2	6.60	5.97	73	241
3	6.50	7.26	76	287
4	6.48	6.01	64	319

F_{H2O} = fluorine extracted with distilled water; F_{OX} = fluorine extracted with acid oxalate; F_{TOT} = total fluorine content; km = distance from summit craters; percent are calculated with respect to F_{TOT}.
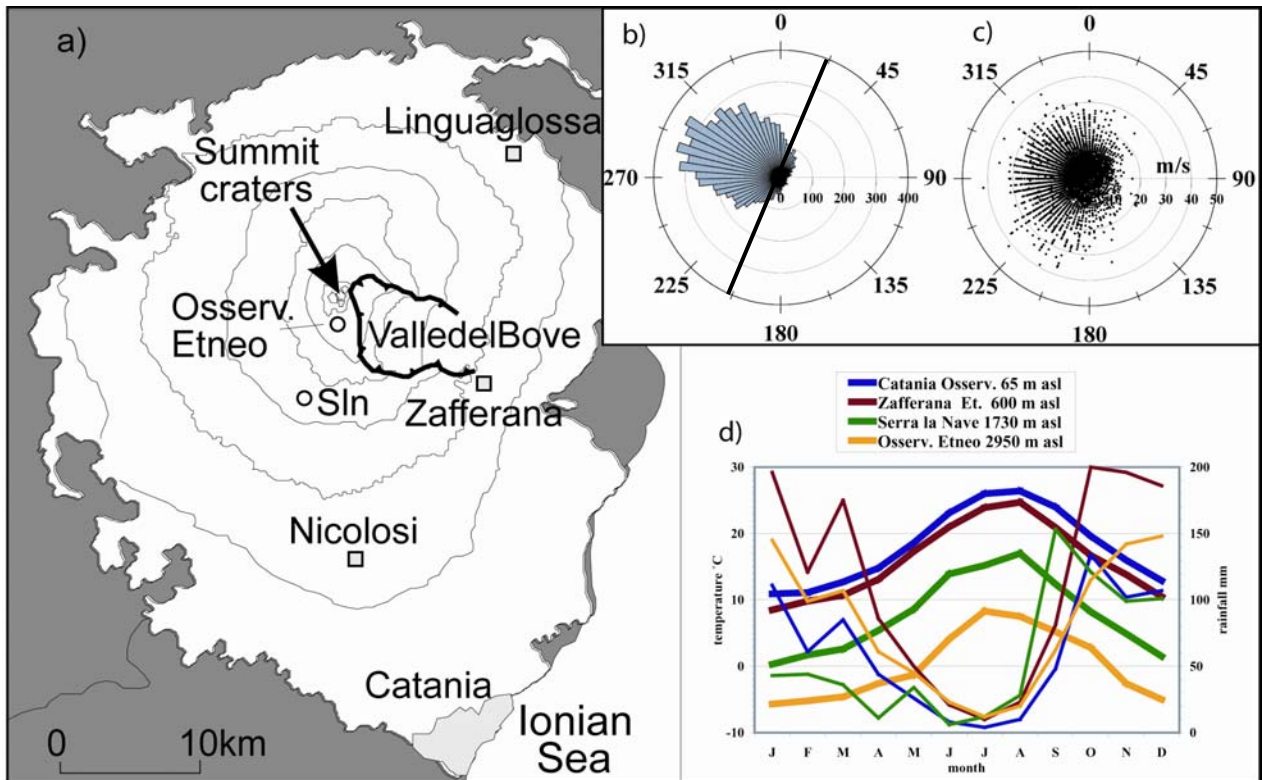
Fig. 1 – a) Mt. Etna area: volcanic products are in white, while underlying sedimentary rocks are in grey; Valle del Bove is a horse-shoe shaped collapse structure on the eastern flank; summit craters are the vent of a permanent volcanic plume; Sln = Serra la Nave; b) wind rose from 700 hPa Birgi station dataset (period 1997-2003), highlighting that the main directions from which wind blows are from W to NW; black line separates the upwind from the downwind sector; c) measured wind speeds in m/s vs. wind direction; d) Average monthly temperatures (thick line) and rainfall (thin line) at different altitudes of the volcano (data from Ferrara, 1975).
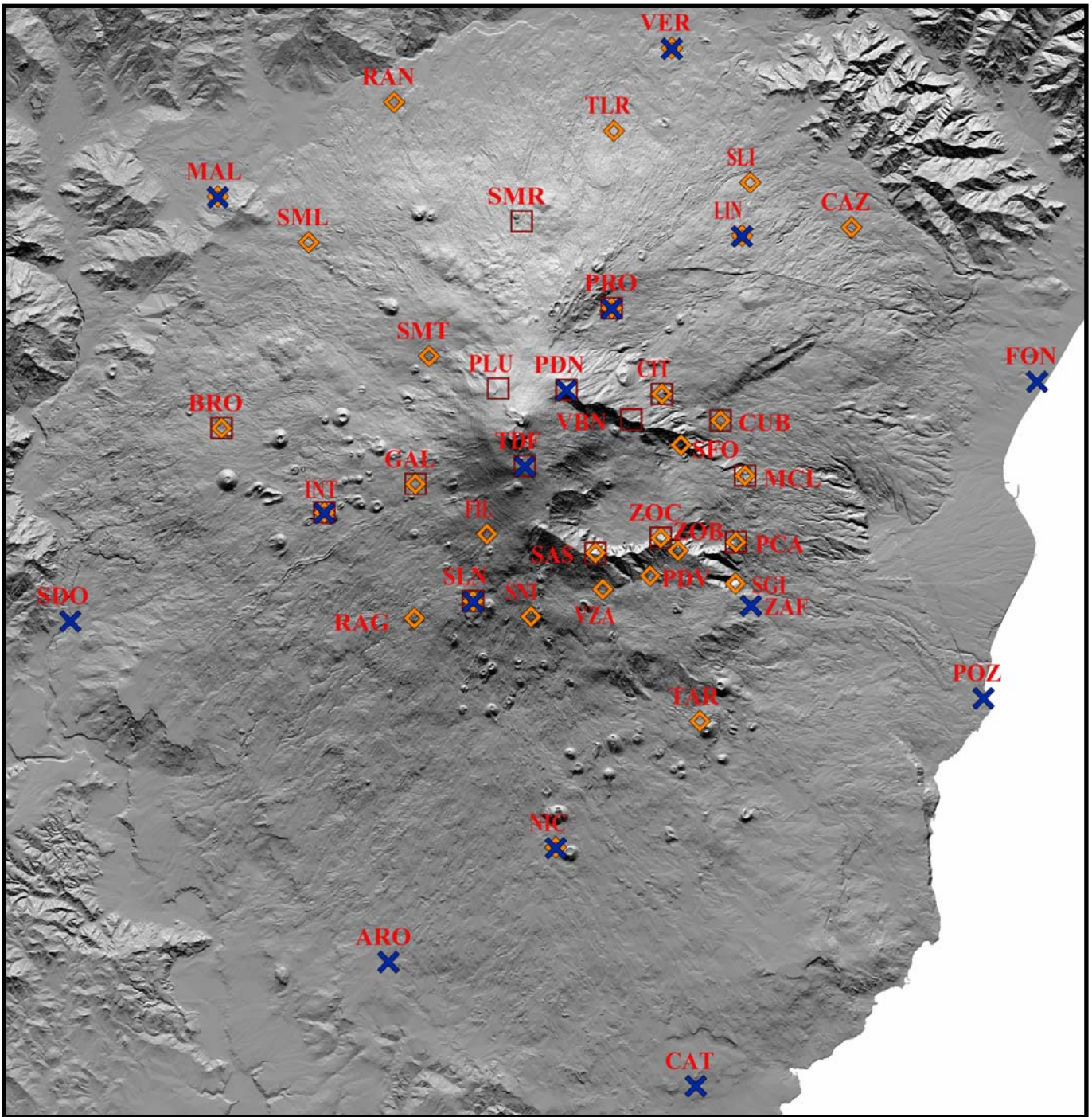
Fig. 2a - Sampling sites position. Blue crosses = Rain gauges; Red squares = Passive samplers; Orange diamonds = Vegetation
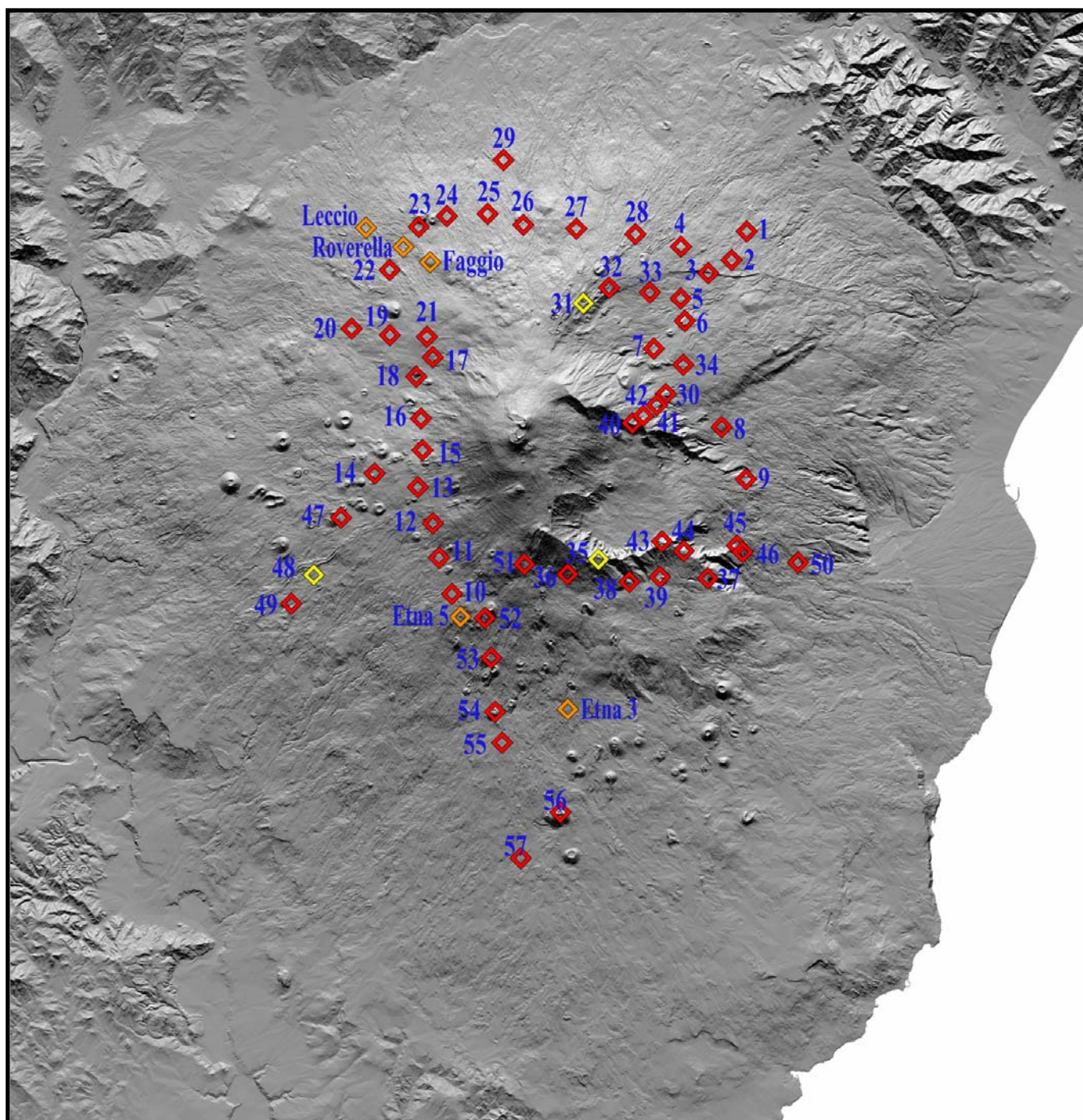
Fig 2b – Soil Sampling sites. Red and yellow diamonds are topsoil sampling sites. On samples taken at sites 31, 35 and 48 (Yellow diamonds) analysis on separate grain fraction were performed. Etna 3, Etna 5, Leccio, Roverella and Faggio (Orange diamonds) are the soil profile sampling sites. Some of the topsoil sampling sites correspond to other media sampling sites (Fig. 2a): 1 = LIN; 8 = CUB; 9 = MCL; 13 = GAL; 17 = SMT; 26 = SMR; 30 = CIT; 32 = PRO; 35 = SAS; 39 = PDV; 40 = VBN; 43 = ZOC; 44 = ZOB; 45 = PCA; 47 = INT; 52 = SLN.
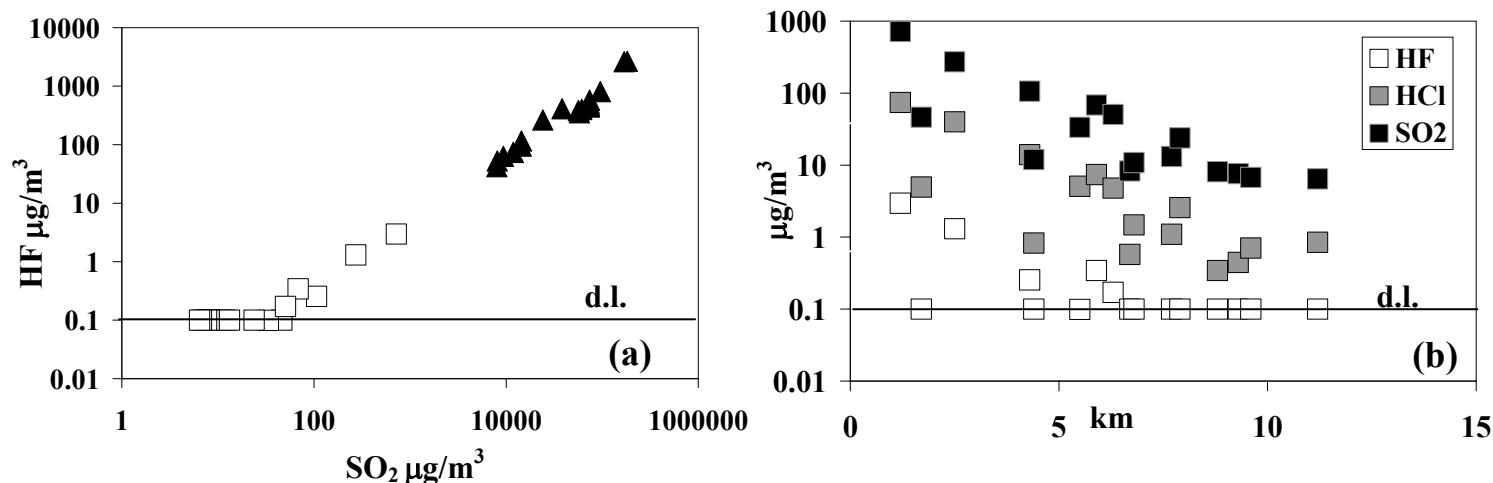
Fig. 3 – a) SO_2-HF scatter plots; squares, time-integrated (1-month exposure period) mean volatile concentrations in air from rural sites on flanks of Etna, measured by passive samplers; triangles: concentrated plume, sampled at summit craters by filter packs; b) time-averaged volatile concentrations at various sites plotted versus distance from summit craters (horizontal solid line labeled "d.l." = HF detection limit)
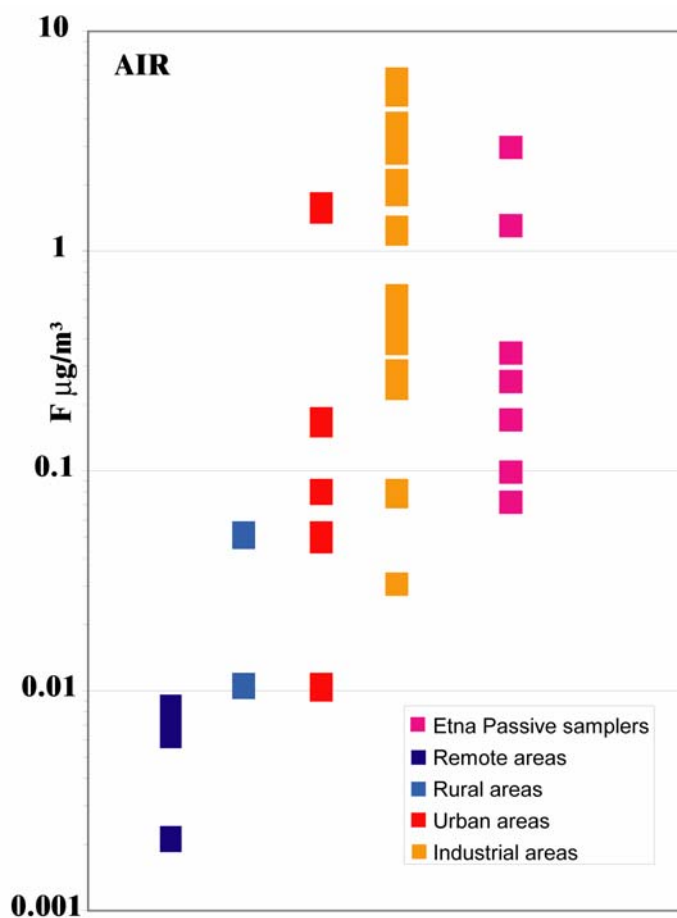
Fig. 4 – Hydrogen fluoride concentrations in air measured in Etnean area compared with literature data (WHO, 2002).
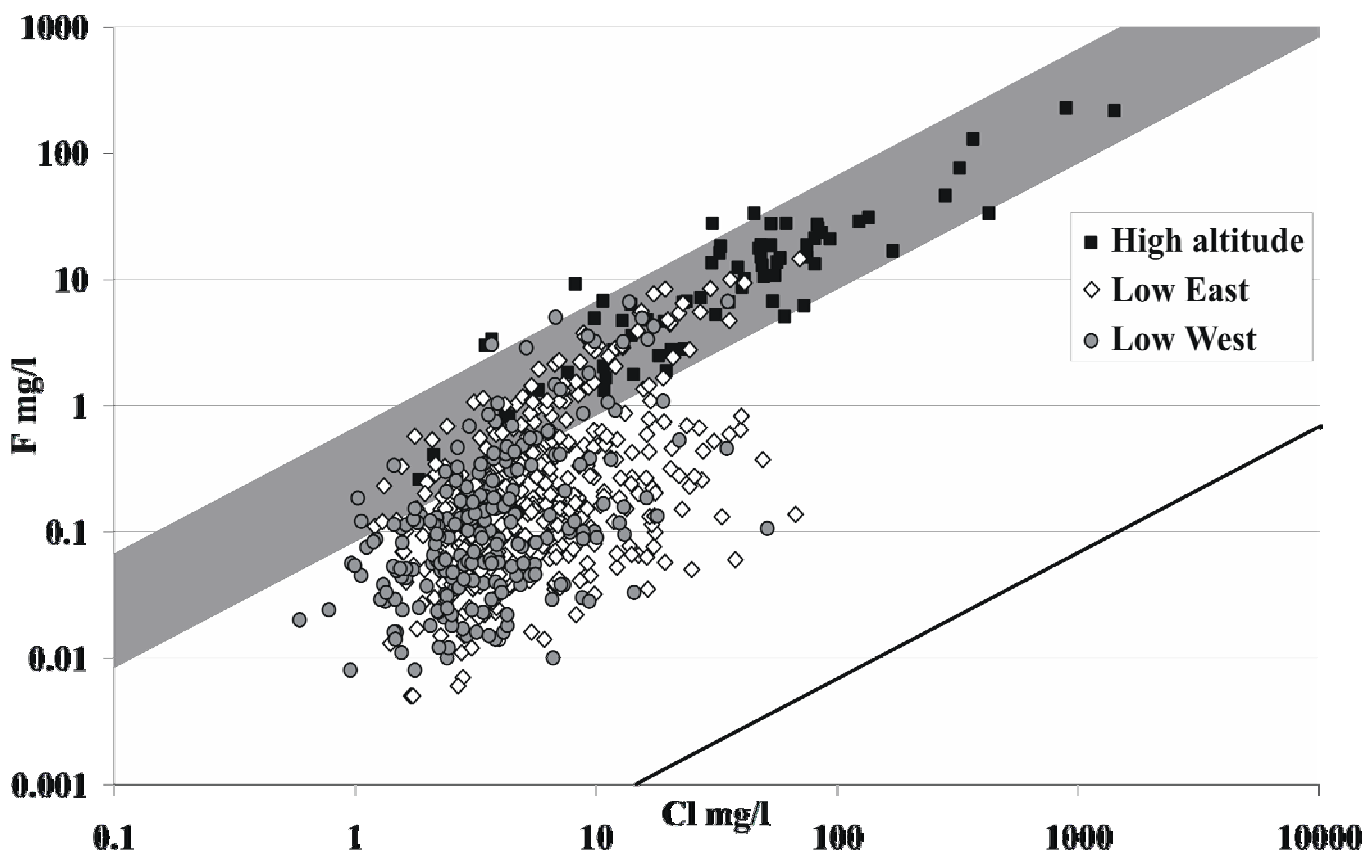
Fig. 5 – Fluoride vs. Chloride scatter plots measured in rainwaters of the Etnean area. High altitude sites are TDF and PDN; low east are ARO, CAT, FON, LIN, NIC, POZ, PRO, ZAF; low west are SLN, SDO, INT, MAL, VER. Grey stripe shows the range of F/Cl ratio measured in summit crater emissions. Black line indicates the F/Cl ratio in seawater.
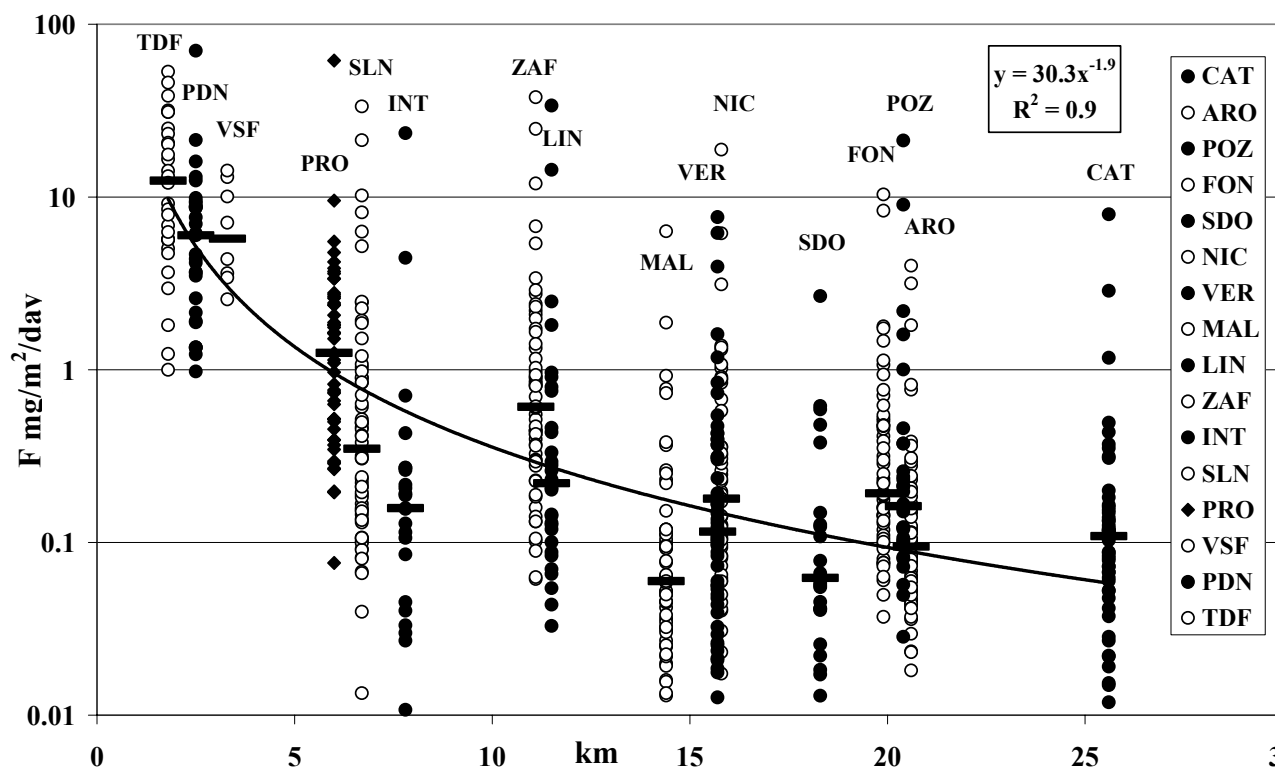
Fig. 6 - Daily bulk fluorine fluxes, calculated from the measured fluorine contents in the rainwater samples, plotted against the distance from the summit craters. Regression line was calculated only for the median values of the whole period (thick marks).
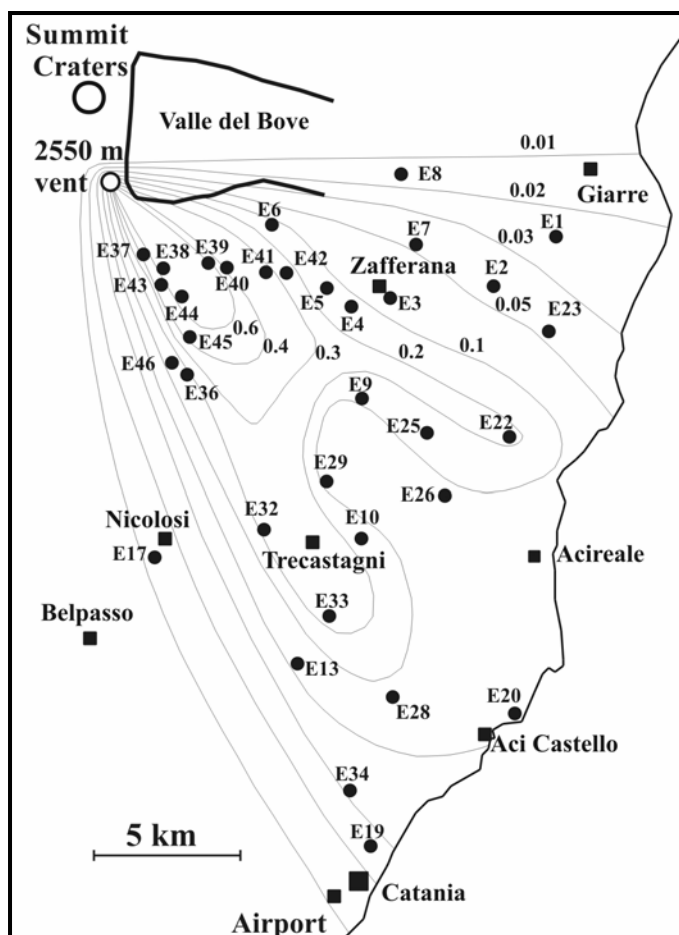
Fig. 7 – Sampling sites of the ashes emitted by a new vent at 2550m altitude during the 2001 eruption. Isolines indicate the deposition values of soluble fluorine leached from ashes (in g/m^2).
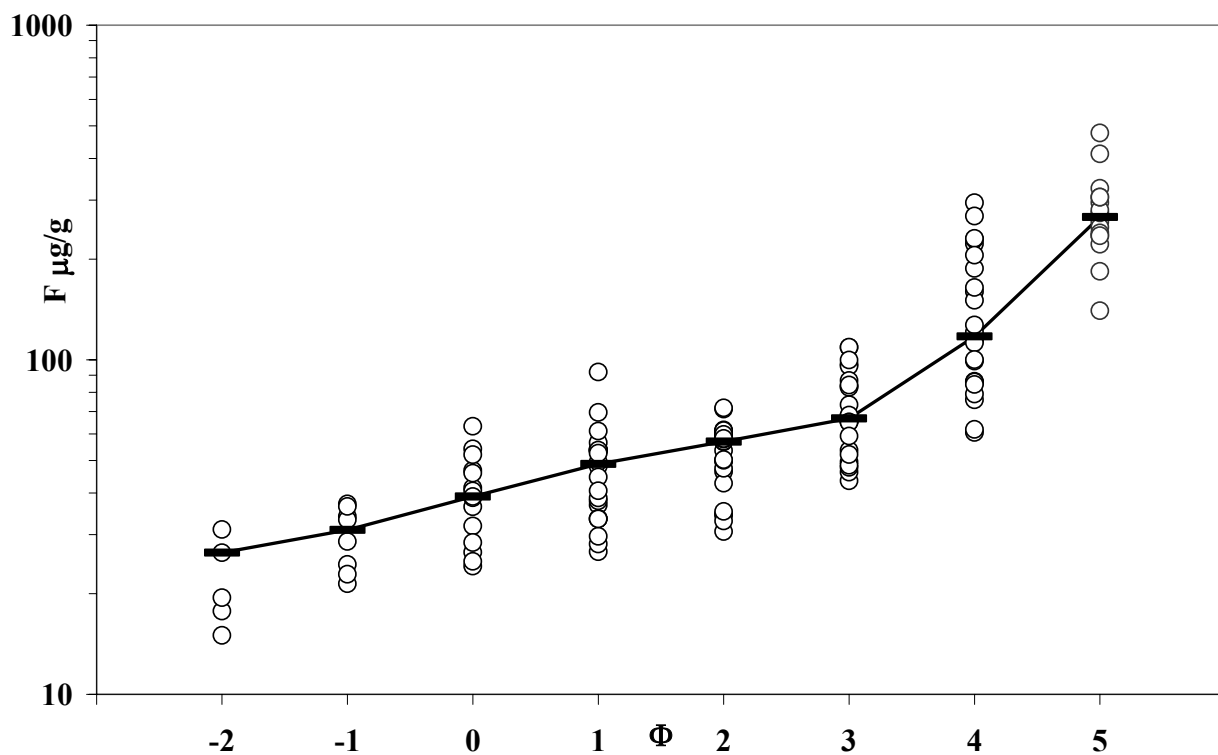
Fig. 8 – Fluorine concentrations in ash leachates of the 2001 eruption plotted versus grain-size. Thick marks are median values.
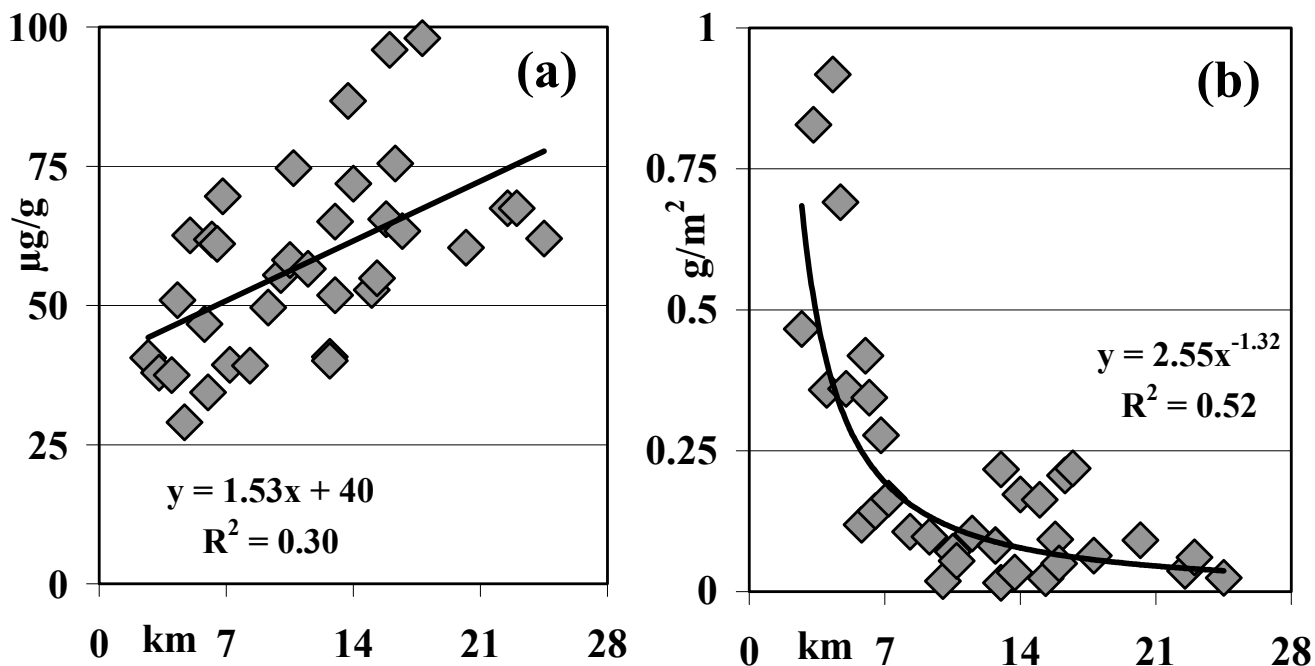
Fig. 9 – Variation with distance from the eruptive vent of (a) concentration of fluorine in ash leachates and of (b) total soluble fluorine deposition.
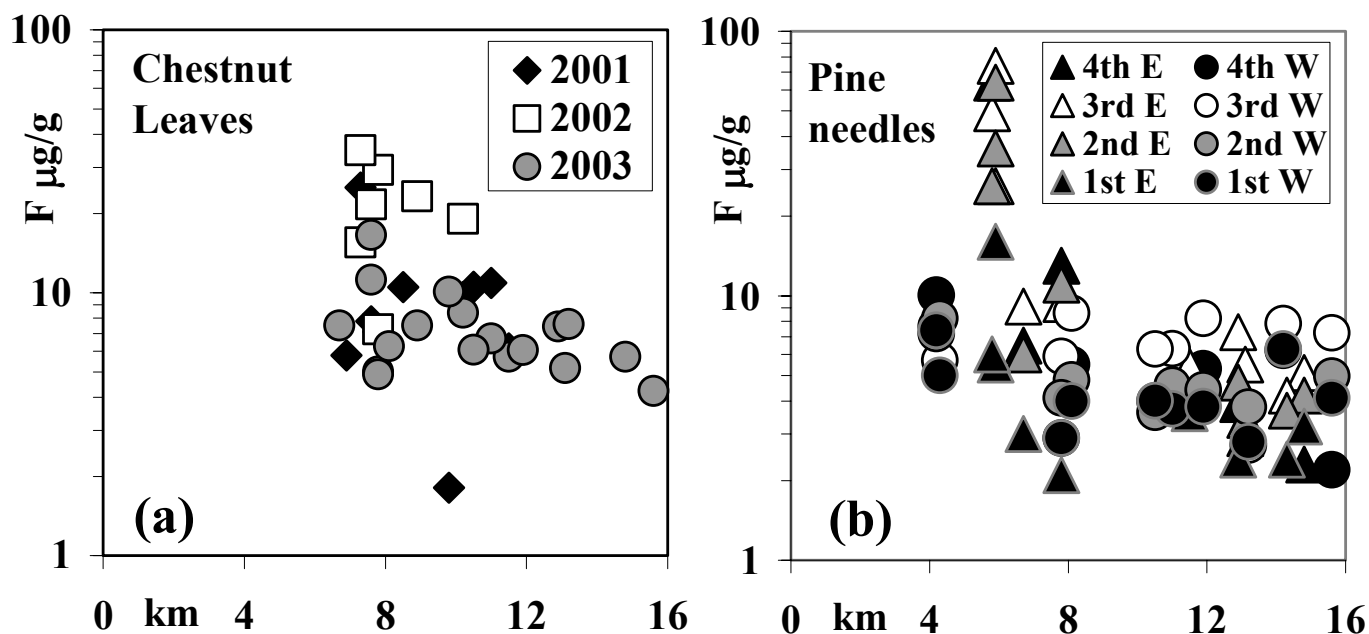
Fig. 10 - Variation with distance from the summit craters of fluorine concentration in (a) chestnut leaves and in (b) pine needles. 1st, 2nd, 3rd and 4th refer to growth year of pine needles (2003, 2002, 2001 and 2000 respectively).
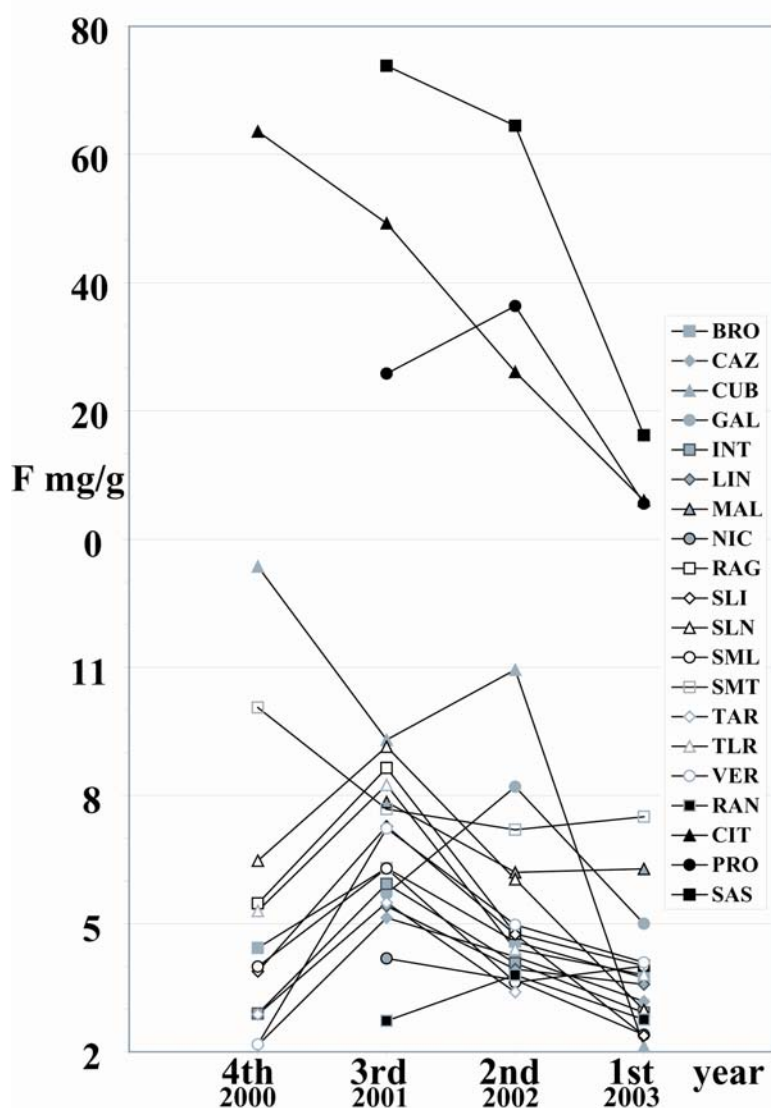
Fig. 11 – Variation with year of growth of fluorine content in pine needles. Note different concentration scale for CIT, PRO and SAS samples.
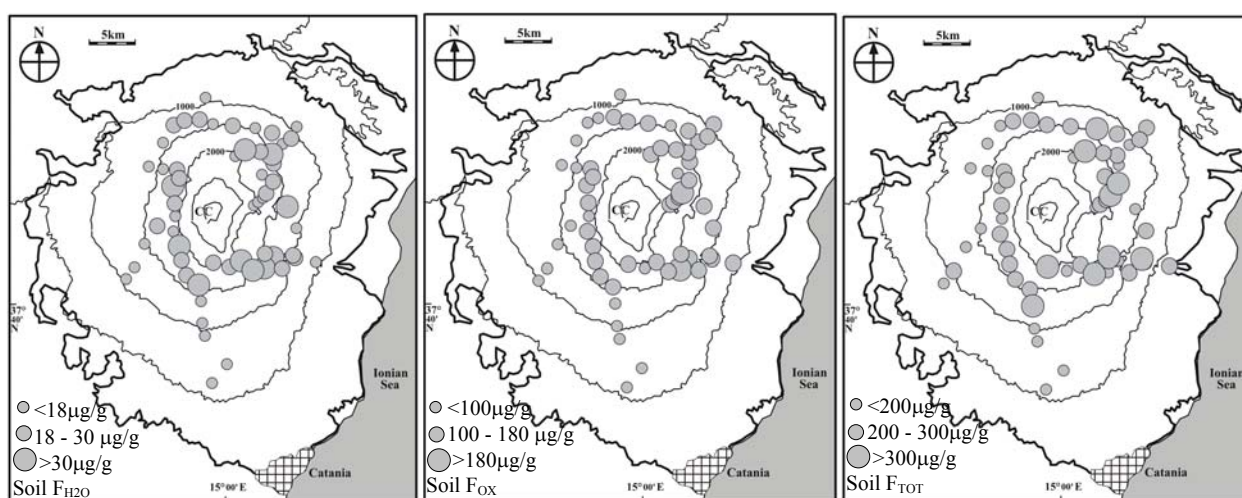
Fig. 12 - Geographical distribution of total (F_{TOT}), acid extractable (F_{OX}) and water extractable (F_{H2O}) fluorine content in the Etnean topsoils.
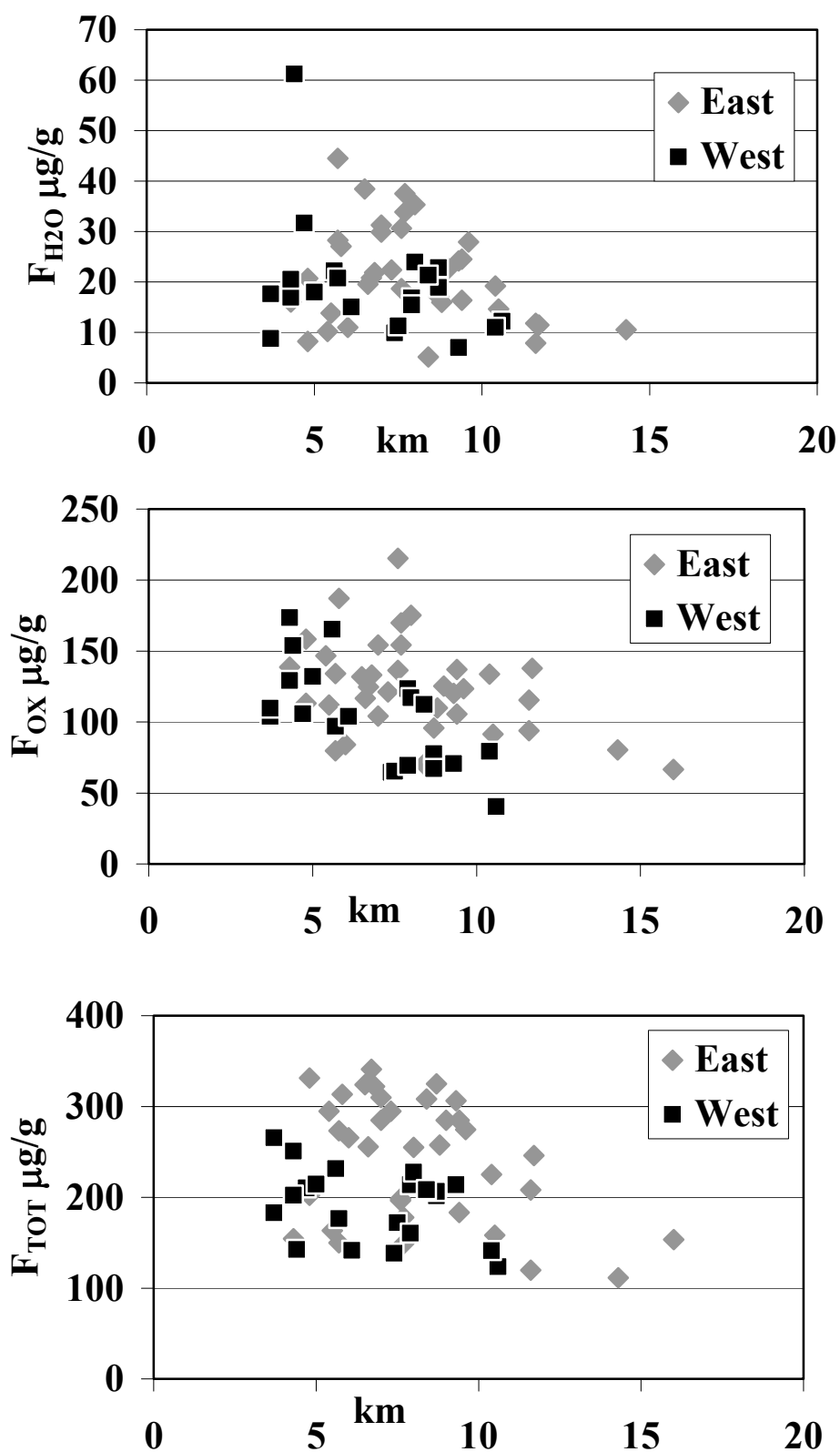
Fig. 13 – Variation with distance from summit craters of total (F_{TOT}), acid extractable (F_{OX}) and water extractable (F_{H2O}) fluorine content in the Etnean topsoils
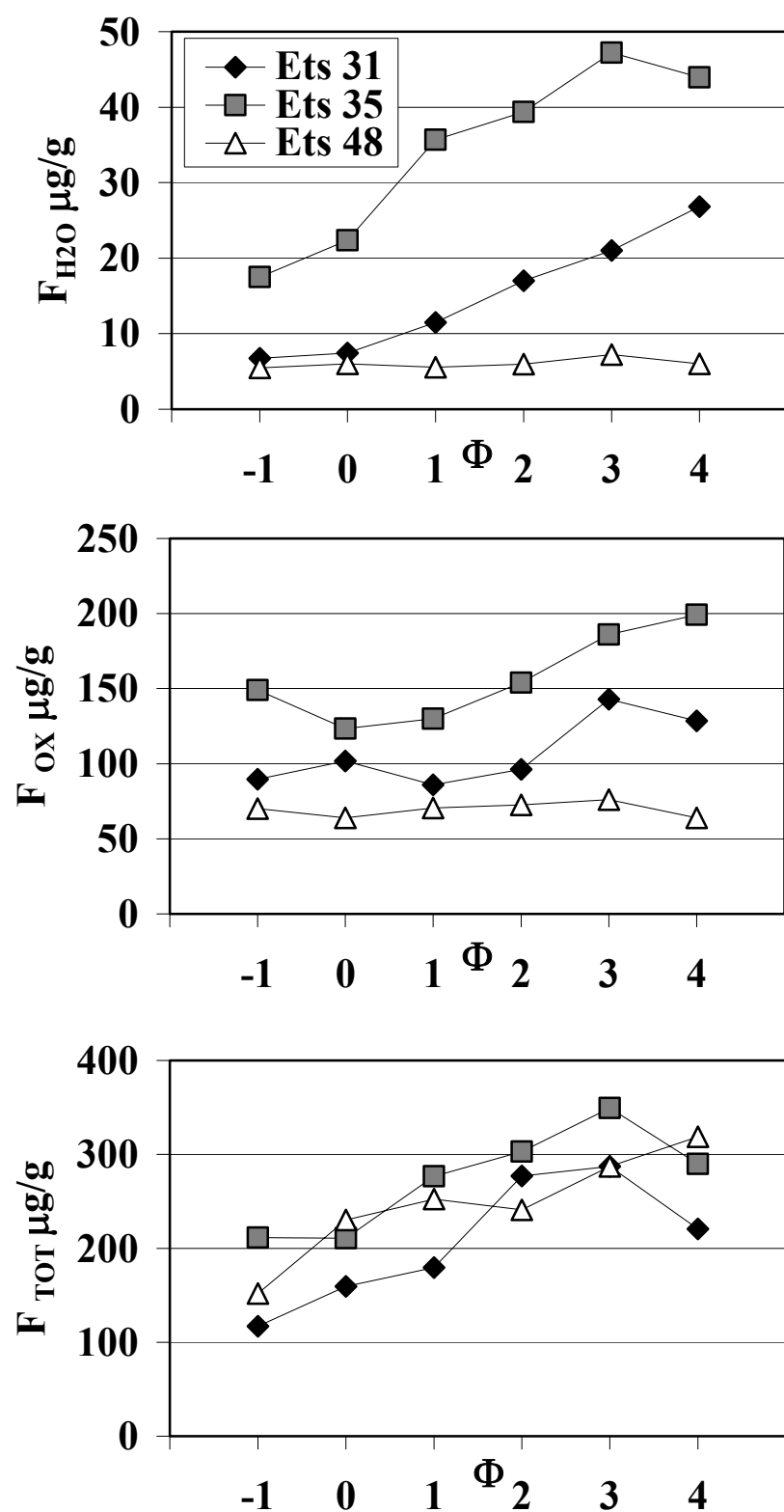
Fig. 14 – Total (F_{TOT}), acid extractable (F_{OX}) and water extractable (F_{H2O}) fluorine content in the Etnean topsoils plotted versus grain-size class.
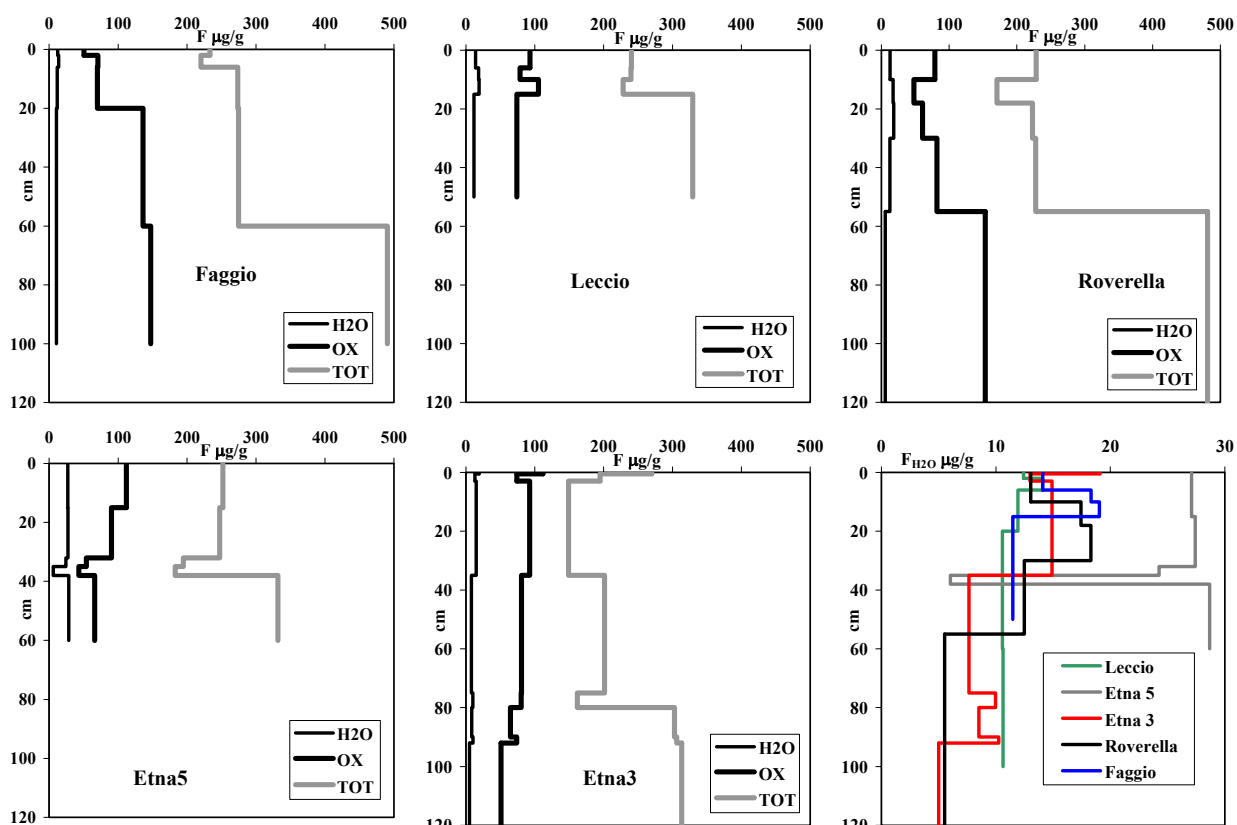
Fig. 15 – Total (F_{TOT}), acid oxalate extractable (F_{OX}) and water extractable (F_{H2O}) fluorine content in the five soil profiles plotted versus depth. In the bottom right graph F_{H2O} of all profiles are plotted together.
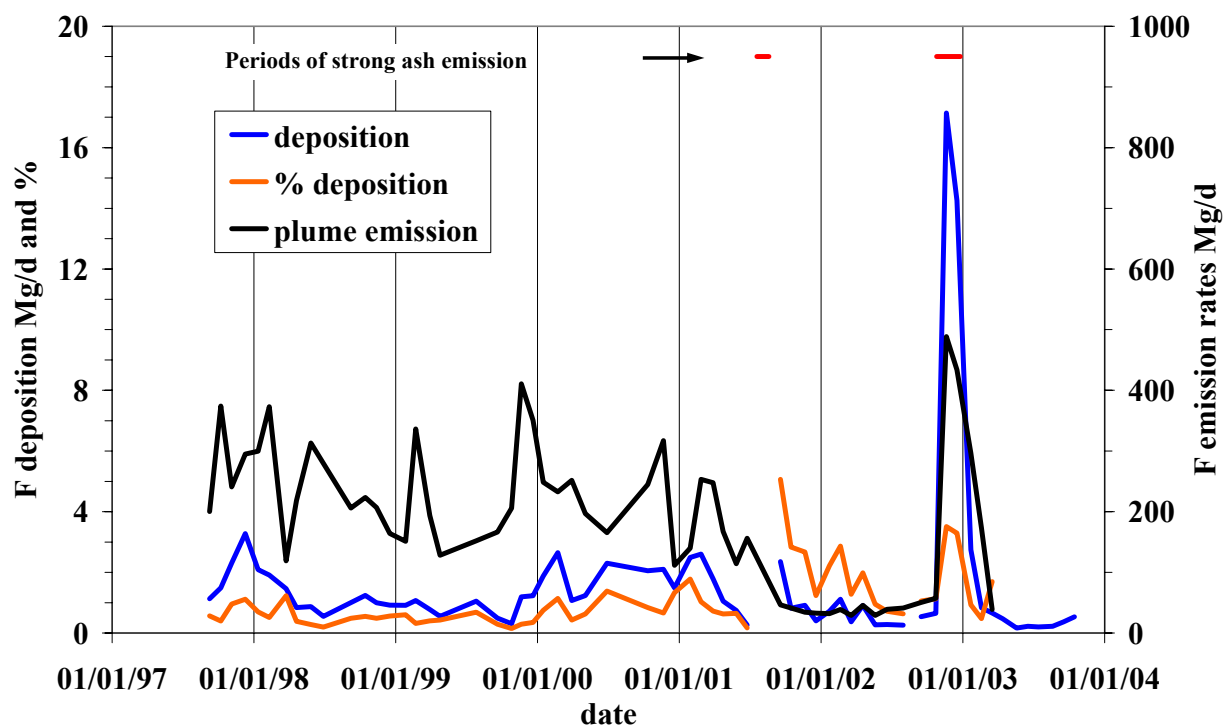
Fig. 16 – Time variations of deposition fluxes at Etna (this study) compared with estimated HF fluxes from the summit craters (see text). All data in Mg·day^{-1}. The mass percentages (%) of plume-derived fluorine scavenged from precipitation on Etna's flanks is also shown.
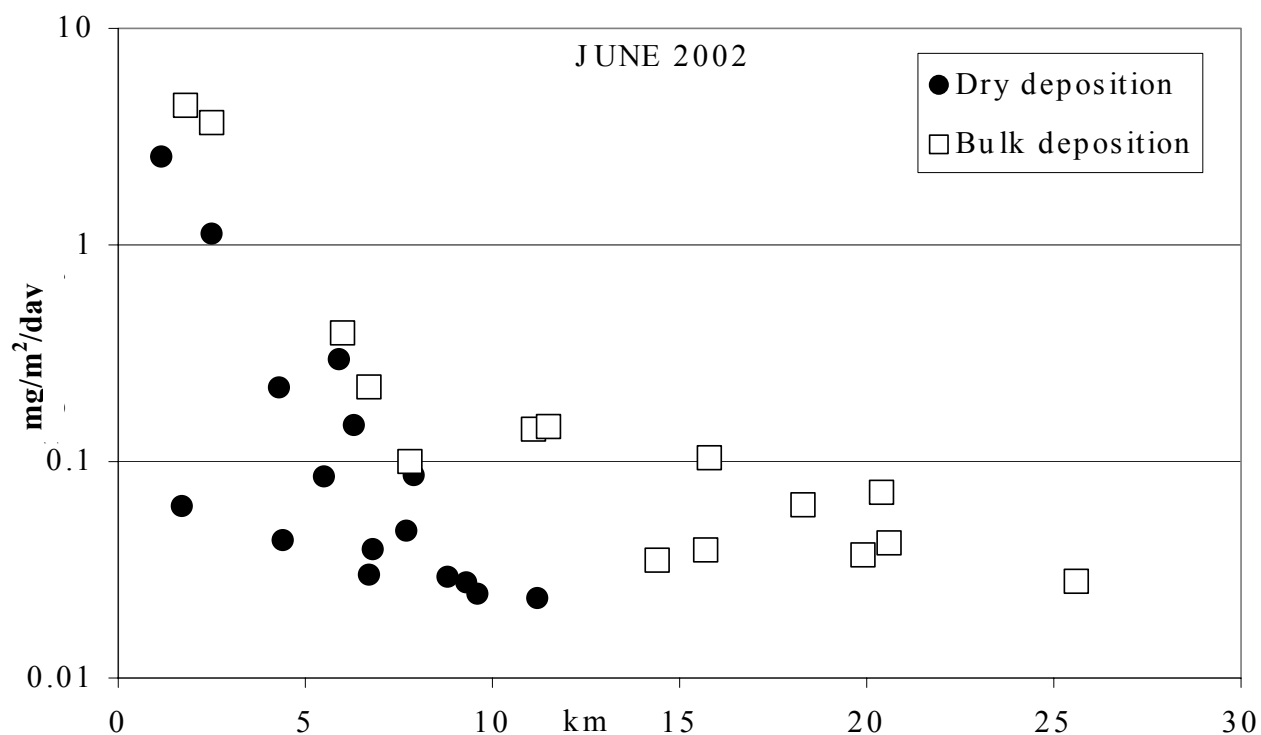
Fig. 17 – Comparison of calculated dry and bulk deposition on the Etnean area in the month of June 2002.
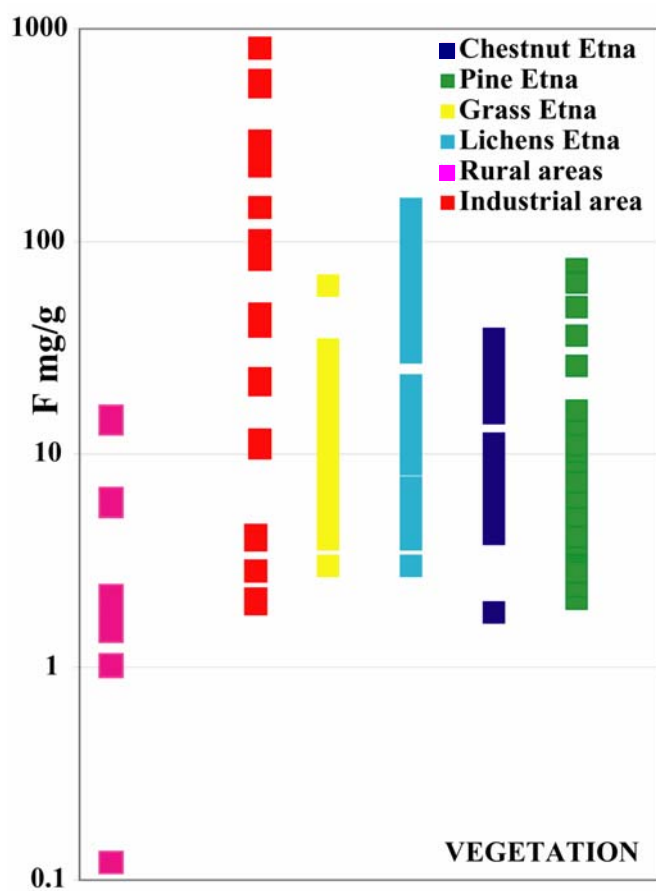
Fig. 18 – Fluorine concentrations measured in Etnean vegetation (this study and Nottcut and Davies, 1989) compared with literature data (WHO, 2002).
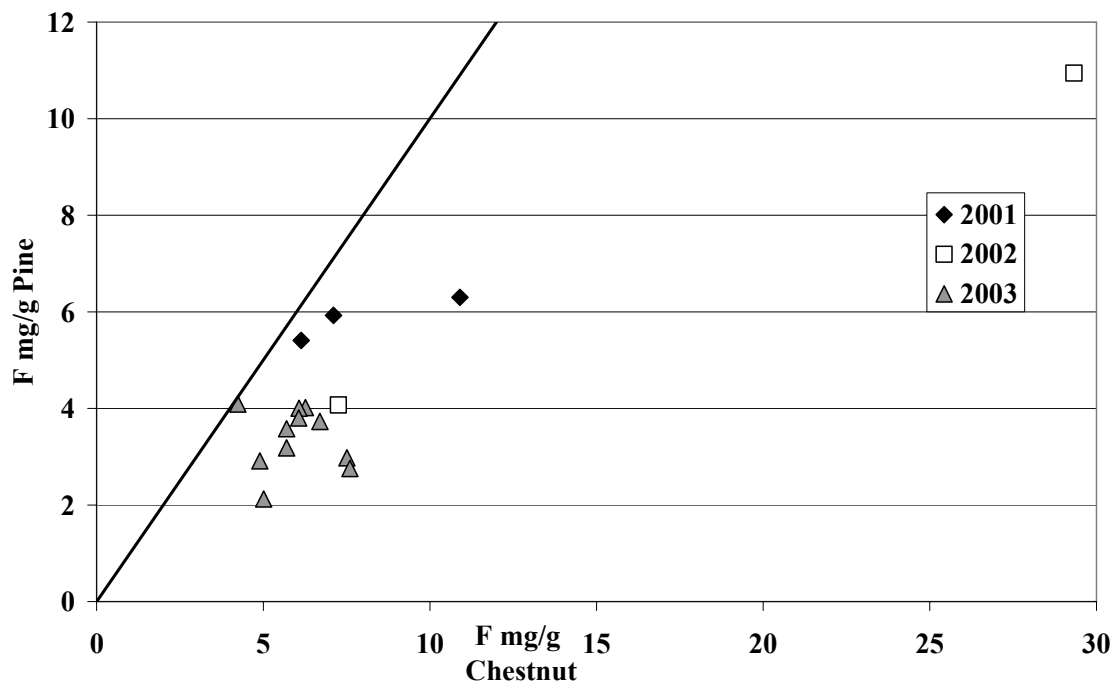
Fig. 19 – Comparison of fluorine concentrations in chestnut leaves and in pine needles collected in the same site. Line indicates isoconcentrations.

Fig. 20 – Picture taken in September 2003 of the sampling site of SAS showing the damages suffered by all trees of the area. The side facing the 2100 m altitude vent of the 2001 lateral eruption (1.5 km to the right) loosed all needle.
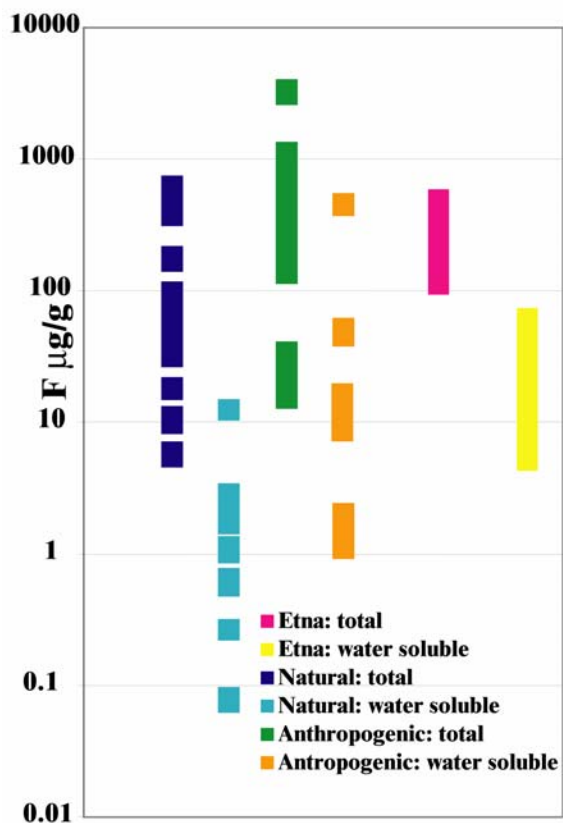
Fig. 21 - Fluorine concentrations (total and water extractable) measured in Etnean soils compared with literature data (WHO, 2002).
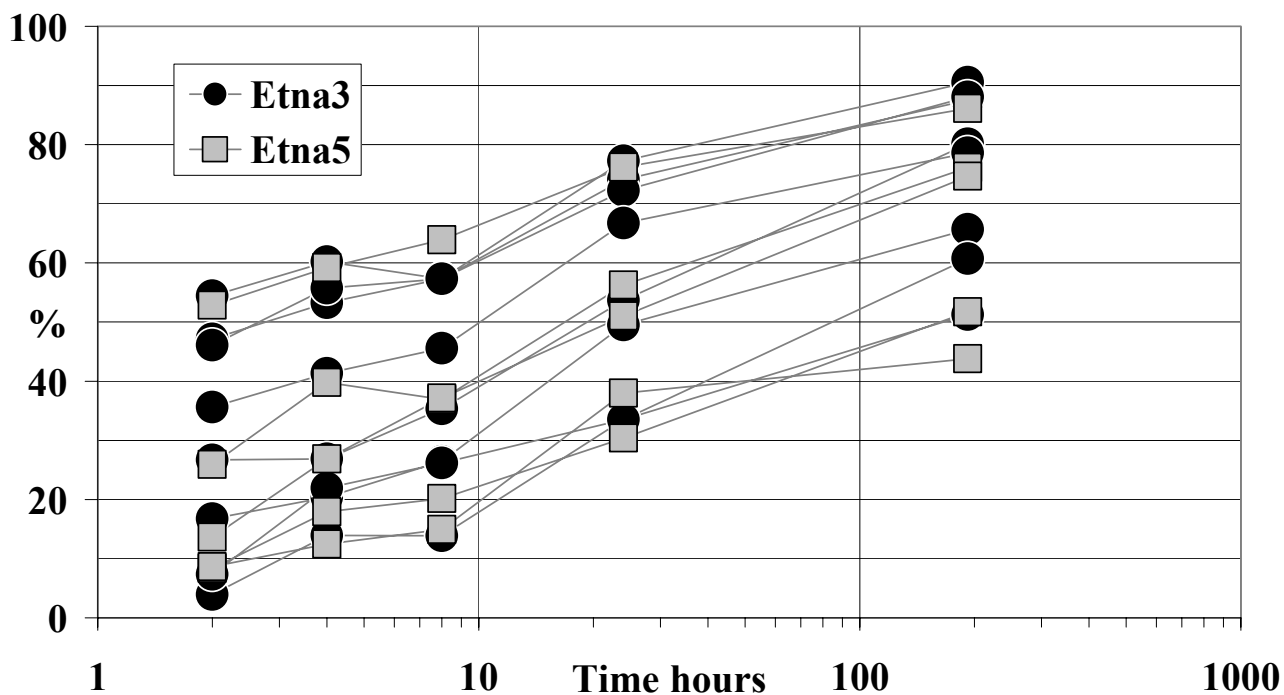

Fig. 22 – Variation with time of the percent of fluorine adsorbed by the different levels of two soil profiles from a solution (natural rainwater) with initial fluorine content of 3.82 mg/l