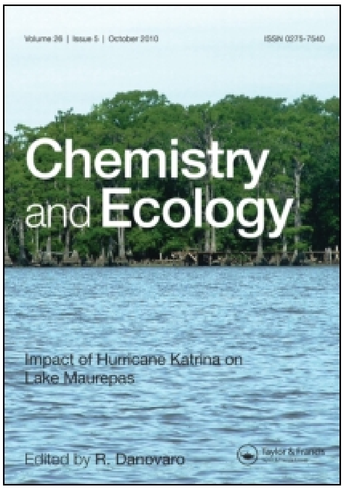

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Contribution of Nitrogen Species to the Surface Aquifers of Volcanic Areas: The Island of Vulcano (Italy)

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Contribution of Nitrogen Species to the Surface Aquifers of Volcanic Areas: the Island of Vulcano (Italy)

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Ammonium and nitrate concentrations have been investigated in water samples from the wells in the island of Vulcano, (Italy). Systematic observations, extended over a period of five years, have verified different trends in the changing concentrations of both species. Nitrate ion is considered as contributed to the unconfined upper ground aquifer by the surface environment, while for ammonium ion a deep origin appears more likely. Significant changes in the activity of the volcanic system appear to affect the distribution of ammonium only, while nitrate levels do not display any important variation.

KEY WORDS Ammonium; Nitrates; Phreatic Waters; Volcanic Areas; Natural Pollution:

INTRODUCTION

Extensive studies of the chemical composition of phreatic waters in the island of Vulcano and of their correlation with the influence of the active volcanic system have shown that nitrogen species are mainly represented by ammonium ion in the fumarolic emissions of the crater (Martini *et al.*, 1980), while both N–NH_4 and N–NO_3 are found in the waters from the wells in the area of Vulcano Porto (Martini, 1980).

The main object of this study is to verify whether, and to what extent, the distribution of those species can be considered an index of natural contamination, possibly affecting the surface environment to a significant degree. A similar role has been recognized already for mercury released by fumarolic activity within the same area (Cellini Legittimo *et al.*, 1986).

Samples from thirty three wells were collected in June and December 1977, and in February 1978, to obtain a general overview of the seasonal influence on the chemical composition of the waters; subsequently, ten specific wells have been selected on the basis of their representativity with respect to the contribution of sea water and volcanic gases which appeared as the main factors affecting the observed variations in time.

From May 1978 to February 1982, nine further samplings have been made on the selected wells, so that the available information covers a span of approximately five years.

ANALYTICAL PROCEDURE

Determinations of nitrogen species have been made by means of a potentiometric method, using ion selective electrodes (Orion mod. 95-12 for ammonium, Orion mod. 93-07 for nitrates), on water sampled stored in pyrex bottles at a pH value of about 2 to avoid redox reactions possibly due to the activity of bacterial flora. The levels of detection are 1 μeq/L for ammonium and 7 μeq/l for nitrates. Accuracy is 5% for both ions.

Standard methods of atomic absorption spectrophotometry have been used for lithium and manganese analyses; chlorides have been determined by potentiometric titration with silver nitrate.

RESULTS AND DISCUSSION

In order to refer the observed concentrations of nitrogen compounds to a standard value of salinity for the samples investigated, lithium was chosen as an index because, in spite of its reduced concentration, it is not influenced by ephemeral variations in the surface environment nor by seasonal effects, thus providing a suitable measure for comparison.

Figure 1 gives the locations of the 33 wells taken into account at the beginning of the investigation; after three samplings 10 of them were selected as sufficiently representative of the different kinds of the observed variations.

Figures 2 and 3 report the results obtained for ammonium and nitrate concentrations respectively, plotted against lithium values, in the first phase of the study. The representation of ammonium and nitrate values by plotting them against a practically constant component (lithium) appeared to the authors as the simplest procedure to give a comprehensive idea of the variability of concentrations. It is possible to observe for both nitrogen species a rather homogeneous cloud, with some peaks of concentrations. For ammonium the three wells indicated by an asterisk in Figure 1 appeared strongly affected by a high tide of marine water, so that they were excluded from further investigation. The highest values of nitrates cannot be referred to a similar influence, and appear rather concentrated in a narrow area where the use of fertilizers for

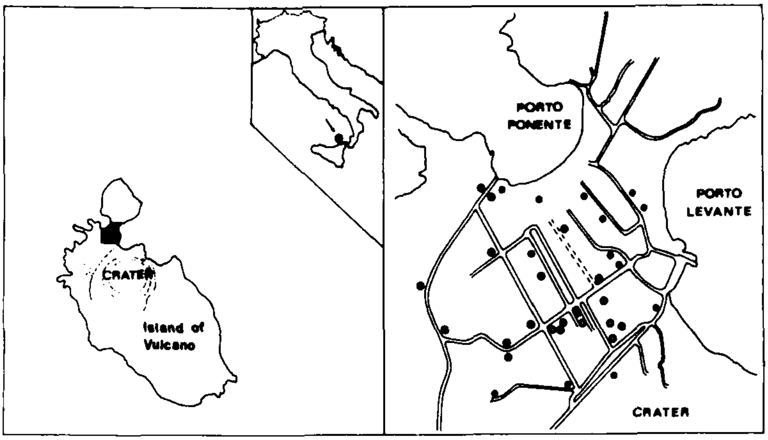

FIGURE 1 Locations of studied wells ○ samples considered at the beginning of the research ● samples selected for further investigation * samples possibly influenced by high tide.

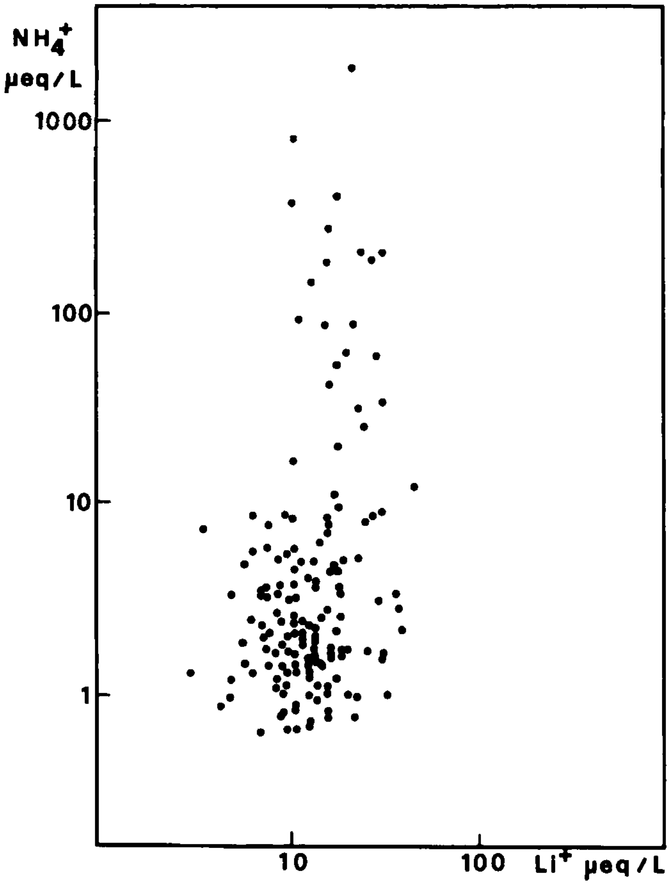

FIGURE 2 Relation between ammonium and lithium concentrations.

agricultural purposes can be claimed as a source of these significantly higher nitrate values.

On the basis of these initial data, different factors appear to affect the distribution of the two nitrogen species; from Figure 4 it is possible to verify the relatively constant nitrate values in comparison with the more variable ammonium concentrations. Higher values of ammonium are observed in wells located along the fracture pattern of the volcanic system, while the more random nitrate distribution appears influenced possibly by the sedimentary

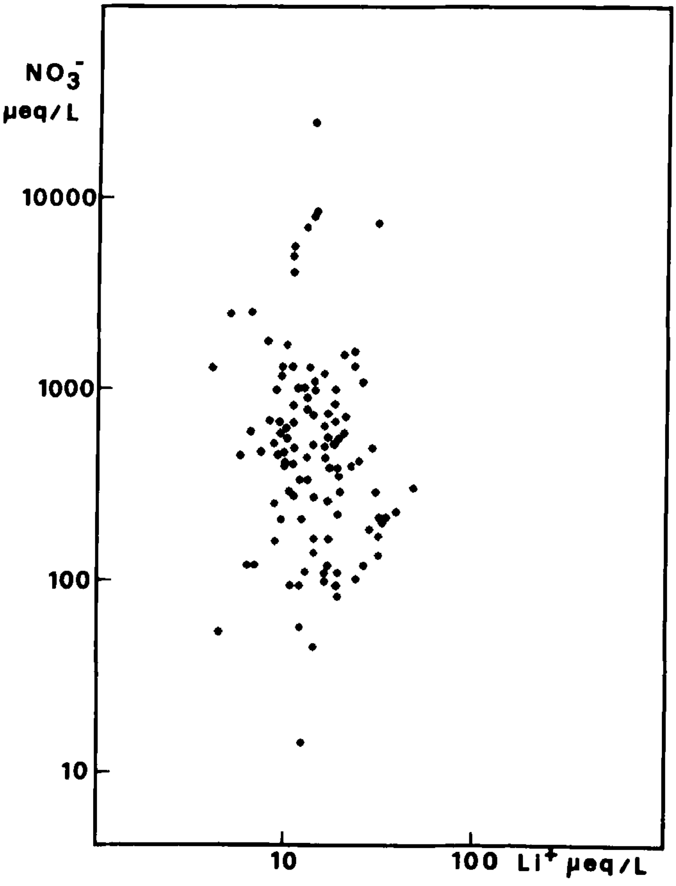

FIGURE 3 Relation between nitrate and lithium concentrations.

cover. This situation was subsequently confirmed by observations extended through 1984, so that a simple inference can be safely drawn: nitrate ion is contributed to the unconfined upper level of ground waters by the surface environment, whereas ammonium appears rather as a deeply originated species which contributes to modification of the surface environment.

To check its possible source from an input of fluids of deep origin NH_4^+ concentrations have been plotted against Mn^{2+} values (Figure 5); manganese can persist in this oxidation state in a reduced

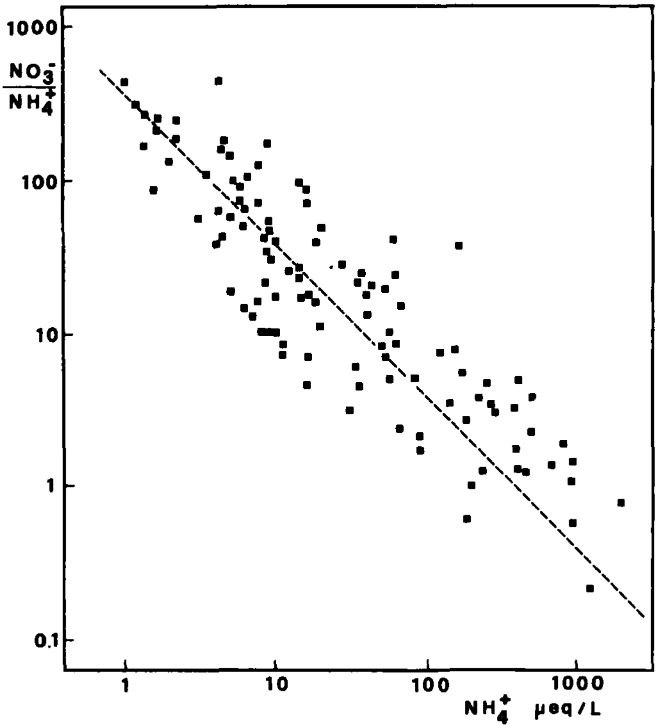

FIGURE 4 Relation between the ratio nitrate/ammonium and ammonium concentrations.

environment only, while it is quickly oxidized and then precipitated in a surface, oxygen-rich environment. Both the visual distribution and the statistical significance (99% by the chi square test) appear to provide the same indication, that is manganese and ammonium are likely derived from the same source.

Since the mean concentration of nitrate is much higher than that of ammonium, the problem of a possible dynamic equilibrium between the two species, producing ammonium through chemical and/or biological reduction of nitrates of superficial origin, can be examined. According to previous investigations (Hammer and MacKichan, 1981; Todd and McNulty, 1976; Stumm and Morgan, 1970), however, the extent of such a process appears limited, and any important modification of the ammonium concentrations because of the contribution of nitrate species seems to be ruled out.

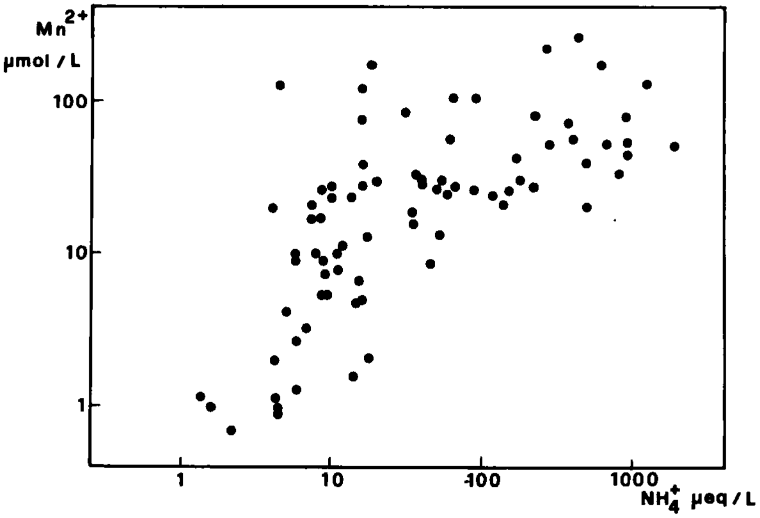

FIGURE 5 Relation between manganese and ammonium concentrations.

This being so, another interesting point seems to arise from the results of the extended observations of nitrogen species concurrent with variations in the volcanic system. Important changes in the composition of fumarolic fluids have been detected, which also involved ammonium concentrations (Martini and Cellini Legittimo, 1984; Martini *et al.*, 1986); in Figure 6 a comparison between ammonium content in fumarolic condensates and in phreatic waters is shown, in order to identify a possible correlation. The absolute concentrations of different components of fumarolic fluids can vary according to the changing contributions of ground and/or meteoric water, which in turn is normally greatly influenced by seasonal variations; it appears suitable to take into account the ratio of ammonium to chloride, considered as a reference, to smooth out any fluctuations not strictly related to the activity of the volcano itself. An opposite behaviour of the quantities is displayed through April 1981, while subsequently we can observe a more synchronous variation. By applying the hypothesis of a direct influence of deeply originating fluids on ammonium concentrations in phreatic waters, any change in the surface water body should occur as a delayed response to variations in fumarolic emissions; that is, according to

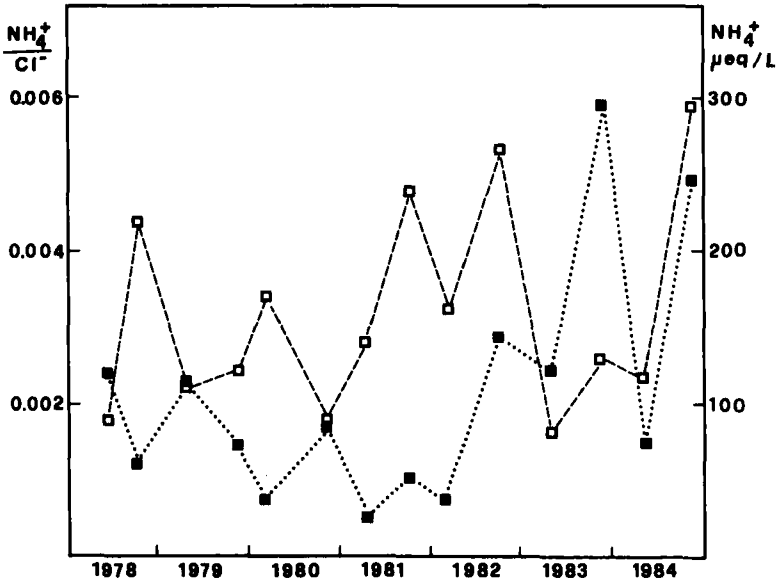

FIGURE 6 Variations in time of the ratios ammonium/chloride in fumaroles (■) and of ammonium content in phreatic waters (□).

the behaviour observed up to April 1981. A substantial change occurred after that date, which can be interpreted both as a more direct or a more delayed influence of fumarolic fluids and should thus correspond to a substantial change in the system as a whole.

By taking into account the general interpretation of fumarolic composition and its evolution in time, a more direct influence appears likely as a consequence of increased seismic activity and of increased magmatic character of the fumarolic components (Martini, 1986). This problem, however, is outside the scope of the present study.

CONCLUSIONS

The investigation of the distribution of nitrate and ammonium ions in the phreatic waters collected from the wells of Vulcano Porto (Italy) during a period of about five years has provided information on the behaviour of the two nitrogen species.

Nitrate ions are probably contributed by circulation of surface waters in the upper layers of the sedimentary cover, with possible direct influence of fertilizers; ammonium concentrations appear more likely to be related to the contribution of the gaseous phase of magmatic origin. Because of this, approximately constant nitrate values were observed throughout all the period considered, while variations of some extent were evident for ammonium.

The present levels of nitrate are within the limits accepted for human consumption; concentrations of ammonium appear to exceed the accepted limits in several instances.

An increased activity of the magmatic system appears responsible for the recent higher concentrations of ammonium.

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