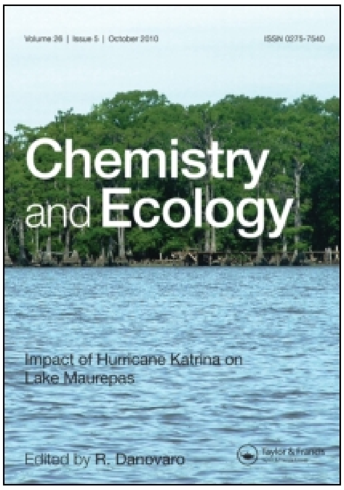

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Environmental Pollution Due to Natural Factors: A Case Study in A Volcanic Area (Vulcano Island, Italy)

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ENVIRONMENTAL POLLUTION DUE TO NATURAL FACTORS: A CASE STUDY IN A VOLCANIC AREA (VULCANO ISLAND, ITALY)

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A major influence on the environment of active volcanic areas is expected from continuous input of chemical species pertaining to fumarolic activities occurring during inter-eruptive intervals.

The systematic investigations carried out during thirteen years in the island of Vulcano (Italy) showed also substantial contributions to phreatic waters and soils of minor constituents and trace metals from volcanic rocks with no negligible influence on growing crops.

Greater extents of these phenomena have been observed for products of hydromagmatic volcanic activity or of long-lasting weathering processes.

KEY WORDS Environment, pollution, volcanic activity, rock weathering, soils.

INTRODUCTION

Volcanic activity is normally considered as consisting of eruptive episodes producing lava flows or explosive columns; a major influence on the environment, however, can be expected from the continuous output of chemical species through fumarolic activity which characterizes the inter-eruptive intervals.

With the few exceptions of volcanoes in persistent activity of Hawaiian type (effusion of fluid lava flows) or Strombolian type (small explosions with moderate lava flows), most other volcanoes are characterized by long-lasting quiescent stages with fumarolic emissions of varying intensities.

Systematic studies have been in progress since 1977 in the island of Vulcano (Italy) where fumaroles of limited amplitudes represent permanent activity after the last eruptive event of 1888–1890. Chemical composition of the emitted gases, of phreatic waters, of rocks, of soils and plants, have been considered, and a rather definitive picture has been obtained about the input to the surface environment of chemical species released by the volcanic system, and about the changes produced by this natural phenomenon.

Earlier, partial accounts about these results have been published (Coradossi and Martini, 1981; Martini *et al.*, 1988; Martini, 1989); a comprehensive evaluation of the whole phenomenon is attempted below.

SUMMARY OF VOLCANIC ACTIVITY

General information about eruptive activity at Vulcano dates back to Greek authors; Homer in the Odyssey and Thucydides in the War of Peloponnesus (VI and V century B.C., respectively) describe the forges of the god Vulcano, emitting smoke during the day and flames during the night. Vigorous activity was subsequently reported in 183 B.C., continuing through their times, by the Latin authors Strabo and Pliny the Elder, writing during the first decades of the Roman Empire (De Fiore, 1921).

A large gap followed and a strong eruption was again reported in A.D. 1444; a permanent activity stage with fumarolic emissions and episodic explosive phenomena continued through August 1888, when the last eruptive event began (Mercalli, 1883; Mercalli and Silvestri, 1891).

Violent explosions with ejection of large bombs have been observed up to March 1890; after this, no other eruption occurred, but significant gas and vapour output is still continuing with fluctuating intensities.

The rocks pertaining to past volcanic activity span in composition from trachybasalts to rhyolites, and are characterized by variations within a relatively narrow interval of volatile components; among these components fluorine and chlorine have substantial mean concentrations (1500 and 3000 ppm, respectively)

Figure 1a Gypsum aggregate with tabular shapes in oxidized ash layer.

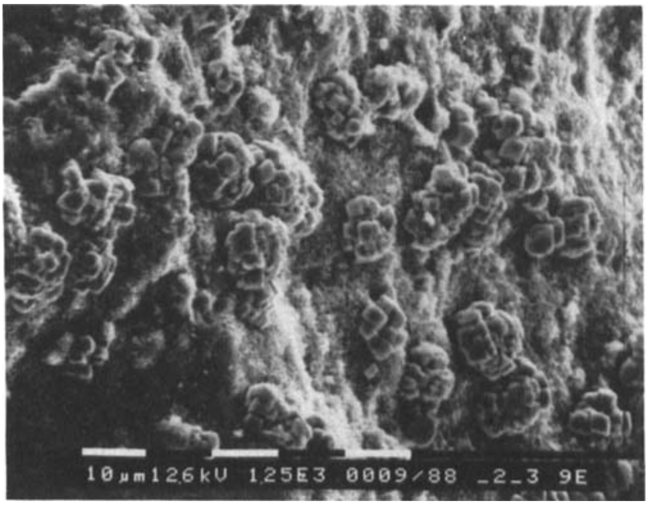

Figure 1b Fluorite aggregates with cubic form in grey ash layer.

Figure 1c Individual halite crystal, enclosed in a clay matrix.

and represent the most leachable species possibly introduced into the environment by the weathering of fresh bedrock material (Coradossi and Martini, 1981).

The participation of important quantities of water in eruptive events occurred during the last centuries, producing hydromagmatic deposits which appear to have undergone an early syn-depositional alteration process (Capaccioni *et al.*, 1988). Encrusting minerals like calcium sulphate, calcium fluoride and sodium chloride, as observed in Scanning Electron Microscope images (Figure 1a, b, c) have been ascribed to these processes; according to their solubilities in aqueous solutions, such components can be leached away even through a weak alteration of surface waters.

Table 1 Flux estimates of major and several minor constituents of emissions of the fumaroles of Vulcano (Martini *et al.*, 1988)

	Tonnes/year
H_2O	88,000
CO_2	38,000
SO_2	2,750
HCl	1,650
H_2S	260
HF	16.5
B	5.8
Zn	0.036
Cu	0.013
Sb	0.011
Pb	0.010
Cd	0.0025
Bi	0.0017
Tl	0.0006
Hg	0.0005

When considering the possible modification of the environment, the bulk of the eruptive rocks outcropping around the presently active cone "La Fossa" appear thus as the possible source of important concentrations of major and trace components derived from the same volcanic products. The few observations on the physical–chemical properties of fluids emitted by the crater fumaroles subsequently to 1890 are summarized in Sicardi (1940). A more complete set of data from periodical investigations has been obtained since 1977; according to the extent of the variations observed, fluctuations in the relative importance of different components have been defined, and some kind of forecast of the possible evolution of the active system has been provided (Martini, 1989).

On the basis of the estimated total output of fumaroles (Faivre Pierret *et al.*, 1982; Sabroux, 1982), the flux of major and several minor constituents has been calculated as reported in Table 1.

ENVIRONMENTAL CHANGES

The mobilization of chemical species due to weathering of volcanic rocks, or of the input of gaseous components from fumarolic activity, results in some kind of modification of the environment, mainly revealed by the composition of phreatic waters acting as general collectors of surface and shallow circulation.

It is thus possible to verify the extent of this process by measurement of changes in the chemical composition of the unconfined aquifers in the northwest sector of the area surrounding the active crater (Vulcano Porto, Figure 2).

Figures 3, 4 and 5 report the variations in time of major and minor components observed from 1977 to 1989, referred to as the mean values for 25 wells; the large number of samples allows a smoothing out of any accidental influence which could affect the water body, and the trend in composition revealed by this can be justified by well defined processes.

A statistical factor analysis procedure (Davis, 1973; Joreskog *et al.*, 1976) has

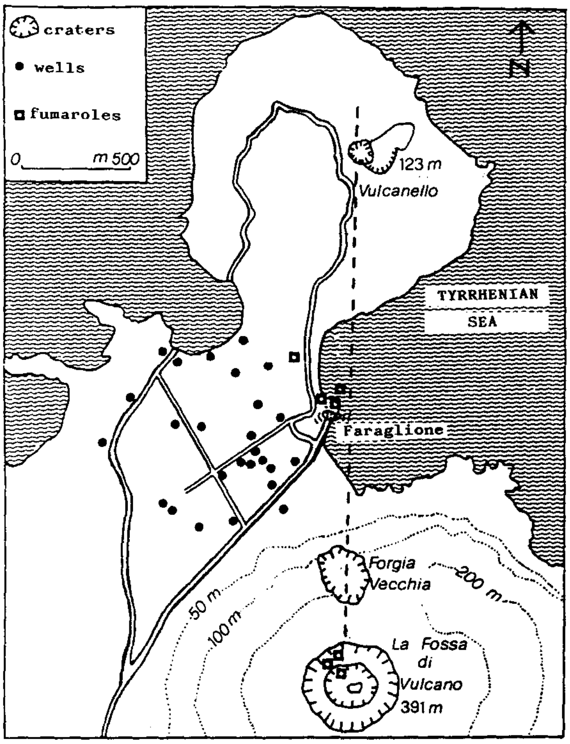

Figure 2 Location of the wells of Vulcano Porto.

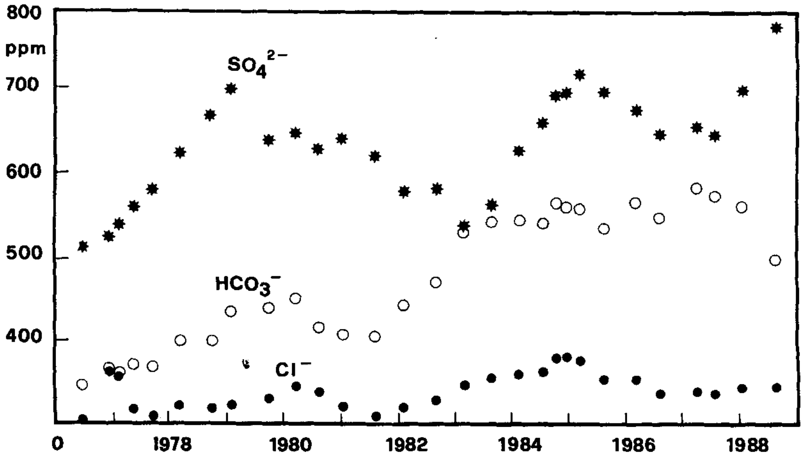

Figure 3 Variation in time of the mean concentrations of sulphate, bicarbonate and chloride in well waters.

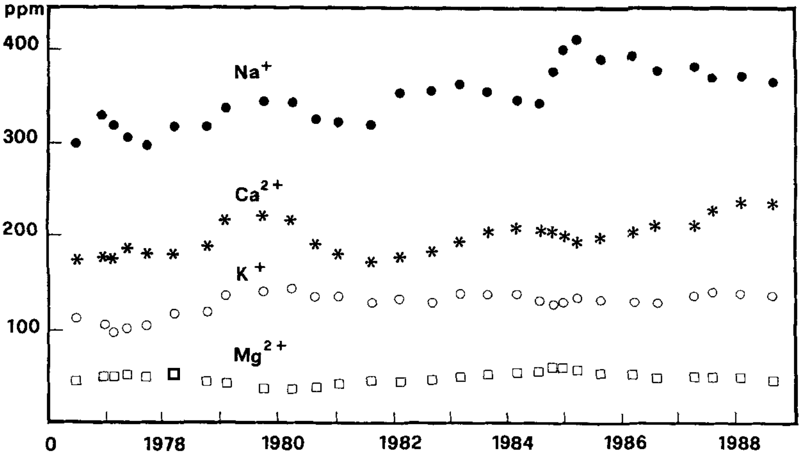

Figure 4 Variation in time of the mean concentrations of sodium, calcium, potassium and magnesium in well waters.

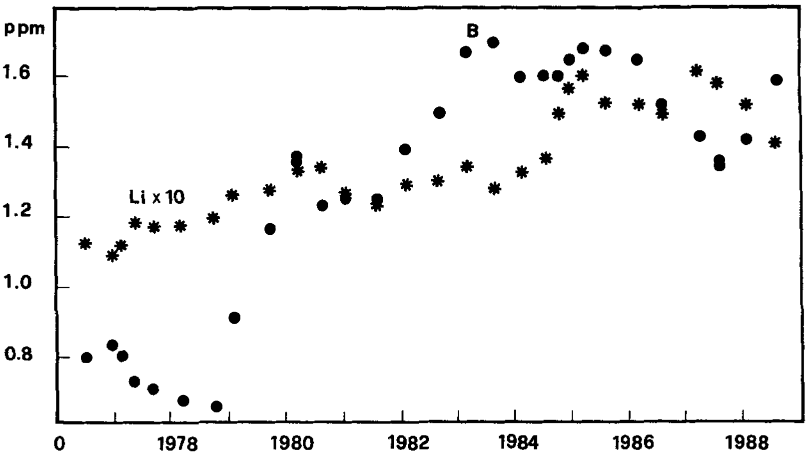

Figure 5 Variation in time of the mean concentrations of lithium (Li) and boron (B) in well waters.

Table 2 Main factors identified from statistical analysis: the values of the variance explained indicate the degree of influence of a single factor on the observed chemical composition

Factor	*Associated variables*	*Variance explained*
1	HCO_3^-, Na^+, K^+, Li^+	0.398
2	Ca^{2+}, SO_4^{2-}	0.132
3	Mg^{2+}, Cl^-	0.094

been used to derive further information about these processes. The original analytical data are simplified and combined according to their natural correlations, and a minimum number of factors representing different influences on the system considered is obtained; three natural mechanisms principally can explain the observed chemical picture (Table 2). The first factor indicates that the most important process appears related to the input of carbon dioxide from the deep uprising gaseous flow into the shallow circulating aquifer; an aggressive character of the waters results, producing a weak extent of rock weathering with consequent mobilization of sodium, potassium and lithium.

Significant concentrations of ammonium can also be associated with the same process (Cellini Legittimo *et al.*, 1988). The second factor can be explained by the reaction of circulating waters with products of the early syn-depositional change following hydromagmatic processes; as already pointed out above, secondary precipitation of gypsum, fluorite and halite takes place as the consequence and the solutions dissolving these secondary minerals display a sharp $CaSO_4$-character as well as a stoichiometric balance between calcium and sulphate, with minor contributions of fluorine and sodium chloride. Trace metals (Cu, Zn, Pb, Cd, Tl, etc.) have been observed to be preferentially associated with waters of $CaSO_4$-composition, and are likely to be derived from the same process.

A further contribution, mainly represented by chlorine and magnesium, can be ascribed to the influence of deep-seated aquifers of marine-like composition, which can occasionally inflow into the overlying water bodies. The same circulation processes can affect the composition of soils to a similar extent and, consequently, of the crops growing in this area; some investigation of this kind has been carried out recently (Cellini Legittimo *et al.*, 1986) and a marked influence on the concentrations of mercury has been detected.

DISCUSSION

The mobilization of chemical species as the result of fumarolic activity and of the alteration of volcanic products, directly affects the unconfined aquifer feeding the wells of Vulcano Porto, the composition of soils and consequently the plants growing within this area.

In order to assess the consequences of this general modification of the environment, let us consider the effect of the chemical input produced by volcanic activity.

Carbon dioxide is provided at a discontinuous rate to the shallow water body, and variations of this input have been observed throughout the present investigation. The weak acidity of the resulting solutions, and the consequent leaching of sodium, potassium and lithium, cannot be considered as a permanent character, since it depends on the CO_2 input, on the rate of neutralization by rock weathering, and also on the intensity of rainfall. Heavy rains, acting as a diluting factor, can modify the final result of the complex phenomenon of rock weathering to a large extent. The same can apply to ammonium associated with the gaseous phase to CO_2 exhalation, and also to magnesium and chloride which should derive from the input of an underlying marine-like water body. The concentrations of all these species depend on external factors, so that their influence on the environment hardly represents a permanent character.

A different situation arises in consideration of the contribution of solutions circulating in volcanic products involved in syn-depositional changes. Significant quantities of calcium sulphate, along with not negligible concentrations of fluorine and other trace elements, are provided to the shallow aquifer, and no natural mechanism can remove them to any significant extent. The only limiting factor is the saturation of the solutions with respect to gypsum and fluorite; saturation concentrations, however, still persist and a permanent change will be produced.

Trace metals are likely to be absorbed in some way by clay minerals which are formed as secondary products of weathering processes, so that a progressive enrichment of metal concentrations in soils will result.

A permanent change in the environmental conditions is then the consequence of the combined syn-depositional processes affecting volcanic deposits and the subsequent mobilization effected by circulating solutions.

These conditions are very likely to be produced to a certain extent in any volcanic area still involved in some kind of active phenomena; fresh rocks from recent eruptive events, however, can undergo a minor degree of change and a limited input of chemical species into the environment can occur. Volcanic systems where past hydromagmatic activity, or where long-lasting weathering processes already occurred, are in contrast, preferential sites for a greater modification of the chemical character of the surrounding environment.

SUMMARY AND CONCLUSION

The most impressive aspects of volcanic activity are represented by powerful explosions and blazing lava flows, but a major influence on the environment can be expected through long-lasting fumarolic activities, characterizing inter-eruptive intervals in most volcanic systems.

Carbon dioxide and gaseous sulphur compounds can dissolve in shallow and surface aquifers, strongly increasing their aggressiveness and giving rise to a significant extent of rock weathering; trace elements are then mobilized, possibly producing permanent changes in the chemical character of the areas surrounding active centres.

Thirteen years of systematic investigations carried out on the island of Vulcano (Italy), at present showing fumarolic activity after the last eruptive phase a hundred years ago, allowed collection of a large number of data on the chemical compositions of gases and phreatic waters from dug wells. With the help of statistical procedures, the main processes influencing the composition of waters can be distinguished; among them, reactions of circulating solutions with magmatic rocks appear the most effective in the mobilization of trace metals in the surrounding areas. The composition of soils can be affected accordingly, with significant consequences for growing crops.

All these processes can occur to a certain extent in any volcanic area; greater modifications in the environment, however, can be expected where hydromagmatic activity or long-lasting weathering processes have already produced a greater change of bedrock materials.

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