

Natural Gases Hazard (CO₂, ²²²Rn) within a quiescent volcanic region and its relations with seismotectonics: the case of the *Ciampino-Marino* area (Alban Hills volcano, Italy)

Pizzino L. (1), Galli G. (1), Mancini C. (2), Quattrocchi F. (1), Scarlato P. (1)

(1) Istituto Nazionale di Geofisica, Via di Vigna Murata 605, 00143, Rome, Italy; e-mail: pizzino@ingv.it

(2) Dipartimento di Ingegneria Nucleare, Università La Sapienza di Roma, Piazza S. Pietro in Vincoli 10, 00185, Roma

Abstract: Groundwater surveys were performed by gridding in details (around 300 sites by measuring water temperature, pH, redox potential, electrical conductivity, ²²²Rn, alkalinity and by calculating the pCO₂), throughout the *Ciampino* and *Marino* towns within the Alban Hills quiescent volcano (Central Italy). Following several episodes of dangerous CO₂ exhalation from soils occurred in the last 20 years and other historically known, the work had the aim to assess the *Natural Gases Hazard* (NGH) including the Rn-indoor hazard. The NGH was therefore defined in this region as the potentiality of an area to become in future seat of poisonous peri-volcanic gases exhalations in soils and in lower atmosphere (comprising buildings), with prevailing CO₂ component. CO₂ was found “carrier” for the other poisonous minor and in trace components (H₂S, CH₄, Rn, etc.). This assessment was performed firstly by extrapolating the aquifer CO₂ and Rn conditions, discriminating sectors where, in future, CO₂ flux-concentration measures in soils as well as Rn-indoor measures have to be detailed. A preliminary Rn-indoor survey was performed (around 200 sites among private houses, schools, and public dwellings): the highest values were found in correspondence of the highest pCO₂ values and high Rn values in groundwater, testifying i.e., convection and enhanced permeability in peculiar sectors of the main aquifer, i.e., along the bordering faults and inside the gas-trap of the *Ciampino Horst*. Here “continuous gas-phase micro-macro seepage mechanism is invoked to explain the high peri-volcanic gases flux.

Keywords: *Natural Gases Hazard, Rn-indoor Hazard; Alban Hills quiescent volcano, Central Italy.*

1. Introduction

The two municipalities of *Ciampino* and *Marino* are located inside the Alban Hills quiescent volcanic structure, 20 Km SE from Rome (Fornaseri *et al.*, 1963). Throughout the volcano as a whole, the *Ciampino-Marino* sector is particularly affected by a steady-state diffuse natural gases exhalation as well as by historically remembered episodes of strong differential degassing, often in occasion of seismic events (Quattrocchi & Venanzi, 1989; Quattrocchi & Calcara, 1994; Calcara *et al.*, 1995; Quattrocchi & Calcara, 1998; Lombardi *et al.*, 1999; EC Programs 1996-1998 b). In February 1998 the two administrations exploited a convention with ING aimed at studying the diffuse gaseous

exhalations, grossly evaluated of volcanic origin, being essentially CO₂, H₂S and trace gases as radon (Giggenbach *et al.*, 1988; Quattrocchi & Venanzi, 1989; Duchi *et al.*, 1991; Quattrocchi & Calcara, 1998). The main task of the convention was to deliver to the local authorities, to the Civil Protection Department and to the scientific community, both *i*) a tool to know, prevent and eventually reduce the *Natural Gases Hazard (NGH)*, onwards intended as *hazard by diffuse gaseous exhalations of natural origin and Rn-indoor hazard*, and *ii*) a further scientific knowledge about the *unrest activity* of the Alban Hills quiescent volcano (Amato & Chiarabba, 1995; Delaney *et al.*, 1996; Kerner *et al.*, 2000).

The NGH is referred mainly to the nature and evolution of endogenous fluids circulating inside the shallower reservoirs of the volcano, namely aquifers, in which a mixing occurs among huge meteoric circulation and deep fluids, mainly gases of volcanic and thermo-metamorphic origin (onwards referred as *peri-volcanic* type). The knowledge of the saturation conditions of dangerous peri-volcanic gases dissolved inside the main aquifer of the volcano is a pre-requisite to assess the prone-areas where degassing may occur at surface and where the fluxes and concentration of these gases must be analysed in soils and indoor. The final composition of the gases at surface is controlled by gas-liquid separation processes, as inferred by the dissolved gases composition and by the isotopic data (C, He), which exclude shallow origin and exhibit slight mantle component (Quattrocchi & Calcara, 1998; EC-Program 1996-1999 b; Chiadini & Frondini, 2000).

Therefore this work focused the new detailed survey in groundwater, solely inside the two municipal territories (60 Km²), by analysing physic-chemical patterns, CO₂ and ²²²Rn. Successively a few hazardous sectors were analysed as regards Rn-indoor conditions in dwellings, also in view of the impending application in Italy of recent European Community laws (i.e., *VII EC Directivity 29/96*). Radon is the main marker of the fluids convection regime setting up, of fault interaction and of U-Th minerals rich host-rocks (i.e., Quattrocchi *et al.*, 1999; Kemski *et al.*, 1999; Zhu *et al.*, 1999; Mancini *et al.*, 2000).

The need to accomplish this kind of geochemical micro-zonation hazard assessment –for the first time so greatly detailed throughout the Alban Hills- arisen in November 1995, following an episode of strong peri-volcanic degassing (prevalent CO₂, up to 99% in volume and traces of H₂S, CH₄, Rn, SO₂ of secondary origin, etc...). It endangered the life of people, also inside dwellings, occurring in an area of 25 km² inside the two municipal territories (Quattrocchi *et al.*, 1998), comprising *Ciampino downtown*, *Marino downtown*, *S. Maria delle Mole* and the “Natural Gases Manifestation of *Cava dei Selci*” (onwards called MNGCS, as a limited asphyxiated sulphurous pool area of 70 m x 50 m). This site

was recently affected by another debate and warning to the Civil Protection Department: on 18/09/1999, early in the morning, a bovine murrain (30 beasts) occurred inside the MNGCS, properly caused by the poisonous peri-volcanic gaseous mixture exhalation inside the asphyxiated pool. In particular, there are historical and recent collations, either documented or narrated, about episodes of dangerous differential gaseous gushing, often in occurrence of narrow and far tectonic events throughout MNGCS and surroundings (i.e., seismicity, fault activity, hydro-fracturing, etc..., Funicello, personal communication, 1995). These episodes aroused a big concern, also in newspapers and TV, whose first effect resulted in awakening the local authorities and public opinion as regards the phenomenon: the presence of dangerous exhalation sites, characterised by a steady-state flux of a mixture of peri-volcanic gases, where life is infeasible.

The gases expelled from the MNGCS, along a N-S elongated belt, together with those expelled from the *Zolfoforata* pool (Chiodini & Frondini, 2000; Quattrocchi *et al.*, 2001), derived from gas liquid separation processes, constitute alone the 15-20% of the total CO₂ degassing budget throughout the Albani Hills, being totally around $4.2 \cdot 10^9$ moles/years.

A recently funded GNV project (*Gruppo Nazionale di Vulcanologia*) is dealing with the diffuse gaseous emissions throughout all the Italian quiescent and active volcanoes, with the main task to locate in details the most dangerous NGH prone-areas and to calculate the diffuse CO₂ fluxes as a whole in each area (Chiodini *et al.*, 1995; Chiodini *et al.*, 1998).

In order to fully evaluate the NGH we have to know in details for each areas: the ongoing geodynamical processes, the water-rock interaction processes as a whole, the local hydrogeological patterns and aquifer depletion with time (Capelli *et al.*, 1999; Giordano *et al.*, 2000; Mangone, 2000), the isotopic and chemical origin and evolution of fluids, the possible gas micro and macroseepage mechanisms (Brown, 2000) and the possible *convection regime* conditions setting up.

The temporal monitoring, possibly continuous and automatic, is the last step, prerequisite for a real-time comprehension of the evolution of phenomena and of the role of fluids in seismo-volcanic processes (Dall'Aglia *et al.*, 1990; Quattrocchi *et al.*, 1992; EC-Program 1996-1999 a; Quattrocchi & Calcara, 1998; Quattrocchi *et al.*, 2000; Galli *et al.*, 2000). Indeed, the scientific community is shading on light an ever-growing importance of the role of fluids in the first crustal strata in the earthquake triggering processes, especially in quiescent/active volcanic structures, geothermal areas and extensive regime structures, as the Alban Hills volcano (Fournier, 1987; Hills *et al.*, 1993; Delaney *et al.*, 1996, Quattrocchi, 1999).

2. Seismo-volcano tectonics and hydrogeology patterns

The Alban Hills Quaternary volcanic complex comprises an area spanning around 1500 km², located South-eastward of Rome (Fig. 1): on the West side it is bordered by the Tyrrhenian Sea, South-eastward and Eastward by the carbonate Meso-Cenozoic Apennine chain (Tiburtini-Prenestini massifs) and finally North-westward by the Sabatini quiescent volcanic structure, pertaining to the *Roman Comagmatic Province* (RCP onward) as the Alban Hills volcano (Washington, 1906; Fornaseri *et al.*, 1963; Locardi *et al.*, 1976; Funicciello & Parotto, 1978; De Rita *et al.*, 1988; Kerner *et al.*, 2000). Petrologically, the Alban Hills volcano is characterised by a particularly high and sometimes discontinuous potassium enrichment relative to silica (Freda *et al.*, 1997). Volcanites have rather uniform chemical compositions being inside the K-foiditic to tephrite field of the TAS diagram (Total Alkali-Silica, see Le Bas *et al.*, 1986), both for the major pyroclastic products of the Tuscolano-Artemisio greatest caldera and for the lava bodies. The composition is noteworthy different with respect to other Quaternary volcanoes, throughout the Tyrrhenian margin of Italy (mostly trachytic to phonolitic), representing an exception on world scale. A rock classification system was suggested by De Rita *et al.*, (1988) on the basis of interpreted phases of activity and dormancy of the volcano. However, since this system was introduced, it has been shown that the original identification of four major cycles oversimplified the volcano history (Kerner *et al.*, 2000; Marra, 2000). In fact, recent interpretations suggest that some eruptions (e.g., *Vallerano lava*) were not vented from the main Tuscolano-Artemisio caldera, but from other minor hypothesised vents (i.e. *Bagni Albule* local vent, *Castiglione* crater, *Pantano Borghese*, *Vallerano-Cecchignola* structure, *S. Maria delle Mole* lava body, *Albano* crater lake, etc.) where actually strong degassing and hot-reduced waters have been located (Quattrocchi & Venanzi, 1989; Calcara *et al.*, 1995; Quattrocchi & Calcara, 1998 and ING unpublished data).

The volcanic structure was established starting from around 700.000 years ago, during different eruptive steps in the frame of the extensive tectonics linked to the Tyrrhenian Sea opening, involving lessening relationships with the crust in its thinning (Locardi *et al.*, 1976; Faccenna *et al.*, 1994 a,b; Montone *et al.*, 1995; Kerner *et al.*, 2000). Two different tectonic regimes affected the Alban Hills during Quaternary (Funicciello & Parotto, 1978; Marra, 1999; 2000): *i*) a main NE-SW extension, corresponding to the volcanoes alignment of *Roman Comagmatic Province*. Focal mechanism of recent seismicity are consistent with this main system (Amato *et al.*, 1994); *ii*) localised convergence with transpression

originating at restraining bends of the N-striking right-lateral shear zone. NE-SW oriented compression halts activity on the extensional faults may have cut off magma supply to the volcanoes. A consistent geodynamic model, capable to explain the mechanism of the superposition of NE-SW and NW-SE σ_3 orientations, provides the existence of N-S strike-slip lines.

The Alban Hills region is characterised by frequent seismic swarms, typical of recent volcanism domains; they are concentrated along a NW-SE belt, that intersects the Western sector of the volcanic structure, in correspondence of the belt where the gaseous manifestations are concentrated (Quattrocchi & Venanzi, 1989; Amato *et al.*, 1994; Calcara *et al.*, 1995; Delaney *et al.*, 1996). The Alban Hills earthquakes are characterised by low-medium magnitude (generally $M < 5.0$) and the seismic swarm duration is highly variable. The hypocenters distribution analysis exhibited apparently the clustering of earthquakes just along the South-western sector of the main caldera, following two preferential alignments: N-S to the west and NW-SE to the South of the structure. Altogether, since 1700 up to date, around 3500 events were listed (historical or recorded), and around half of those are clustered during the period 1870-1900. The last energetic seismic swarms occurred on 1981 and 1989, while during the '90, the Alban Hills seismicity was very scarce, excluding the isolate earthquake of $M_d=3.8$ occurred in June 1995. It was located in the Southern sector of the Rome town, probably connected to the *Cecchignola-Laurentina* micro-seismogenic segment (Calcara & Quattrocchi, 1995; Marra, 1999; 2000; Quattrocchi & Calcara, 1998), where very recently we found hot and CO_2 -Rn rich groundwater (ING – unpublished data).

An open debate is still ongoing about the Alban Hills “dormant stage” and its “unrest activity”: the latter is mainly revealed by ground deformation data, shallow depth seismic swarms, geomorphological anomalies (Amato and Chiarabba, 1995; Delaney *et al.*, 1996; Kerner *et al.*, 2000), diffuse degassing from crust-mantle strata, geothermal reservoir at depth and volcanic structure swelling as a whole (Zuppi *et al.*, 1997; Giggenbach *et al.*, 1988; Quattrocchi & Venanzi, 1989; Duchi *et al.*, 1991; Quattrocchi & Calcara, 1998; Quattrocchi *et al.*, 2001). The most intense degassing area (*Ciampino-Marino*) corresponds to the area of maximum ground uplift recorded in the last century (Amato & Chiarabba, 1995; Delaney *et al.*, 1996) and to the present day highest energy seismic belt.

Recently, detailed time history has been reconstructed by geomorphological, petrological and geochronological investigations, indicating that, after a period of dormancy as long as 200 Ka (spanning between 0.25 and 0.045 Ma), the Alban Hills volcano appears to have

begun recently (0.45 ka) a new eruptive cycle, rather than the late waning stage of the previous volcanic activity. The most recent inferring of this cycle lasted probably up to 7.5 Ka, as found inside the Albano crater lake (Radicati di Bronzolo *et al.*, 1981; Villa *et al.*, 1999; Kerner & Renne, 1998).

Available information about the Meso-Cenozoic carbonate basement underlying the volcanic edifice point out that the volcanic region was involved in a recent tectonics (Funicciello & Parotto, 1978; Amato & Valensise, 1986); it makes horst and /graben sequences inside the basement itself. Grossly, the state of art of the Alban Hills knowledge suggests that the boundaries of these structures are coincident with the areas of highest peri-volcanic degassing (i.e., the *Ciampino Horst*, the *Lavinio-Pomezia Horst*, the *Ardea Transfer Basin* of Faccenna *et al.*, 1994, Quattrocchi *et al.*, 2001), despite more detailed information are recommended. Only recently, by using the drillings data (CMP and AGIP data, ENEL, 1987, 1990 and data managed within a GIS in progress by the “*Roma Tre*” University, see in Capelli *et al.*, 1999; Giordano *et al.*, 2000; Mangone, 2000), the boundary between the Plio-Pleistocenic clays and the overlying volcanites was detailed, being located at different depths. Moreover the thickness of the clays was found variable, being minimum at the structural highs, as in the case of the *Ciampino* area (after Toro, 1977; Di Filippo & Toro, 1980; Mangone, 2000). The *Ciampino Horst* was found limited Eastward by a N-S up to NNE-SSW fault system, well recognisable by the meso-structural and hydrogeological surveys and by the analyses of the carbonate ejecta (Parotto & Funicciello, 1978, alignment A), corresponding to a clear positive gravimetric gradient drop. Another line, with apparent N-S trend, was shaded on light by the gravimetric anomalies Eastward from Albano (Parotto & Funicciello, 1978, alignment B). These above-mentioned lines precisely delineate a polygon where the thickness of the Neogenic clayey cycle is minimum and the peri-volcanic gaseous flux was grossly evaluated as maximum, despite never detailed up to date. Two hypotheses have to be constrained to explain the spatial and temporal CO₂ anomalies: *i*) the *Ciampino Horst* as main geologic structure which possibly acts as funnel-shaped trap for the gas of deep origin, allowing some peculiar micro and macro-seepage process to occur and *ii*) the variation of volumetric flux due to the modification of geometry/width of the fracture field as the prevalent mechanism explaining the “episodic” nature of strong differential degassing.

The clays overlying the carbonate basement have the function of impervious *aquiclude*, as bottom of the shallow multistrata aquifers inside the volcanic cover. The continuity of the clayey Neogene was assessed also on hydrogeological basis (Lombardi *et al.*, 1975; Boni

et al., 1979 1981; Capelli *et al.*, 1999; Mangone, 2000). If the Neogenic clays are fractured along peculiar weakness planes, the gaseous flux from below may upraise. Each sector of the Alban Hills main aquifer, having radial hydrogeological patterns, is characterised by highly variable permeability, as a consequence of the presence of *i)* fault systems *ii)* alternance of inter-bedded lavas (highly pervious if fractured) and pyroclastic rocks (impervious if cemented); *iii)* impervious lahar tongues, like that discovered, also by analysing the DEM image, along the NW-SE *Ciampino-Albano* line, possibly due to a recent episode of the Albano Lake overflowing (Funicello, personnel communication, 2000). The evolution of the piezometric surface in the last 30 years was recently studied in details just in the *Ciampino-Marino* sector (Mouton, 1977; Ventriglia, 1990; Mangone, 2000), finding a maximum depletion of 45 meters, while inside the *Ciampino* town it reaches about 25 meters. Obviously, this static level drop, increasing in time the deep gas/water ratio, facilitates the reaching of the thresholds of dissolved gases over-saturation inside the groundwater body. This process may involve an enhanced probability that diffuse free-gases exhalations may interest sectors progressively wider, spreading the hazardous areas. A quantitative analysis is in progress by using the available data-set (Principe *et al.*, 1994; Chiodini & Frondini, 2000). As a consequence, free-gas phases may reach the surface more frequently, and finally poisonous thresholds for human health may be exceeded, mainly as regards CO₂, H₂S and radon.

3. Method

Two groundwater surveys were accomplished: the first one in the period February 1998–April 1999, and the second in January 2000, contemporaneously to the aquifer depletion study (Mangone, 2000). As a whole 277 sites have been sampled among private wells, municipal wells, springs and public fountains (Table 1; data referred to the public fountains are omitted). The surveys were performed in a very detailed gridding, sampling several wells and springs for each square kilometre. Geo-referenced file cards was compiled for each sample site and inserted within a GIS (Capelli *et al.*, 1999). The following measurements were performed: water temperature, pH, redox potential (Eh), electrical conductivity (onwards named EC), ²²²Rn, alkalinity (HCO₃). A *Crison*TM (Model 524) instrument was used for the EC and temperature determination; it allows temperature compensated EC measurements referred to 20°C. The pH and Eh measurements were performed by using an *Orion*TM (Model 205 A) potentiometer coupled with *Mettler*

*Toledo*TM electrodes (Model InLab 412). The bicarbonate ions content was determined by acidic titration (HCl 0.05 N). The groundwater temperature values are expressed in °C, EC in $\mu\text{S}/\text{cm}$, Eh in mV, bicarbonates in meq/L.

The *EDA Instruments*TM facility (Toronto, Canada) was used to accomplish the measurement of radon dissolved in groundwater (expressed in Bq/L). It is made up by a *vacuum-stripping suit-case* (RU 200 unit), *Lucas Cells* (ZnS_{Ag}) and by an *α -particle counting- photomultiplier* (RD 200 unit). A second method was tested recently on the last 70 samples to deepen the inter-comparison (Mancini & Giannelli, 1995; Belloni *et al.*, 1995; Galli *et al.*, 1999; Mancini *et al.*, 2000). While the first method exhibits an error within 20% as a whole, the second do not exceeds the 1-5%.

The pCO_2 (CO_2 partial pressure) was calculated by a simple code, by using the following formula:

$$\log (\text{pCO}_2) = \log [\text{HCO}_3] - \text{pH} - \log K_0 - \log K_1$$

where $[\text{HCO}_3]$ is expressed in moles/l, K_0 e K_1 are known equilibrium constants, temperature dependent, defined as: $K_0 = [\text{H}_2\text{CO}_3]/(\text{pCO}_2)$, and $K_1 = ([\text{HCO}_3] \cdot [\text{H}^+])/[\text{H}_2\text{CO}_3]$. The above-mentioned code uses as input data the ionic strength, water temperature, alkalinity and pH for each sample.

Radon indoor measures were performed by using reliable and certified methodologies (Cohen & Cohen, 1983; EPA, 1987; De Luca & Mancini, 1991), adopting the *Activated Charcoal Collector* (ACC onwards) facility. It is based upon the capability of the activated charcoal to adsorb the radon gas; by means of a process of dry distillation of the organic and/or animal residuals (20 g for each ACC), inside a range of temperature between 400 and 600 °C, a porous substratum of charcoals can be obtained, which becomes “active” after a treatment with phosphoric acid and zinc chloride, working as catalysts. The absorption is ruled by the Henry law: $v = kp$, where v is the volume of the adsorbed gas, for each mass unit of charcoal, p is its partial pressure and k is an adsorption coefficient. Typical k values are around 4000 Bq per gram of active charcoals, for each Bq/cm^3 of radon in air. After use the ACC has to be regenerated in order to eliminate the existing residuals (mainly radon daughters); it is accomplished by heating at temperatures ranging from 100 to 120°C, for a duration of 10÷12 hours. The chosen exposure time (duration of the ACC exposure in the environment to be analysed) is 48 hours, however different time interval may be used. Collectors were analysed by employing a γ -spectrometer. Pulses

coming from a NaI(Tl) detector, opportunely processed, are sent to a multi-channel analyser obtaining a spectrum due to radon daughters and background. After cutting the background, the ^{222}Rn concentration is obtained by dividing the number of net counts related to ^{214}Pb and ^{214}Bi peaks, as follows (formulas and details in Mancini *et al.*, 2000):

- by the exposure time (i.e., 48 hours);
- by a calibration factor, resulting from the used collector type (geometry, dimension, etc...), the exposure time and the *water gain* (water adsorbed by the activated charcoal);
- by the counting efficiency, estimated by using a collector with known radon activity;
- by a *Decay Factor*, that accounts for radon decay from the median exposure time to the measuring time.

4. Results

4.1 Groundwater survey

Firstly, general maps of the pCO_2 distribution and ^{222}Rn concentration in groundwater are showed (Fig. 2, 3), comprehending both the *Marino* and *Ciampino* territories; secondly more detailed information are focused where the NGH assessment was found critical (keeping constant the population distribution for the investigated area as a whole). Specific sectors were discriminated by empirical thresholds with respect to the two main components of the NGH: the “ CO_2 exhalation potential hazard” in soils and buildings and the “Rn-indoor potential hazard”. In the following data presentation, the term “ CO_2 exhalation potential hazard” will be intended as the relative potentiality of an area to become seat of poisonous natural gases exhalations in soils and in lower atmosphere (comprising dwellings), with prevailing CO_2 component. This potentiality was extrapolated firstly by considering the CO_2 conditions within the main Alban Hills aquifer. This is considered both the main interface between the “gas source strata” and the “living strata” and the main “buffer pillow” of uprising peri-volcanic gases. Where the main aquifer is over-saturated in deep CO_2 or near to the saturation, the probabilities that the excess free-gas may arrive at surface increase noteworthy. Similarly, where the radon in solution reaches high values, high Rn-indoor levels may be expected, testifying i.e., convection and enhanced permeability in peculiar sectors of the main aquifer, thus defining in details the most powerful candidate Rn-indoor prone-areas. However we have in mind

that, in the final NGH assessment, the “Rn-indoor potential hazard” component evaluation is more complex than the evaluation needed for the “CO₂ exhalation potential hazard” component, depending mainly upon the prevailing role undertaken by the CO₂, as “carrier” or “diluting” agent for radon, respectively as detailed after.

The most important result is apparent observing the pCO₂ map (Fig. 2): a clear differentiation between a “polygon” characterised by high pCO₂ values (> 0.5 bars, clustered within the areas of *Marino* downtown, *Ciampino* downtown, the surrounding of the MNGCS and the *S. Maria delle Mole* sector) and the remaining part of the two municipal territories, characterised by low values of pCO₂. A clear and continuous linear structure, elongated around the NNE-SSW direction, divides the two sectors: it is probably the Eastern fault of the *Ciampino Horst*, previously discussed. This result clearly points out the power of the fluid geochemistry methods to discriminate fault systems and geologic buried structures as horsts.

Considering the average pCO₂ value on the totality of the samples (0.27 bar) we defined a threshold of 0.5 bar to assess an “hazardous anomaly”. The found average value of pCO₂ is in very good agreement with the average value of 0.2 bar referred to the Alban Hills structure as a whole (grossly calculated on 400 sites sampled by AGIP, see in Principe *et al.*, 1994; Chiodini & Frondini, 2000). This value is two times greater than the typical pCO₂ value found throughout the RCP as a whole and four times greater than the value estimated for the Central Italy sector (Chiodini *et al.*, 1995).

In particular, inside the *Marino* and *Ciampino* municipalities we distinguished three zones characterised by three different hazard threshold for the pCO₂: <0.1, 0.1-0.5 and >0.5 bars. These three pCO₂ threshold levels, being arbitrary, may be newly defined if the study will be extended throughout a spreader region: at the moment, they have been considered the soundest thresholds for a correct evaluation of the NGH of this peculiar “geochemical hazard micro-zonation”.

The first area is characterised by calculated values of pCO₂ > 0.5 bars. Here we assess an high hazard for CO₂ exhalations in soils and buildings. It comprises the sectors of: *Cava dei Selci*, and *S. Maria delle Mole* inside the *Marino* territory, the bulk of the *Ciampino* village (comprised the “*Vigna Fiorita*” residence), inside the *Ciampino* territory. Recently (November 2000) inside the *Vigna Fiorita* residence, during an excavation of some buildings new gaseous pools have been discovered with 99% of CO₂, 700 ppm of H₂S, traces of CH₄ (IGF unpublished data) and 258 Bq/l of ²²²Rn in the free gaseous phase.

Effectively, during random check-out measurements at soils within the sectors of *Cava dei Selci*, *S. Maria delle Mole* and surroundings, very high CO₂ values were measured (up to 99 % in volume in soils and up to 2 % inside some building basements) where the calculated CO₂ partial pressure in groundwater befitting reached around 1 bar and more. The measured CO₂ flux in this area was found effectively very high (i.e., inside the MNGCS the values reach $2.71 \cdot 10^{-7}$ g/day, see Chiodini & Frondini, 2000 and unpublished data of Carapezza *et al.*, 2000). This correlation between the CO₂ fluxes effectively found in test-sectors and the pCO₂ evaluation in groundwater over a spread area stresses the power of the adopted method for the NGH assessment, based essentially on the aquifer conditions extrapolation.

The second zone is characterised by calculated values of pCO₂ comprised between 0.1 and 0.5 bar and here we assessed a medium hazard for CO₂ exhalations from soils and inside buildings (i.e., *Parco Colonna*, and the *Cemetery area* in the *Marino* territory, a restricted sector of *Valle Cupella* and the western sectors of the *Ciampino airport* in the *Ciampino* territory).

The third zone is characterised by calculated values of pCO₂ < 0.1 bar and here we assessed a low hazard for CO₂ exhalations from soils and inside buildings. It includes more or less the remaining part of the *Marino* and *Ciampino* territories.

Within the *Ciampino* and *Marino* territories, it is possible to locate the sites affected in the recent past (around 40 years, Table 2) by noticeable natural gases exhalation and gas-gushing episodes. It is noteworthy the fact that among the 10 cases listed in Table 2, 8 occurred just inside areas assessed by the present work to be of high hazard for the peri-volcanic gases exhalations from soils and inside buildings. This evidence makes exploitable our extrapolation method based firstly upon the aquifer data, to evaluate the CO₂ exhalation hazard and to assess where CO₂ flux and concentration in soils and Rn-indoor measurements have to be intensified. The remaining two cases indeed occurred in zones assessed in this work to be of medium-low hazard; however both are located close to the *Valle Cupella Well* which deserved attention (since its discovery, on April 1998) as a consequence of the water temperature, reaching 26°C with respect to background value of 12°C. This fact spur us to consider that also areas classified here of medium-low NGH may be affected by episodes of peri-volcanic gases gushing, if adjacent to those with high NGH and thermal anomaly, induced by the peri-volcanic heat and mass transfer from below.

Other considerations have to be done analysing the distribution of radon concentration in groundwater, pertaining the two municipal territory.

The map of Radon in groundwater (Figure 3) is surely less easy and clear than of pCO₂ to frame the anomalies in the geo-structural settings, as a consequence of the dis-homogeneous and random distribution of the anomalies. In fact, high ²²²Rn concentration values in groundwater (more than 150-200 Bq/L), with spikes-values reaching 350 Bq/L matched with the areas of *Frattocchie*, *S. Maria delle Mole*, *Selve Nuove* and *Colle Oliva* sectors, while lower values (≈ 50 - 60 Bq/L) were measured in the areas of *Ciampino* downtown, *Marino* downtown, *Cava dei Selci*, and in the sectors crossed by the *Nettunense* road, also where high pCO₂ values were calculated. A high hazard level for Rn-indoor in soils and building has been assigned to this sectors.

The average value calculated considering the totality of the samples was found equal to 100 Bq/L: this value is around ten-fold higher than the national average, as expected in a volcanic and tectonically active area, like the Alban Hills volcano (Quattrocchi *et al.*, 1999).

The radon concentration level in groundwater does not necessarily matches with a correspondent Rn-indoor hazard as explained later.

Finally, considering the main Rn-enrichment factors i.e., volcanic rocks thickness, U-Th series minerals abundance, radon decay laws, state of fracturing and granulometry, permeability, crystalline structures of matrix, convection conditions setting up, rate of circulation inside the aquifer/reservoir (Varhegyi, *et al.*, 1992), gradients of pressure, temperature and concentration, transport facilities, presence of carrier/stripping agents, the presence of this rare gas in solution has a noteworthy more dis-homogeneous distribution than CO₂. Recent unpublished studies regarding radon concentration in soils throughout the Alban Hills region (Lombardi S. *et al.*, 2000 unpublished data of Regione Lazio, 2000) confirm our inferring from groundwater geochemistry.

4.2 Rn-indoor survey

During the Rn – indoor surveys, performed from October 1998 to September 1999, the radon concentration was measured inside private and public buildings (schools, municipal facilities, working edifices, private houses), sampling 190 sites as a whole (Table 3). Totally 68 private houses were selected (47 inside *Ciampino* and 21 inside *Marino*), 38 schools either public or private (20 inside *Ciampino* and 18 inside *Marino*) and various labour-dwellings. The analyses were accomplished during two different periods of the year, October-April (winter in the text) and May-September (summer in the text), to check

the seasonal differences in the Rn-indoor accumulation inside buildings. In fact, the Rn exhalation from soils has been demonstrated to be influenced by the meteorological conditions, i.e. atmospheric pressure, soil moisture, wind patterns, rain/snow episodes. In particular the enhancing of ^{222}Rn exhalation is favoured by low-pressure and dry soil conditions, while it resulted attenuated in presence of high atmospheric pressure, low wind, wet or even frozen soils (Biancotto & Marinaro, 1997).

The figure 4 exhibits the histograms of the Rn-indoor distribution during the studied period as a whole (winter and summer together); moreover, the singled-out winter data (central histogram) and summer data (lower histogram) are shown separately. The average of the two seasons together is 282 Bq/m^3 . Thus, against the above mentioned expectations, in the studied area the differences between winter and summer data are minimal, being 284 and 280 Bq/m^3 respectively. This first inference is not so reassuring, since also in summer the *Ciampino* and *Marino* areas may be affected by high indoor radioactivity. For a better comprehension of the data collected during our surveys, we report as comparison the results gathered by other Rn-indoor studies performed either in Italy or abroad (Poffin *et al.*, 1992; Gundy *et al.*, 1993; Kemski *et al.*, 1996; Biancotto & Marinaro, 1997).

These kind of studies in Italy were performed by the ENEA institution (*Ente Nazionale per le Energie Alternative*). A first national screening research about the “indoor air quality”, pertaining the Italian population was performed in 1982. The most complete study however has been accomplished from 1989 to 1994 by the ANPA institution (*Agenzia Nazionale per la Protezione Ambientale*) and by the ISS (*Istituto Superiore di Sanità*), comprising around 5000 houses located in 200 municipalities spread over all the Italian territory; fifty municipalities with more than 100.000 inhabitants were included within the sample (Bochicchio *et al.*, 1994). The average value of the Rn-indoor concentration resulted to be 77 Bq/m^3 , exhibiting different background levels among regions. The lowest averaged values ($25\text{-}40 \text{ Bq/m}^3$) were found in Calabria, Basilicata, Liguria and Marche regions, while the highest (100 Bq/m^3) are referred to Lombardia, Friuli-Venezia-Giulia, Lazio (where *Marino* and *Ciampino* are located) and Campania regions. Abroad averaged Rn-indoor background of 108 Bq/m^3 in Swedish, 49 Bq/m^3 in Germany, 46 Bq/m^3 in the U.S.A and 21 Bq/m^3 in the U.K. were found.

There is an EC Directivity stated on 21/2/1990 concerning the suggested thresholds to the radon indoor exposure. This directivity fixed a Rn-indoor maximum threshold of 400 Bq/m^3 for pre-existing buildings (constructed by using ancient criteria too) and of 200 Bq/m^3 for the modern buildings. Above these thresholds, which correspond to a maximum

radiation dose of 8 and 4 mSv/year respectively, it should be opportune to take actions in order to cut down radioactivity level.

Coming back to our specific surveys, we observed that 77% of the samples exhibited Rn-indoor values less than 400 Bq/m³, while the remaining 23% of the buildings exceeding the threshold are located within the following zones: *Cava dei Selci*, *S. Maria delle Mole*, *Ciampino* downtown (*Vigna Fiorita* residence) and *Marino* downtown.

The Rn-indoor values found in this study resulted particularly high, if compared with those gathered by the ANPA and ISS above-mentioned study; where only the 5% of the 5000 investigated buildings exceeded the threshold of 200 Bq/m³, and only the 1% exceeded that of 400 Bq/m³.

For a better graphical data comprehension, the 8 Rn-indoor values found inside the control rooms of the *Marino* Aqueduct and inside a house of the *Vigna Fiorita* residence (all values exceeding 2000 Bq/m³), were omitted in the histogram referred to the summer semester period. As shown in Table 3, the Rn-indoor values measured in certain sites are extremely high (up to 60000 Bq/m³), representing very dangerous levels in case of prolonged exposition. It is very interesting the situation found during the month of July 1999 within the *Vigna Fiorita* residence, where two narrow houses (50 metres far) were analysed: built following the same constructive criteria, inside the first building works were accomplished recently, with the purpose to cut down the NGH induced by the CO₂, H₂S and radon, while in the second no building-works were performed. As reported in Table 3, the first house exhibited very low Rn-indoor levels (values < 200 Bq/m³, in green), while inside the second house the Rn-indoor concentrations are very high (values of 1026 and 5467 Bq/m³, in violet). Furthermore, the situation is alternatively quite good when labour-dwellings are concerned, as showed in Figure 5, where the histogram of Rn-indoor distribution inside the school buildings (classes, refectories, etc...), the Fire Brigade buildings of *Marino*, and the *S. Pietro* mineral spring bottling plant, are reported. All these sites exhibited values below 400 Bq/m³, with levels slightly higher inside the basements of only two schools.

Figures 6 and 7 show the histogram of Rn-indoor distribution inside various investigated environments, referred to the winter and summer semesters respectively. When possible, three floors of the buildings have been considered: basements (hobby rooms, wine vaults, etc...), ground floor, first floor and/or upstairs. The results are significant as it may be observed either by the histograms or by the Table 3: the highest Rn-indoor values were found in the basements (average of 557 and 459 Bq/m³ for winter and summer semesters,

respectively), as expected (Biancotto & Marinaro, 1997; Nero & Nazaroh, 1984; Semkov, 1990; Morawska & Phillips, 1993), the maximum values reaching even 1700 Bq/m³. In other floors the values are decidedly lower, reaching at the first floor and upstairs the maximum values of 844 Bq/m³ (“*Vigna Fiorita*” residence of *Ciampino*).

The environmental and geophysical-geochemical variables affecting and concurring to determine the final Rn-indoor values are: the host-rock underlying the soils strata, the kind of strata reached by the foundations, the local fracture field up to the surface, the depth of the first aquifer, the Rn enrichment in the aquifer, convection conditions setting up inside the reservoir, presence of faults, etc... Other invoked variables may be porosity of the building walls, insulation thickness from the soil/foundations, natural or man-made ventilation, foundation air-conduits for canalising radon exhalation from soil out of the building. The different combination of these variables explains the great difference found among very narrow edifices (see Table 3, minimum and maximum values). The first floors and upstairs exhibit radioactivity levels, when detectable, almost entirely induced by the building materials. The soil-radon source loses progressively importance upstairs, unless air convective conditions are established inside the edifice. The revealed differences among the first floors and upstairs are minimal, mainly as a consequence of the great homogeneity of building materials in the investigated area.

5. Discussion: fluid geochemistry anomalies and degassing processes

5.1 Spatial anomalies: a trap inside the basement or an highly fractured sector?

Throughout the Alban Hills volcanic structure, under the Neogenic clays, the Mesozoic carbonate basement is seat of a low-medium enthalpy reservoir (Zuppi *et al.*, 1974; Giggenbach *et al.*, 1988; Quattrocchi & Venanzi, 1989; ENEL, 1990; Duchi *et al.*, 1991; Quattrocchi & Calcara, 1998), whose outcomings at surface are very rare. The knowledge about the thermal reservoir is still scarce, as a consequence of the masking factor constituted by the huge meteoric circulation within the volcanic cover. Our recent studies (Mancini *et al.*, 2000; Quattrocchi *et al.*, 2001) make the hypothesis of a deep reservoir temperature inside the carbonate basement reaching around 220°C against the 150°C evaluated by previous authors (Duchi *et al.*, 1991). This hypothesis was constrained by using the geochemical data pertaining to the newly drilled *Ardea S. Stefano* hot well (ARDH site, 54°C at surface, Fig. 1, see details in Quattrocchi *et al.*, 2001).

However, the main aquifer is essentially cold, and only locally it receives gaseous exhalations, with apparent thermal signature, ascending from the underlying carbonate basement. In average, an increasing trend of groundwater temperature from 12 to 18°C going from East to West, exceeding 20°C at *Ciampino*, Morena, Vallerano-Laurentina, Frattocchie, Ardea and Northward from Anzio, was evaluated throughout the Alban Hills as a whole. A progressive increasing in electrical conductivity is correlated to that inferred in water temperature, spanning from 4 to 15 $\Omega^{-1} \text{ cm}^{-1} \times 10^{-4}$. Groundwater may be drawn away from the typical bicarbonate alkaline and earthy-alkaline chemistry, resulting from volcanic rocks leaching (leaching of leucite, analcime, halloysite, micas, K-feldspar, etc...). This geochemical evolution of meteoric groundwater is usual when the circulation is fast, shallow and not contaminated by peri-volcanic gases. When indeed this contamination occurs, as verified just in some sectors of the *Ciampino* and *Marino* municipalities, the acidic and reduced gaseous input increases noteworthy the leaching power of groundwater. Consequently groundwater is enriched *i)* by sulphate ion originated by the arrival in solution of reduced species containing sulphur and/or after leaching of sulphide deposits; *ii)* by chlorine ion arisen from acidic volatile compounds and possibly from the “metamorphosed” groundwater of the deep reservoir (Fournier, 1987) and *iii)* mostly by bicarbonate ion⁻ drastically upraised, where CO₂ input batches are dissolved.

As the data apparently show, the CO₂ and radon distribution in groundwater throughout the two territories exhibited different patterns. In both cases the spatial anomalies do not follow linear trends but exhibit a spread anomalous shape, more random for Rn and more homogeneous for CO₂. This difference may be explained in part as a consequence of the different origin of the two species and in part induced by their different geochemical behaviour and geo-dynamic transport patterns, as explained before. The CO₂ has a “primary” and deeper origin, originating both by the direct degassing of the deep magma chamber, whose presence was inferred by tomographic and geo-structural studies (Amato & Chiarabba, 1995; Delaney *et al.*, 1996), and by the thermo-metamorphic degassing. Therefore the geometry and linear boundaries of the CO₂ spread areal anomalies may give strong indication about the buried geological structure, which explain the shape and width of the anomaly itself.

In other geodynamical settings CO₂ is enriched properly where the structural patterns are favourable to its uprising, i.e., along faults, involving linear anomalies. On the contrary, in this peculiar case, it is strongly evident that the CO₂ spread anomaly corresponds properly to the polygon of the *Ciampino Horst*, bordered by faults. Among which the clearest is an

almost NNE-SSW fault, inferred in the past by other methodologies (geo-structural, hydrogeological and gravimetric, see Toro B., 1977; Di Filippo & Toro, 1980; Capelli *et al.*, 1999; Giordano *et al.*, 2000).

Therefore we identified a buried funnel-shaped gas trap, whose presence involves an intermediate step refilled gas reservoir under the clays allowing a huge flux uprising by a “continuous gas-phase micro-macro seepage mechanism”(Brown, 2000).

Moreover, the macro-seepage is additionally facilitated at the boundary of the horst, by using the fracture field, which generates the trap itself as further preferential pathway for gases to escape at surface. Anyway, the presence of a gas-trap at intermediate depth between source and surface is the main pre-requisite of the *Ciampino-Marino* uncommon NGH prone-area throughout Italy. This result is in good agreement with the dissolved gases chemistry considerations made by Chiodini & Frandini, (2000): the *Ciampino* gas manifestations originate from degassing of shallow groundwater at low temperature which previously dissolved a deep gas (single-step separation from liquid).

5.2 Temporal anomalies: phase separation or modification in the geometry/width of fracture field ?

Episodes of gas-gushing and strong exhalations have been observed and narrated from historical times in specific sectors of the Alban Hills volcano. These occurred mainly during earthquakes, exhibiting to people and scientists as hot groundwater, random thermal signature and gases gushing (CO₂, H₂S), mostly in *Marino-Ciampino*, *Morena*, *Laurentina*, *Ardea* and *Tivoli* sectors (see in Boni *et al.*, 1981, Quattrocchi & Venanzi, 1989; Calcara *et al.*, 1995; Quattrocchi & Calcara, 1998; Funicello, unpublished data). This correlation suggests a common cause between gaseous release at surface and stress-strain release at depth. In the past we tried to explain this close correlation by the phase-separation thermodynamic process enhanced or triggered in correspondence of extensive episodes (Fournier, 1987; Quattrocchi & Calcara, 1998).

Anyway a simpler mechanism may be mentioned, mostly in absence of earthquakes, namely a temporal variation in the volumetric flux induced by a variation in the real fracture network and by the effects of gas expansion as it ascent, namely a fracture width positive variation with consequent positive variation of the gas flux (Brown, 2000).

At the moment, we have not enough data and case histories to state definitively the prevailing mechanism generating temporal variation of peri-volcanic fluxes at surface.

5.3 Stripping and carrier role of the CO₂ flux on dissolved Radon

The radon concentration level in groundwater does not necessarily matches with a correspondent Rn-indoor hazard: despite both CO₂ and radon data contribute to the NGH assessment as a whole, the specific contribution of each gas specie has to be evaluated in different manner, as a consequence of their intrinsic geochemical characteristics and dynamical patterns (origin, transport, geochemical mobility fields, chemical bonds, etc.).

Sectors under study were assessed of high Rn-indoor potential hazard despite having low radon concentration in groundwater. It was inferred on the basis of the evidence that, exceeding certain CO₂ fluxes from below, corresponding to pCO₂ values in groundwater around > 0.8 bar, the “*stripping effect*” of the uprising peri-volcanic gases (mainly CO₂) is prevailing with respect the “*carrier effect*” of the same gases during the transport at surface of the dissolved minor and trace gases of shallower origin, namely Rn. Thus, if under certain peri-volcanic gaseous fluxes the Rn and CO₂ enrichment in solution are strictly parallel and correlated, in the case of huge CO₂ flux the radon signature in groundwater drop down, being enriched apparently in the gas phase, as occurs at the MNGCS and surroundings. Here the radon measured i.e., on 15/1/99, in liquid and gaseous phases was 8 Bq/L and 104 Bq/L respectively (around ten times more in the gaseous phase with respect to the liquid one, as consequence of the partitioning due to the “*stripping effect*”). Thus, radon follows preferentially the gaseous phase in transition through aquifer to surface, finally being strongly enriched at the soil and basement level. Therefore, we decided to include inside the high “Rn-indoor potential hazard” areas also sectors characterised by medium-low dissolved radon in groundwater, nevertheless characterised by CO₂ partial pressures overlying a certain “stripping threshold”, here defined at 0.8 bars. The test Rn-indoor discussed measurements effectively confirmed the soundness of this assessment criteria.

6. Conclusions

The multidisciplinary and multiparametric approach is the main prerequisite to the natural hazards assessment, i.e. to the *Natural Gases Hazard* (NGH) here defined as “*hazard by diffuse gaseous exhalations of natural origin (i.e., peri-volcanic type) and Rn-indoor hazard*”

A fluid geochemistry micro-zonation was successfully accomplished in an Alban Hills test-site also to deepen the geodynamical processes inside a quiescent volcanic area, although characterised by a specific *unrest activity*. This micro-zonation approach is highly requested in other volcanically quiescent areas, i.e., throughout the *Roman Comagmatic Province* as a whole.

We evaluated in details the “CO₂ exhalation potential hazard” (as main part of the NGH) here intended as the potentiality for an area to become seat of poisonous natural gases exhalations either in soils or in lower atmosphere (comprising dwellings), with prevailing CO₂ component. This evaluation was performed firstly by extrapolating the aquifer physico-chemical and CO₂ patterns, discriminating sectors where in future CO₂ flux measurements and gases concentration tests in soils have to be detailed. The choice to start the NGH study from groundwater conditions arises by the fact that, where the main aquifer is over-saturated in CO₂, the probabilities that the excess of deep gases may arrive at surface increase noteworthy.

At the same time, where radon reaches high values in solution, high “Rn-indoor potential hazard” (as part of NGH) is expected and effectively found in the study area, testifying i.e., convection and enhanced permeability in peculiar sectors of the main aquifer. Therefore, the method turned out to be very sound in defining accurately the most powerful candidate CO₂ exhalation hazardous areas and Rn-indoor prone-areas assessing the NGH as a whole. Nevertheless, looking for a final NGH final evaluation, the Rn-indoor component is more complex, depending upon the prevailing role of CO₂: as “*carrier*” or “*stripping-diluting*” agent, respectively. In fact, there is a strict link and a positive correlation between CO₂ and Rn in groundwater below the 0.8 bar pCO₂ threshold, followed by either a more random behaviour in groundwater or an enrichment in the free-gas phase, exceeding this pCO₂ threshold. The first specie -CO₂- was found to be the main component of the peri-volcanic gases, with a “*carrier*” role for the other minor and trace components either of volcanic origin (as H₂S, CH₄, CO, etc...) or of shallower origin (crustal as He and Rn, CH₄ from oil accumulation); the second, properly ²²²Rn, as a gaseous trace element with a complex behaviour, mainly testifying *i*) enhanced permeability at depth, *ii*) pervious fracture field and possibly *iii*) fluid convection at depth.

The new results added such a significant detail of the pCO₂ distribution in groundwater, that now we are able to distinguish clearly a NNE-SSW regional fault, around 5 Km elongated, corresponding to the Eastern border of the *Ciampino Horst*, previously defined by other Earth Science methodologies, stressing the power of fluid geochemistry micro-

zonation method in locating buried faults. The evident NNE-SSW fault separates a western sector of the entire studied area -prone to hazardous CO₂ flux from depth- from a eastern one, without any appreciable NGH. Therefore we discovered a buried gas trap with the role of a funnel-shape structure for canalising deeply originated gases. Its presence involves an intermediate step permanently refilled gas reservoir, under the thinned Neogene clays. It allows a huge flux by a “continuous gas-phase micro and macro seepage mechanism” (Brown, 2000) and strongly affects the final chemistry of the dissolved gases.

The drilling of a deep well, reaching the carbonate basement of the Alban Hills, is strongly recommended: it may involve a conspicuous task forces drilling project (i.e., ENEL, AGIP, ING, Latium Region and Municipalities), with the main purpose to solve a lot of scientific questions about the nature of the first crustal strata of this volcano (i.e., if seat of a medium enthalpy reservoir of 220°C as critically reviewed by using our data).

We advise also the need of a geochemical network planning in the surroundings of the MNGCS, to install at least one remote continuous gas monitoring station (UNI standards for human health) of the following parameters: CO₂, CH₄, H₂S, Rn and possibly CO and SO₂ and the atmospheric parameters; while two or three stations must be installed to monitor aquifer by a versatile multiparametric configuration (i.e., GMS II prototype, Quattrocchi *et al.*, 2000), inserting the Rn sensor (Galli *et al.*, 2000).

Even before the intervention of toxicologists, radio-protection experts, sanitary subjects and urbanists, a *Natural Gases Hazard* assessment micro-zonation have to be managed by scientists devoted to the geophysical, geochemical, geo-structural and hydrogeological comprehension of the ongoing geodynamical process: a slow Earth degassing. This geodynamical process preferentially is enhanced throughout peculiar structural settings as quiescent and active volcanoes, extensive structures, geothermal areas, active fault systems and seismogenic segments, as well as gaseous trap-reservoir prone-structures.

In future we don't exclude new dangerous differential peri-volcanic degassing: they are expected to occur at extremely localised sectors inside the areas advised hazardous in this work; the situation may become critical mostly if the aquifer static level will keep decreasing as happened during the last 25 years (around 1 meter/year decreasing rate), allowing spreader narrow sectors to be interested by the phenomena (i.e., *Vigna Fiorita Residence*) If these degassing episodes will occur in presence of animals or human beings, lethal consequences are not excluded. The 1995-1999 degassing episodes and the highly probable human death caused the lethal peri-volcanic degassing on December 29, 2000, are

emblematic of what may occur in future, and with worse outcomes, if the area will not be taken under severe monitoring and without actions of the City Councils.

Anyway a wide knowledge of the NGH by people and local authorities and a sound urbanistic re-arrangement, accompanied by new regulations in force for NGH subjected areas, are indispensable measures to reduce to minimum levels the risks for human health.

Acknowledgements: We are grateful to the *Ciampino* and *Marino* Municipalities, which partially funded this work. We are grateful to the private citizens rendering available the sampling in their houses. Thank R. Funicello for the continuous hints and encouragement during the geochemical monitoring and finally thank to G. Capelli who gave information about the hydrogeological settings of the Alban Hills region.

6. References

- Amato A. and Valensise G.: 1986, Il basamento sedimentario dell'area Albana: risultato dello studio degli ejecta dei crateri idromagmatici di Albano e Nemi, *Rend.Soc.Geol.It.* **35**, 761-767. (In Italian)
- Amato A., Chiarabba C., Cocco M., Di Bona M. and Selvaggi G.: 1994, The 1989-1990 seismic swarm in the Alban Hills volcanic area, central Italy, *J.Volc.Geoth.Res.* **61**, 225-237.
- Amato A. and Chiarabba C.: 1995, Recent Uplift of the Alban Hills Volcano (Italy): evidence for magmatic inflation, *Geoph.Res.Lett.* **22 (15)**, 1985-1988.
- Belloni P., Cavaioli M., Ingrao G., Mancini C., Notaro M., Santaroni P., Torri G. and Vasselli R.: 1995, Optimization and comparison of three different methods for the determination of Rn-222 in water, *Science of the Total Environ.* **173/174**, 57-61.
- Bianconi R. & Marinaro M.: 1997, Radon tra natura e ambiente costruito, *Proc. Meeting "Radioprotezione, Territorio, Interventi, Informazione"*, Mestre, 24-26/11/97. (In Italian)
- Bochicchio F., Campos Venuti G., Nuccetelli C., Piermattei S., Risica S., Tommasino L., Torri G.: 1994, Indagine nazionale sulla radioattività naturale nelle abitazioni, *ANPA e IIS, Special Volume* Roma. 257 pp (In Italian)
- Boni C., Bono P., Capelli G., Funicello R., Lombardi S., Parotto M., Rossi F.M. and Ventura G.: 1979, Lineamenti idrogeologici, idrogeologici e idrochimici della Regione Albana: primi risultati della campagna 1977-1979, *Proc. I Sem. Info. PFE-EG, CNR, Pisa.* (In Italian)
- Boni C., Bono P. and Capelli G.: 1981, Nuove osservazioni su idrogeologia, geochemica e termalismo dell' Area Albana (Lazio Meridionale), *Proc. II Sem. Info. PFE-EG, CNR, Pisa*, **2**, 64-84. (In Italian)
- Brown A. (2000): Evaluation of possible gas micro-seepage mechanism, *AAPG Bull.* **184 (11)**, 1775-1789.
- Calcara M., Lombardi S. and Quattrocchi F.: 1995, Geochemical Monitoring for seismic surveillance in the Alban Hills region, *Special Volume: "The Volcano of Alban Hills"*, Eds. R. Trigila, 283 pp. 243-265.
- Capelli G., De Rita D., Cecili A., Giordano G., Mazza R., Rodani S. Bigi G.: 1999, Cities on volcanoes: groundwater resources and management in a highly populated volcanic region. A GIS in the Colli Albani region, Rome, Italy, *Proc. Int. Symp. on Engineering Geology, Hydrogeology and Natural Disaster with emphasis on Asia.* Kathmandu, Nepal, September 28-30, 1999, NGS, IAEG, IUGS and IDNDR.

- Chiodini G., Frondini F., Ponziani F.: 1995, Deep structures and carbon dioxide degassing in Central Italy, *Geothermics* **124**, 81-94.
- Chiodini G., Cioni R., Guidi M., Raco B., Marini L.: 1998, Soil CO₂ flux measurements in volcanic and geothermal areas, *Applied Geochemistry* **13** (5), 543-552.
- Chiodini G., Frondini F.: 2000, Carbon dioxide degassing from the Alban Hills volcanic region, Central Italy, *Chemical Geology*, in press.
- Cohen B.L. and Cohen E.S.: (1983, Theory and practice of radon monitoring with charcoal adsorption, *Health Physics* **45**, 501-508.
- Dall'Aglio M., Quattrocchi F., Venanzi G.: 1990, La stazione automatica per lo studio dei precursori geochimici nei Colli Albani: il prototipo del sottosistema geochimico della rete sismica nazionale dell'ING, *Proc. IX Convegno GNGTS 1990, CNR-Roma*, 95-100. (In Italian)
- Delaney P., Amato A., Borgia A., Chiarabba C. and Quattrocchi F. (1996): The Restless Volcano of the Alban Hills, Central Italy, *Proc. AGU Fall Meeting 1996, San Francisco, U.S.A.*
- De Luca A. and Mancini C.: 1991, The measurement system for ²²²Rn, monitoring with charcoal adsorption collectors, *Health Physics* **61**, 543-546.
- De Rita D., Funicello R. and Parotto M.: 1988, Carta Geologica del Complesso Vulcanico dei Colli Albani, *Prog. Fin. "Geodinamica", SELCA Eds., CNR-Rome, Italy*. (In Italian)
- De Rita D., Funicello R. and Rosa C.: 1992: Volcanic activity and drainage network evolution of the Colli Albani area, *Acta Vulcanologica* **2**, 185-198.
- Di Filippo M. and Toro B.: 1980, Analisi gravimetrica delle strutture geologiche del Lazio Meridionale, *Geologica Romana* **19**, 285-294.
- Duchi V., Paolieri M. and Pizzetti A.: 1991, Geochemical study on natural gas and water discharges in the Southern Latium (Italy): circulation, evolution of fluids and geothermal potential in the region, *J. Volc. Geoth. Res.* **47**, 221-235.
- EC Program: 1996-99 b, Automatic Geochemical Monitoring of Volcanoes (AGMV), *EC Contract N. ENV4-CT96-0289 EC Community, DG XII, Bruxelles, Belgium*.
- EC Program: 1996-99 b; Geochemical Seismic Zonation (GSZ). Seismic Hazard Zonation: a multidisciplinary approach using fluid-geochemistry methods, *EC Contract N. ENV4-CT96-029, EC Community, DG XII, Bruxelles, Belgium*.
- ENEL: 1990 Esplorazione Geotermica dei Colli Albani, *Special Volume*, 143 pp, Pisa. (In Italian)
- ENEL-DST "La Sapienza": 1987, Controllo delle Variazioni temporali del chimismo di alcune acque e gas nella regione dei Colli Albani, *Rapporto Attività UNG dell'ENEL e DST "La Sapienza"*, 120 pp. (In Italian)
- EPA: 1987, EERF standard operating procedures for ²²²Rn measurement using charcoal canisters, *EPA Pubbl.* **520/5-87-005**.
- Faccenna C., Funicello R. and Mattei M.: 1994 a, Late Pleistocene N-S shear zone along latium Thyrrhenian margin: structural characters and volcanological implications, *Boll. Geof. Teor. Appl.* **36**, 141-144.
- Faccenna C.: 1994 b, Structural and idrogeological features of Pleistocene shear zones in the area of Rome, *Ann. Geof.* **37** (1), 121-133.
- Fornaseri M., Scherillo A. and Ventriglia V.: 1963, La regione vulcanica dei Colli Albani, *Eds. A.T.E.D. Bardi, CNR-Roma*, 561 pp. (In Italian)
- Fournier R.O.: 1987, Conceptual models of brine evolution in magmatic-hydrothermal systems, *In "Volcanism in Hawaii, U.S.G.S. Prof. Paper N. 1350, Chapter 55*, 1487-1506.
- Freda C., Gaeta M., Palladino D.M. and Trigila R. (1997): The Villa Senni eruption (Albani Hills, Central Italy): the role of H₂O and CO₂ on the magma chamber evolution and on the eruptive scenario, *J. Volc. Geoth. Res.* **78**, 103-120.

- Funiciello R. and Parotto M.: 1978, Il substrato sedimentario nell'area dei Colli Albani: considerazioni geodinamiche e paleogeografiche sul margine tirrenico dell'Appennino centrale, *Geologica Romana* **17**, 233-287. (In Italian)
- Galli, G., Guadoni C. and Mancini, C.: 1999, Radon Grab sampling in water by means of Radon transfer in activated charcoal collectors, *Il Nuovo Cimento* **22C** (3-4), 583-587.
- Galli, G., Mancini, C. and Quattrocchi, F.: 2000, Groundwater radon continuous monitoring system (a-scintillation counting) for natural hazard surveillance, *PAGEOPH* **157**, 1-27.
- Giggenbach W.F., Minissale A.A. and Scandiffio G.: 1988, Isotopic and chemical assessment of geothermal potential of the Colli Albani area, Latium region, Italy, *Applied Geochemistry* **3**, 475-486.
- Giordano G., Mazza R., Pizzino L., Quattrocchi F., Cecili A., Capelli G., De Rita D. and Biggi G.: 2000, Geologic hazards in a highly populated volcanic region, Colli Albani volcano, Rome, Italy, *Proc. EGS Gen. Assembly, Amsterdam, The Netherlands, April 2000*.
- Gundy S. A., Darby S. C., Miles J. C. H., Green B. M. R., Cox D. R.: 1993, Factors affecting indoor radon concentrations in the United Kingdom, *Health Phys.* **64**, 2-12.
- Hills D.P. and 18 al.: 1993, Seismicity remotely triggered by the Magnitude 7.3 Landers California Earthquake, *Science* **260**, 1617-1623.
- Kemski J., Klingel R., Sieml A.: 1996, Classification and mapping of radon affected areas in Germany, *Environ. Int.* **22** (1), 789-798.
- Kemski J., Siehl A. and Valdavia-Manchego M.: 1999, Mapping and prediction of geogenic radon potential in Germany, *Il Nuovo Cimento* **22** (3-4), 295-300.
- Kerner D.B. and Renne P.R.: 1998, $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of Roman Volcanic Province Tephra in the Tiber River Valley: age calibration of Middle Pleistocene sea-level changes, *Am.Bull. Geol.Soc.* **110**, 740-747.
- Kerner D.B., Marra F. and Renne P.R.: 2000, The history of Monti Sabatini and Alban Hills volcanoes: groundwork for assessing volcanic-tectonic hazards for Rome, *J.Volcan.Geoth.Res.*, in press.
- ICRP: 1994, Protection against radon 222 at home and at work, *ICRP-Publ.* **65**, 45.
- Le Bas M., Le Maitre R.W., Streckeisen A. and Zanettin B.A.: 1986, Chemical classification of volcanic rocks based on total alkali-silica diagram, *J. Petrol.* **27** (3), 740-745.
- Locardi E., Lombardi G., Funiciello R. and Parotto M.: 1976, The main volcanic groups of Latium (Italy): relationships between structural evolution and petrogenesis, *Geol.Rom.* **15**, 279-300. (In Italian)
- Lombardi S.: 1975, Il ruolo dell'idrologia nei confronti del vulcanismo freatico albano, *Geologica Romana* **14**, 29-39. (In Italian)
- Lombardi S., (Project Leader) et 22 al.: 1999, Final Report of the "Geochemical Seismic Zonation" EC Program, *EC Contract N. ENV4-CT96-0291, DG XII, Brussels, Belgium*.
- Mancini C. and Giannelli G.: 1995, Determination of waterborne ^{222}Rn , using AC canisters, *Health Physics* **69**, 408-410.
- Mancini C., Quattrocchi F., Guadoni C., Pizzino L. and Porfidia B.: 2000, ^{222}Rn study throughout different seismotectonical areas: comparison between different techniques for discrete monitoring, *Ann. Geof.* **43** (1), 1- 28.
- Mangone G.: 2000, Valutazione del depauperamento delle risorse idriche nel settore nord-occidentale dei Colli Albani e suoi possibili effetti sul Natural Gases Hazard, *Degree Thesis*, University "Roma Tre" 127 pp. (In Italian)
- Marra F.: 1999, Low-magnitude earthquakes in Rome, structural interpretation and implications for the local stress-field, *Geoph. J. Intern.* **138**, 231-243.
- Marra F.: 2000, Strike-slip faulting and block rotation: a possible triggering mechanism for lava flows in the Alban Hills ?, *J. Struct. Geol.*, in press.

- Martini M., Giannini L., Prati F., Tassi F., Capaccioni B. Iozzelli P.: 1994, Chemical characters of crater lakes in the Azores and Italy: the anomaly of lake Albano, *Geochem. J.* **28**, 173-184.
- Montone P., Amato A., Chiarabba C., Buonasorte G. and Fiordelisi A.: 1995, Evidence of active extension in Quaternary volcanoes of Central Italy from breakout analysis and seismicity, *Geoph.Res.Lett.* **22**, 1909-1912.
- Morawska L. and Phillips C. R.: 1993, Dependence of the radon emanation coefficient on radium distribution and internal structure of the material, *Geoch. Cosmoc. Acta* **57**, 1783-1797.
- Mouton J.: 1977: Contributo allo studio delle acque sotterranee dell'Agro Romano e Pontino, *Proc. Meeting "L'acqua nella Pianura Pontina*, Latina. 156 pp. (In Italian)
- Nero A. V. and Nazaroh W. W.: 1984, Characterising the source of indoor radon, *Rad. Prot. Dosim.* **7** (1-4), 23-39.
- Poffijn A., Uyttenhove J., Drouguet B. and Tondeur F.: 1992, The radon problem in schools and public buildings in Belgium, *Rad. Prot. Dosim.* **45**, 499-501.
- Principe C., Romano G.A. and Vannozzi D.: 1994, GEOCH data bank: geochemical data of natural fluids from Italian active volcanoes under surveillance. Reference Manual, *Geoinformatica* **2**, 75-82.
- Quattrocchi F. and Venanzi V.: 1989, Sulla scelta di un sito per il monitoraggio di parametri idrogeochimici per lo studio di premonitori sismici nell' area dei Colli Albani, *Proc. VIII Convegno GNGTS 1989, CNR - Roma*, 259-266.
- Quattrocchi F., Amato A., Calcara M., Chiarabba C. and Funiciello R.: 1992, Anomalie geochimiche correlabili alla sequenza sismica nell'area settentrionale dei Monti Vulsini (Castel Giorgio, Febbraio 1992), *Proc. XI Convegno GNGTS 1992, CNR-Roma*, 59-70.
- Quattrocchi F. and Calcara M.: 1994, Groundwater chemistry in some Italian seismic areas: space and time correlations with tectonic features and seismic activity, *Mineral. Magaz.* **58**, 750-751.
- Quattrocchi F. and Calcara M.: 1998, Test-sites for earthquake prediction experiments within the Colli Albani region, *Phys. Chem. of the Earth* **23** (9/10), 915-920.
- Quattrocchi F., Pizzino L., Guerra M. and Scarlato P.: 1998, Geochemical Hazard of the Colli Albani quiescent volcano: CO₂ and ²²²Rn surveillance in Ciampino-Marino-Rocca di Papa area, *Proc. Int. Symp. «Cities on Volcanoes», Rome-Naples, 28/6-4/7/98, p. 114.* (In Italian)
- Quattrocchi F., Di Stefano G., Pizzino L., Pongetti F., Romeo G., Scarlato P., Sciacca U. and Urbini G.: 2000, The Geochemical Monitoring System II prototype (GMS II) installation at the Acqua Difesa well, within the Etna region. first data during the 1999 volcanic crisis, *J. Volc. Geoth. Res.* **101**, 273-306.
- Quattrocchi F., Guerra M., Pizzino L. and Lombardi S.: 1999, Radon and helium as pathfinders of fault systems and groundwater evolution in different Italian areas, *Il Nuovo Cimento* **22** (3-4), 309-316.
- Quattrocchi F.: 1999, In search of evidences of deep fluid discharges and pore pressure evolution in the crust to explain the seismicity style of Umbria-Marche 1997-98 seismic sequence (Central Italy), *Ann. Geof.* **42** (4), 1-29.
- Quattrocchi F., Capelli G., De Rita D., Faccenna C., Funiciello R., Galli G., Giordano G., Goletto D., Mancini C., Mazza R., Pizzino L.: 2001, The Ardea Basin fluid geochemistry, hydrogeology, and structural patterns: new insights about the geothermal unrest activity of the Alban Hills quiescent volcano (Rome, Italy) and its geochemical hazard surveillance, *Proc. WRI-10, Water-Rock Interaction X Int. Conference, Villasimius, Italy, Balkema Eds.*, in press.
- Radicati Di Bronzolo, Huneke F., Papanastassiou J.C. and Wasserburg G.L.: 1981, ⁴⁰Ar/³⁹Ar and Rb/Sr age determination on Quaternary volcanic rocks, *EPSL* **53**, 445-456.

- Semkov T. M.: 1990, Recoil emanation theory applied to radon release from mineral grains, *Geoch. Cosmoc. Acta* **54**, 425-440.
- Toro B.: 1977, Gravimetry and deep structure of the Sabatinian and Alban volcanic areas (Latium), *Geologica Romana* **15**, 301-310.
- Varhegyi A., Hakl J., Monnin M., Morin J.P. and Seidel J.L.: 1992, Experimental study of radon transport in water as test for a transportation micro-bubble model, *J. Appl. Geophys.* **29**, 37-46.
- Ventriglia U.: 1990, Idrogeologia della Provincia di Roma. Regione Vulcanica dei Colli Albani. *Assess. LL-PP, Provincia di Roma* **3**, 253 pp (In Italian)
- Villa I.M., Calanchi N., Dinelli E. and Lucchini F.: 1999, Age and evolution of the Albano crater lake (Roman Comagmatic Province), *Acta Vulcanol.* **11**, 305-310.
- Washington H.S.: 1906, The Roman Comagmatic Region, *Pubbl. 57 Carnegie Inst.*, Washington, 145 pp.
- Zhu H.C., Charlet J.M. and Tondeur F.: 1999, Indoor radon levels in relation to geology in Southern Belgium, *Il Nuovo Cimento*, **22** (3-4), 353-358.
- Zuppi G.M., Fontes J.C. and Letolle R.: 1974, Isotopes du milieu et circulation d'eaux sulfurees dans le Latium, *In Isotope Techniques in Groundwater Hydrology, IAEA Editor Vienna* **1**, 341-361.

Figure captions

Figure 1: Geological sketch of the Alban Hills district. MA: Marino town; CIA: Ciampino town; MOR: Morena town; TIV: Tivoli town; MNGCS: Natural Gas Manifestation of Cava dei Selci; ZFR: Zolforata gas-pool; ALBU: Bagni Albule thermal and gas spring; ARDH: Thermal Well Ardea; TA: Tuscolano Artemisio caldera; VLR-CECCH-LAUR: Vallerano-Cecchignola-Laurentina; PNT BRG: Pantano Borghese crater; CAS: Castiglione crater (modified from Chiodini et al., 2000).

Figure 2: Map of the pCO₂ distribution in groundwater of the Marino and Ciampino municipalities.

Figure 3: Map of the radon distribution in groundwater of the Marino and Ciampino municipalities.

Figure 4: Rn-indoor distribution in public and private dwellings of the Marino and Ciampino municipalities in the period October-1998-December 1999 (upper histogram), October 1998-April 1999 (winter in the text, central histogram), May 1999-September 1999 (summer in the text, lower histogram).

Figure 5: Rn-indoor distribution inside labour-dwellings of the Ciampino and Marino municipalities (schools, Marino Fire Brigade building and *S. Pietro* mineral water bottling plant).

Figure 6: Rn-indoor distribution in public and private edifices in the Marino-Ciampino municipalities during winter semester.

Figure 7: Rn-indoor distribution in public and private edifices in the Marino-Ciampino municipalities during summer semester.

Table captions

Table 1: Physic-chemical parameters measured during the geochemical surveys in the Alban Hills area. Temperature is expressed in °C, Eh in mV, Electrical Conductivity in µS/cm, HCO₃ in meq/L, ²²²Rn in Bq/L. Calculated pCO₂ is expressed in bar. Latitude and longitude are kilometric coordinates.

Table 2: Remarkable gaseous exhalations from soils and wells occurred in the past in the Alban Hills volcanic area.

Table 3: Statistical analyses of the Rn-indoor distribution both in the winter or in the summer semesters for basements, ground floors and first/upper floors. Rn-indoor distribution inside both the Marino aqueduct control rooms and *Vigna Fiorita* residence are also reported.