Influence of hydrogeological setting on the arsenic occurrence in groundwater of the volcanic areas of central and southern Italy

Antonella Baiocchi, Francesca Lotti and Vincenzo Piscopo

Abstract: In this study, the relations between the arsenic concentrations in groundwater and the hydrogeological features of some important volcanic areas of central and southern Italy were analyzed. The groundwater resources of these areas are widely used for the local drinking supply by approximately 2 million inhabitants, and they sustain the related economic activities. Based on a review of the published data and new determinations, the As content in the groundwater is presented along with the hydrostratigraphy and structural setting of the different systems and the hydraulic characteristics of the volcanites. The results show that the As content in the groundwater of the volcanic areas of central and southern Italy varies both within the single aquifer system and among the different aquifer systems, often exceeding the maximum admissible concentration of 10 µg/L.

In addition to the well-known relations among the contents of geogenic contaminant in groundwater and volcanic rock composition, water chemistry and hydrothermal activity, the results show that where the flow is relatively fast in a basal aquifer less influenced by uprising of deep fluids, relatively low As concentrations are found. Where the groundwater circulation is more fractioned, the aquifers are hydraulically heterogeneous and the vertical discontinuities permit interactions between the basal aquifer and deep fluids, As concentration in the groundwater has a wider range, frequently exceeding the value of 50 µg/L. In this hydrogeological environment, when tapping the groundwater resources for drinking water, it must be considered that the more vulnerable zones are related to the nature of the substratum of the volcanites, volcano-tectonic structures and hydrothermal areas and to the local response of the aquifer to pumping.

Keywords: arsenic, volcanic aquifer, hydrogeology, hydrochemistry, drinking water.

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Riassunto: *In questo studio sono analizzate le relazioni tra le concentrazioni di arsenico nelle acque sotterranee e le caratteristiche idrogeologiche di alcune importanti aree vulcaniche del centro e sud Italia. Le risorse idriche sotterranee di queste aree sono ampiamente utilizzate per l'approvvigionamento potabile di circa 2 milioni di abitanti, e per sostenere le attività economiche connesse. Sulla base di una revisione dei dati pubblicati e di nuove determinazioni, la distribuzione di As contenuto nelle acque sotterranee è esaminato considerando le caratteristiche idrogeologiche dei diversi sistemi vulcanici ed in particolare l'idrostratigrafia, l'assetto vulcano-tettonico e le caratteristiche idrauliche delle vulcaniti.*

I risultati mostrano che il contenuto di As nelle acque sotterranee delle aree vulcaniche del centro e sud Italia varia sia all'interno del singolo sistema acquifero sia tra i diversi sistemi acquiferi, e spesso risulta essere superiore alla concentrazione massima ammissibile di 10 µg/L.

Oltre alle ben note relazioni tra i contenuti del contaminante geogenico nelle acque sotterranee e composizione della roccia vulcanica, chimismo dell'acqua e attività idrotermale, i risultati mostrano che laddove il flusso è relativamente veloce in un acquifero basale meno influenzato dalla risalita di fluidi profondi, si trovano concentrazioni relativamente basse. Dove la circolazione delle acque sotterranee è invece più frazionata, gli acquiferi sono idraulicamente eterogenei e le discontinuità verticali consentono interazioni tra la falda basale e fluidi profondi, la concentrazione di As copre un intervallo di valori più ampio, superando spesso il valore di 50 µg/L.

Sulla base dei risultati ottenuti, il posizionamento e il metodo di pompaggio dei pozzi ad uso potabile dovrebbero seguire un nuovo approccio, considerato l'impatto che le acque con alta concentrazione di As possono avere sulla salute umana. A tal fine, occorre osservare che le zone più vulnerabili all'interno di questi acquiferi vulcanici sono legate alla natura del substrato delle vulcaniti, alle strutture vulcano-tettoniche e alle aree idrotermali. Dovrebbe inoltre essere sempre verificato che gli effetti del pompaggio sul flusso orizzontale e verticale contengano il mescolamento tra acque di circuiti relativamente poco profondi con quelle di circuiti più profondi, specialmente dove la circolazione delle acque sotterranee è più frazionata. Un approccio integrato che comprenda la zonazione idrogeologica e idrochimica degli acquiferi dovrebbe essere il metodo alla base dell'individuazione delle risorse idriche sotterranee a scopo potabile in ambienti idrogeologici naturalmente contaminati da As.

Introduction

Arsenic (As) occurrence in groundwater circulating in volcanic rocks is a widespread phenomenon and has mainly natural origins. Usually, As in groundwater is related to the presence of the element as a minor constituent of volcanic gases and geothermal fluids or to the leaching of ore deposits containing the element as a major or minor constituent (for example, Ballantyne and Moore, 1998; Smedley and Kinniburgh, 2002; Webster and Nordstrom, 2003).

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The occurrence of As in groundwater in Italy is widely documented and its release covers different origins, such as mineral deposits (in Tuscany and Sardinia), highly reducing environments (alluvial plains in Veneto, Emilia Romagna and Lombardy) and volcanic systems (in Tuscany, Latium and Campania) (for example, Zavatti et al., 1995; Tamasi and Cini, 2004; Scialoja, 2005; Fanfani and Pilia, 2007).

The present work deals with the As content in the groundwater of the volcanic areas of central and southern Italy, documented in, for example, Cremisini et al., 1979; Brondi et al., 1986; Celico et al., 1992; Dall'Aglio, 1996; Aiuppa et al., 2000; 2003; Lima et al., 2003; Aiuppa et al., 2006; Achene et al., 2010. These studies show that several factors control the As mobility in groundwater, such as the water temperature, host-rock composition, water chemistry and the influence of magma-derived volatiles. However, a few studies analyze the As distribution in groundwater while taking into account the influence of the regional and local characteristics of flow in volcanic aquifers (for example, Vivona et al., 2007; Angelone et al., 2009).

Within this framework, this study aims to analyze the relations between the As concentrations in groundwater and the hydrogeological features of some important volcanic areas of central and southern Italy. The groundwater resources of these areas are widely used for the local drinking supply by approximately 2 million inhabitants, and they sustain the related economic activities.

The need to detail the relations between As occurrence in groundwater and the hydrogeological environment comes from the recent revision of quality standards for drinking water (98/83 EC Directive). The maximum admissible concentration has been lowered from 50 to 10 µg/L, and, as a consequence, several local public administrators and water management companies must invest money to ensure that drinking resources are in accordance with the new rules. It is essential, therefore, to readdress the future options for groundwater resource management in keeping with the concept of sustainable yield.

Geological outlines

The volcanoes considered in this study are located in central and southern Italy (Fig. 1).

The volcanoes located along the Tyrrhenian margin from Latium to Campania (Fig. 1) can be related to an orogenic tectono-magmatic association. The Roman Magmatic Province, including the Vulsini, Vico, Cimino, Sabatini, Roccamonfina, Isle of Ischia, Phlegrean Fields and Somma-Vesuvius volcanoes, developed along this margin as a consequence of the intense rifting in the Pliocene-Quaternary

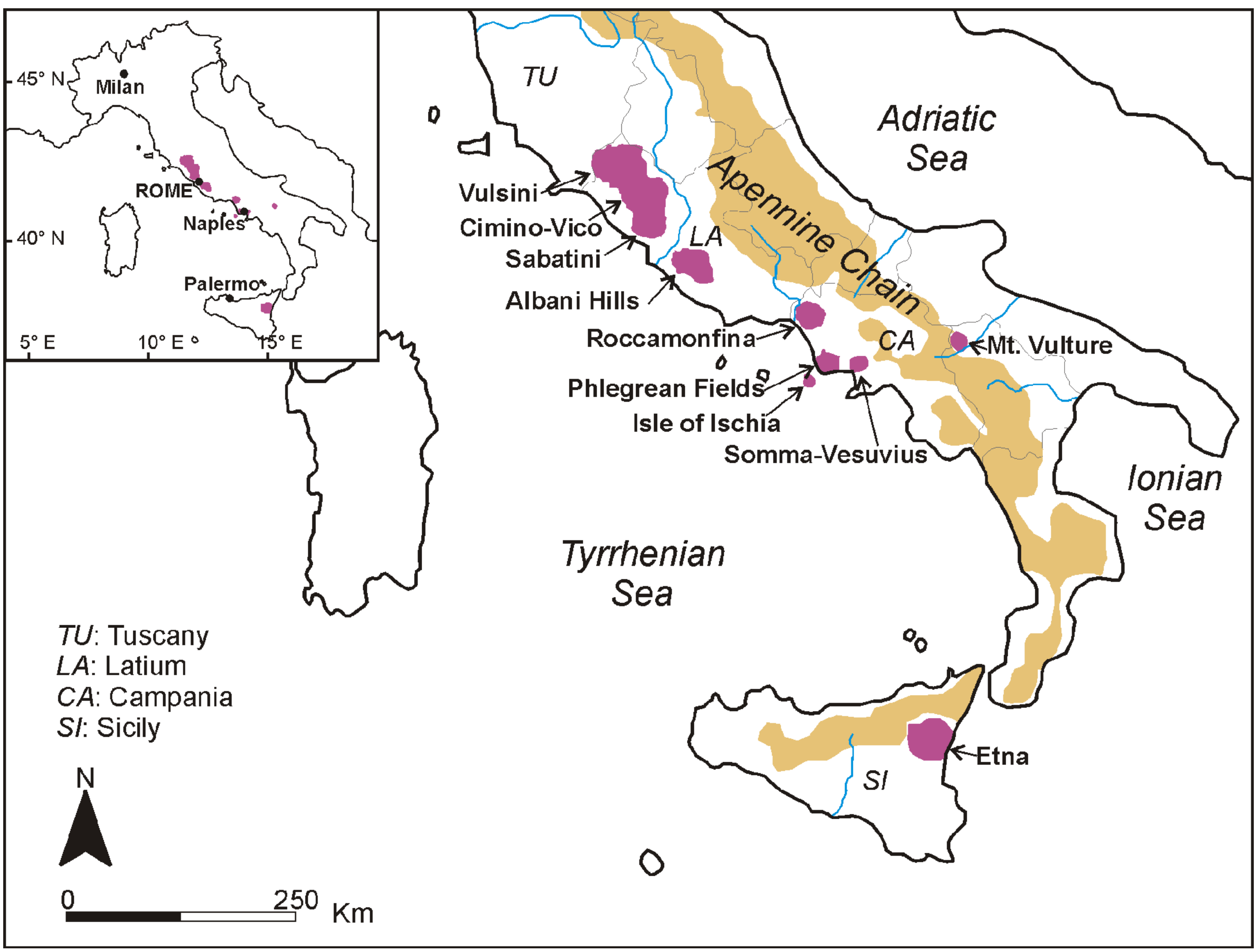

Fig. 1: *Location map of the studied volcanic aquifers in the Italian peninsula.*

that affected the internal Apennine Chain. In this area, the volcanic formations are mostly represented by pyroclastic products with intercalated lavas belonging to distinct magmatic series: potassic series mostly represented by shoshonitic basalts, shoshonites, latites and trachytes, and high potassium series mostly represented by leucitites, leucite-basanites, phono-tephrites and leucite-phonolites (Peccerillo and Manetti, 1985; Beccaluva et al., 2004).

The Mount Vulture volcano, located at the easternmost border of the Apennine compressional front (Fig. 1), shows petrological analogies with the Roman Magmatic Province, although more sodic products involve enrichment in Na-alkali silicate/carbonatite anorogenic components (Beccaluva et al., 2002).

The Etnean area (Fig. 1) falls within the Etna-Iblei-Sicily Channel, an anorogenic volcanic province active from the Late Miocene up to the Present. The Etnean volcanism initially gave rise to tholeiitic products, allowing the coexistence of tholeiitic and alkaline lavas and, subsequently, hawaiite lavas (Gillot et al., 1994).

The structural setting and related magmatic domains of the volcanic areas under investigation affect the heat flow and temperature variation with depth. A strong regional heat flow anomaly (>150 mW/m^2) appears in the peri-Tyrrhenian belt, extending from Tuscany to Campania, as a consequence of a thinning of the lithosphere. In the geothermal fields of Tuscany, Latium and the Neapolitan area (between the Isle of Ischia and the Phlegrean Fields), very high values of heat flow have been found (from 200 up to 400 mW/m^2) with temperatures above 150-300 °C at a depth of 1000 m (Calamai et al., 1976; Mongelli et al., 1989; Cataldi et al., 1995)

Methods

This study is based on a review of the published data on the hydrogeology and As content in groundwater of the main volcanoes of central and southern Italy.

The hydrogeological data come from studies carried out in the last decades dealing with general groundwater circulation, hydrogeochemical characterization and resource evaluation of the volcanic aquifers (Aureli, 1973; Baldi et al., 1973; Ferrara, 1975; Celico et al., 1980; Boni et al., 1981; Celico, 1983; Boni et al., 1986; Watts, 1987; Ferrara, 1991; Panichi et al., 1992; Alvino et al., 1998; Celico et al., 1998; Capelli et al., 1999; Celico et al., 1999; Ferrara, 1999; Valentino et al., 1999; Piscopo et al., 2000; Brusca et al., 2001; Federico et al., 2002; Duchi et al., 2003; Celico and Summa, 2004; Allocca et al., 2005; Capelli et al., 2005; Baiocchi et al., 2006; Piscopo et al., 2006; Fuganti and Sigillito, 2008).

Data on the As content in the groundwater come from more recent studies (Brondi et al., 1986; Aiuppa et al., 2000; Beccari and Dall'Aglio, 2002; Aiuppa et al., 2003; Lima et al., 2003; Aiuppa et al., 2006; Giuliano et al., 2006; Dall'Aglio, 2007; Angelone et al., 2009; Cuoco et al., 2010; Achene et al., 2010). Details on sampling and analytical procedures are given in the cited publications, which involve several analytical techniques (ICP-MS, INAA and GFAAS) of which the accuracy and reproducibility are well known. Unpublished data for 19 waters sampled in wells and springs from the Mount Vulture volcano are also considered; these waters were sampled in 2003 and analyzed with the same techniques (ICP-MS).

The available data from pumping tests regarding the hydraulic characteristics of the aquifers under examination were also acquired (Celico, 1983; Ferrara, 1991; Alvino et al., 1998; Celico et al., 1998; Celico et al., 1999; Ferrara, 1999; Piscopo et al., 2000; Celico and Summa, 2004; Baiocchi et al., 2006; Piscopo et al., 2006; Piscopo et al., 2008). These tests were conducted on wells 10-200 m deep at rates ranging from 0.5 and 80 L/s and by measuring drawdown and recovery in the pumping well. A few data refer to pumping tests conducted at a constant rate over a long time (more than 24 h) with observation wells.

Results

Hydrogeological features

Table 1 summarizes the primary information regarding the volcanoes' hydrogeology from the available literature.

Different aquifer systems can be distinguished in central and southern Italy in relation to the type of volcano, hydrostratigraphy and volcano-tectonic setting. These factors control the boundaries and characteristics of flow in each aquifer system.

The bottom boundaries of the systems depend on the relative permeability of the substratum compared with that of the volcanites and on the occurrence of volcano-tectonic structures that can interrupt the continuity of the low-permeability substratum, allowing interactions with deep aquifers. Based on these general concepts, open and close bottom boundaries can be distinguished for the different aquifer systems in relation to the possibility of the uprising of fluids from deep aquifers toward the more active groundwater circulation hosted in the volcanites of the first hundreds of meters and recharged from direct precipitation (Tab. 1).

When the volcanites are limited laterally by relatively permeable units, groundwater outflow from the volcanic aquifers has been found. In some cases, outflow toward the sea has been found when the boundary is the sea.

The variability of the erupted products and type of volcano affect the hydraulic heterogeneity of the aquifer systems, originating a complex subdivision of groundwater circulation in polygenetic volcanoes, where explosive phases frequently alternate with effusive eruptions (for example, Cimino-Vico-Sabatini system), and a relatively lower permeability variation in central strato-volcanoes (for example, the Somma-Vesuvius and Etna systems).

For most of the systems, continuous, generally unconfined basal aquifers have been found with a potentiometric surface controlled by the topography and/or surface morphology of the substratum of the volcanics. Where there is a frequent vertical variation of relative permeability, several perched aquifers of limited discontinuous extent or overlapped aquifers have been found (Tab. 1).

The volcanic aquifers discharge mainly into the streams and rivers and secondarily into the springs. Numerous springs are related to the perched aquifers and generally discharge less than 0.01 m^3/s, characterizing systems with a more fractioned groundwater circulation. A few springs are related to the basal aquifer and have a significant flow rate (generally less than 0.1 m^3/s); springs with a flow rate up to some cubic meters per second emerge only in the Etna system. Exchanges between the surface water of the volcanic lakes and the groundwater of the basal aquifers have been found with flow mainly from the aquifer toward the lakes. In several cases, groundwater flows from the volcanic aquifers toward the surrounding aquifers and the sea also occur (Tab. 1).

Based on the relative amount of major ions, temperature and salinity, the chemistry of the waters circulating in the volcanic aquifers can be summarized as reported in Table 2. From these parameters, the basal aquifers can be distinguished from the perched aquifers, and those with relatively faster and shorter circuits from those with deeper circuits.

The waters of the basal and perched aquifers are generally characterized by low temperature and salinity, and they show different

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Tab. 1: *Summary of the main hydrogeological features for the studied volcanic aquifers.*

System	Surface area (km^2)	Bottom boundary	Lateral boundaries	Aquifer type	Discharge	Recharge
Vulsini	1733	Generally close: low-permeability sedimentary units	Open and close: sedimentary units and alluvial deposits	Basal aquifer generally unconfined, few perched aquifers	Streams, rivers, basal and perched springs, surrounding aquifers and lake	Mainly by direct infiltration
Cimino-Vico-Sabatini	2800	Close and open: low-permeability sedimentary units sometimes fractured and faulted	Open and close: sedimentary units, and alluvial and coastal deposits	Basal aquifer generally unconfined, several perched aquifers	Streams, basal and perched springs, surrounding aquifers and lakes	Mainly by direct infiltration
Albani Hills	1982	Generally close: low-permeability sedimentary units	Open and close: sedimentary units and alluvial deposits	Unconfined or leaky basal aquifer, several perched aquifers	Streams, rivers, basal and perched springs, surrounding aquifers and lake	Mainly by direct infiltration
Roccamonfina	351	Close and open: low- and high-permeability sedimentary units	Open and close: sedimentary units, and pyroclastic, alluvial and coastal deposits	Unconfined or leaky basal aquifer	Streams, rivers, few basal springs, surrounding aquifers	Mainly by direct infiltration and secondly by flow from carbonate substratum
Phlegrean Fields	64	Open: considerable thickness of volcanics	Sea and open: alluvial and pyroclastic deposits	Unconfined or leaky basal aquifer	Surrounding aquifers and sea	Mainly by direct infiltration
Isle of Ischia	46	Open: considerable thickness of volcanics	Sea	Multi-layered aquifer	Sea and basal and perched springs	By direct infiltration and sea
Somma-Vesuvius	153	Close and open: low- and high-permeability sedimentary units	Sea and open: pyroclastic and alluvial deposits	Unconfined basal aquifer	Surrounding aquifers and sea	Mainly by direct infiltration and secondly by flow from carbonate substratum
Mt. Vulture	76	Generally close: low-permeability sedimentary units	Close: low-permeability sedimentary units	Unconfined basal aquifer	Streams, basal springs and lakes	Mainly by direct infiltration
Etna	1228	Generally close: low-permeability sedimentary units	Sea and close: low-permeability sedimentary units	Unconfined basal aquifer	Rivers, sea and basal springs	Mainly by direct infiltration

hydrochemical facies according to the different rock chemistry and mineralogy, with the exception of the Isle of Ischia system (Tab. 2). In the volcanic areas, mineral and thermal waters discharge from springs and wells related to deeper circuits located near more recent volcano-tectonic structures or where hydrostratigraphy permits the uprising of waters circulating in deep aquifers below the volcanites. These waters are characterized by high temperature and salinity, hydrochemical facies ranging from bicarbonate to sulfate to chloride, and high gas content (mainly CO_2). With the exception of the Isle of Ischia, the flows of mineral and thermal waters are localized and have a limited influence on the total yield of the volcanic aquifers (generally less than 5 %). The Isle of Ischia system shows a complex hydrogeochemistry (Tab. 2) falling within an area characterized by higher heat flow. The system is also recharged by salt-water intrusion and constituted by several overlapped aquifers often communicating via faults and fractures.

The present knowledge regarding the groundwater resources of the volcanic aquifers is based on water budget estimations. The available recharge estimates were developed at the volcanic system scale and on an annual basis, generally considering the average annual values of precipitation and evapotranspiration. This last parameter was evaluated through empirical methods as well as the

Tab. 2: *Summary of the main hydrochemical characteristics for the studied volcanic aquifers*

System	More frequent hydrochemical facies of basal and perched aquifers	More frequent water temperature of basal and perched aquifers (°C)	More frequent water salinity of basal and perched aquifers (g/L)	Mineral and thermal waters
Vulsini	from Ca(Mg) to Na(K)–HCO_3	< 25	< 1.0	Springs and wells: temperature up to 40°C and salinity up to 3 g/L
Cimino-Vico-Sabatini	from Ca(Mg) to Na(K)–HCO_3	< 25	< 1.0	Springs and wells: temperature up to 64°C and salinity up to 4 g/L
Albani Hills	from Ca(Mg) to Na(K)–HCO_3	< 22	< 1.0	Few springs and wells: temperature up to 30°C and salinity up to 2 g/L
Roccamonfina	Ca-K–HCO_3	< 20	< 0.5	Wells: temperature < 20°C and salinity up to 2 g/L; and few springs: temperature up to a 50°C and salinity up to 3 g/L
Phlegrean Fields	from K(Na) to Ca(Mg)–HCO_3	< 27	< 1.0	Springs and wells: temperature up to 95°C and salinity up to 30 g/L
Isle of Ischia	K(Na)-HCO_3, Na(K)–SO_4 and Na(K)-Cl	10-100	0.1-40	
Somma-Vesuvius	K(Na)–HCO_3 and K(Na)–SO_4	< 20	< 1.2	Wells: temperature up to 28°C and salinity up to 15 g/L
Mt. Vulture	from K(Na) to Ca(Mg)–HCO_3	< 20	< 1.3	Springs and wells: temperature < 20°C and salinity up to 5 g/L
Etna	Ca-Mg–HCO_3	< 20	< 1.6	Few springs: temperature < 25°C and salinity up to 3 g/L

Tab. 3: *Estimations of water budget for the studied volcanic aquifers.*

System	Surface area (km^2)	Effective infiltration (L/s per km^2)	Discharge toward rivers and springs (L/s per km^2)	Flow toward surrounding aquifers and sea (L/s per km^2)	Withdrawals (L/s per km^2)	Percentage of withdrawals for drinking water (%)	References
Vulsini	1733	7.36	2.86	2.64	1.86	42	Capelli et al., 2005
Cimino-Vico Sabatini	2800	7.10	2.12	2.04	2.94	15	Capelli et al., 2005
Albani Hills	1982	7.55	1.96	0.27	5.52	31	Capelli et al., 2005
Roccamonfina	351	11.65[a]	>5.98	[c]	3.52	8	Celico, 1983; Boni et al., 1986
Phlegrean Fields	64	7.20	[d]	4.48	2.72	[d]	Piscopo et al., 2000
Isle of Ischia	46	5.55[b]	0.45	8.81	1.68	[d]	Piscopo et al., 2000
Somma-Vesuvius	153	7.75[a]	[d]	4.57	5.89	55	Piscopo et al., 2000
Mt. Vulture	76	7.79	5.11	[d]	2.68	61	Celico and Summa, 2004
Eastern Etna	652	15.85	[c]	3.74[e]	10.84	44	Ferrara, 1975
Western Etna	145	16.63	16.63[f]	[d]		[c]	Aureli, 1973
Etna	1228	15.99	[c]	[c]	12.99	[c]	Ferrara, 1999

a – also recharged by flow from carbonate substratum; b – also recharged by sea; c – not available; d – absent or insignificant; e – including flow toward the springs; f – including withdrawals

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runoff. The recharge estimates were generally verified through the outflow from each volcanic system, considering the flow rate toward the surface waters, springs, surrounding aquifers and withdrawals. For most of the latter components, the data are frequently incomplete or discontinuous due to the lack of an effective monitoring network. Table 3 summarizes the results of the available estimates for each volcanic aquifer. All components are reported as the average value per unit surface.

Arsenic content in groundwater

The As concentrations in groundwater are summarized in Table 4 in terms of mean, range and standard deviation (SD) values for each system under examination.

The As determinations are available for most of the aquifer systems but are not always completely representative of the whole system in term of the sampling numbers and/or the type of sampled water.

There are more complete data for the Cimino-Vico-Sabatini (subdivided into the Cimino-Vico and Sabatini sub-systems), Roccamonfina, Phlegrean Fields, Isle of Ischia, Somma-Vesuvius, Mount Vulture and Etna systems. The reported data are representative regarding the fresh and thermal waters of the Cimino-Vico sub-system, the Phlegrean Fields and Isle of Ischia systems and, mainly, fresh waters for the Sabatini sub-system and the Roccamonfina, Somma-Vesuvius, Mount Vulture and Etna systems.

For the Albani Hills system, only a few data concerning wells and springs of fresh water are available (Tab. 4). For this system, monitoring conducted from 2010 to 2011 by local water management companies on drinking water reported values of As ranging from 10 to 30 μg/L (ACEA, 2011; Acqua Latina, 2011). For the Vulsini system, the As values range from 4 to 27 μg/L in samples collected by the local health and environmental department in 2011 for drinking water supplies (ASL Viterbo, 2011), but no information is given about the type of aquifer sampled. From other datasets concerning 32 springs and 68 wells of the Vulsini system and the Cimino-Vico sub-system supplying local drinking water, mean, minimum, maximum and SD values of 11.2, < 0.1, 45.9 and 11.9 μg/L, respectively, were obtained (Achene et al., 2010).

The highest mean concentration of As and wider dispersion result for the Phlegrean Fields and Isle of Ischia systems. The lowest mean and a reduced variability are given for the Etna, Somma-Vesuvius and Roccamonfina systems. The Mount Vulture system shows a relatively low mean value as well as a low range of values. Intermediate values, compared with those of the previous systems, are found for the Cimino-Vico-Sabatini system.

Tab. 4: *As contents in groundwater of the studied volcanic aquifers.*

System	Number of sampled waters	Water temperature range (°C)	Mean value of As (μg/L)	Range of As (μg/L)	SD (μg/L)	References
Cimino-Vico	65	11-60	45.0	1.6-371	82.6	Angelone et al., 2009
Sabatini	60	10-24	19.3	1.9-128	21.1	Giuliano et al., 2006
Albani Hills	14	13-20	13.9	0.8-37.6	11.2	Dall'Aglio, 2007
Roccamonfina	68	12-25	8.1	0.5-120	14.7	Cuoco et al., 2010
Phlegrean Fields	64	15-95	328	2-6939	1001	Aiuppa et al., 2006
Isle of Ischia	73	11-99	205	0.5-1558	327	Lima et al., 2003
	93	13-100	752	3-8345	1387	Aiuppa et al., 2006
Somma-Vesuvius	55	11-28	8.3	0.9-92	na	Aiuppa et al., 2003
Mt. Vulture	19	10-20	18.8	11.1-48.7	9.0	Unpublished data
Etna	53	9-22	2.8	0.1-21.5	3.3	Aiuppa et al., 2000

na – not available

Hydraulic characteristics of the volcanic aquifers

The available data on pumping tests mainly concern the Cimino-Vico sub-system (Baiocchi et al., 2006) and the Phlegrean Fields (Piscopo et al. 2008), Isle of Ischia (Celico et al., 1999), Somma-Vesuvius (Celico et al., 1998) and Mount Vulture systems (Celico and Summa, 2004). Several tests were performed on these aquifers, which provide a good coverage of the study areas. Most of the tests were conducted on single wells. In this case, specific capacity was calculated after data correction due to the quadratic head losses, or transmissivity values were estimated considering the recovery data of the pumped well. A few data refer to pumping tests conducted at a constant rate over a long time (greater than 24 h) with observation wells.

The frequency plots of specific capacity or transmissivity are shown in Figure 2.

Values of specific capacity ranging from 10^{-2} to 10^{-3} m^2/s (Celico, 1986) and hydraulic conductivity ranging from $7x10^{-5}$ to $4x10^{-3}$ m/s (Alvino et al., 1998) have been reported for the Roccamonfina system and from 10^{-1} to 10^{-3} m^2/s for the Etna system (Ferrara, 1991; 1999). For the Vulsini system, four pumping tests resulted in a transmissivity ranging from 10^{-2} to 10^{-3} m^2/s (Piscopo et al., 2008).

From twenty tests conducted in the Cimino-Vico sub-system and the Vulsini, Phlegrean Fields, Isle of Ischia and Mount Vulture systems, the more detailed available data allow the storativity to be calculated (Piscopo et al., 2008). A mean value of $4.1x10^{-3}$ m^2/s results and the frequency plot is shown in Figure 2.

In general, the response of the volcanic aquifers to pumping often corresponds to the theoretical models of leaky and unconfined aquifers; less frequently, the drawdown-time curve fits with the theoretical model of Theis for confined aquifers (or rather, the fit with the Theis model happens when the test does not last for a long time).

In the volcanic areas, where the rising of fluids from depths through the fractured or faulted zones occurs or a complex hydrostratigraphy and hydrochemical vertical zonation exists, the water temperature and salinity increases during pumping, as shown, for example, in Figure 3. Particularly in the Isle of Ischia, the clear phenomena of deep fluids drawing up for wells near volcano-tectonic structures and of up-coning for wells along the coast were found during pumping.

Discussion

The As content in the groundwater of volcanic areas of central and southern Italy varies both within the single aquifer system and among the different aquifer systems.

The highest As contents characterize the Phlegrean Fields and Isle of Ischia systems, where the highest temperatures of groundwater (Tab. 4) and clear evidence of the uprising of deep fluids have been found (Tab. 1). In these cases, according to Aiuppa et al. (2003; 2006), the main control on the As mobility is related to the groundwater temperature and water chemistry. In these systems, the dispersion of As values is related to the considerable variability of hydrochemical facies (Tab. 2), which is explained by considering the vertical and horizontal division of the groundwater circulation due to the presence of overlapped aquifers interacting differently with deep fluids.

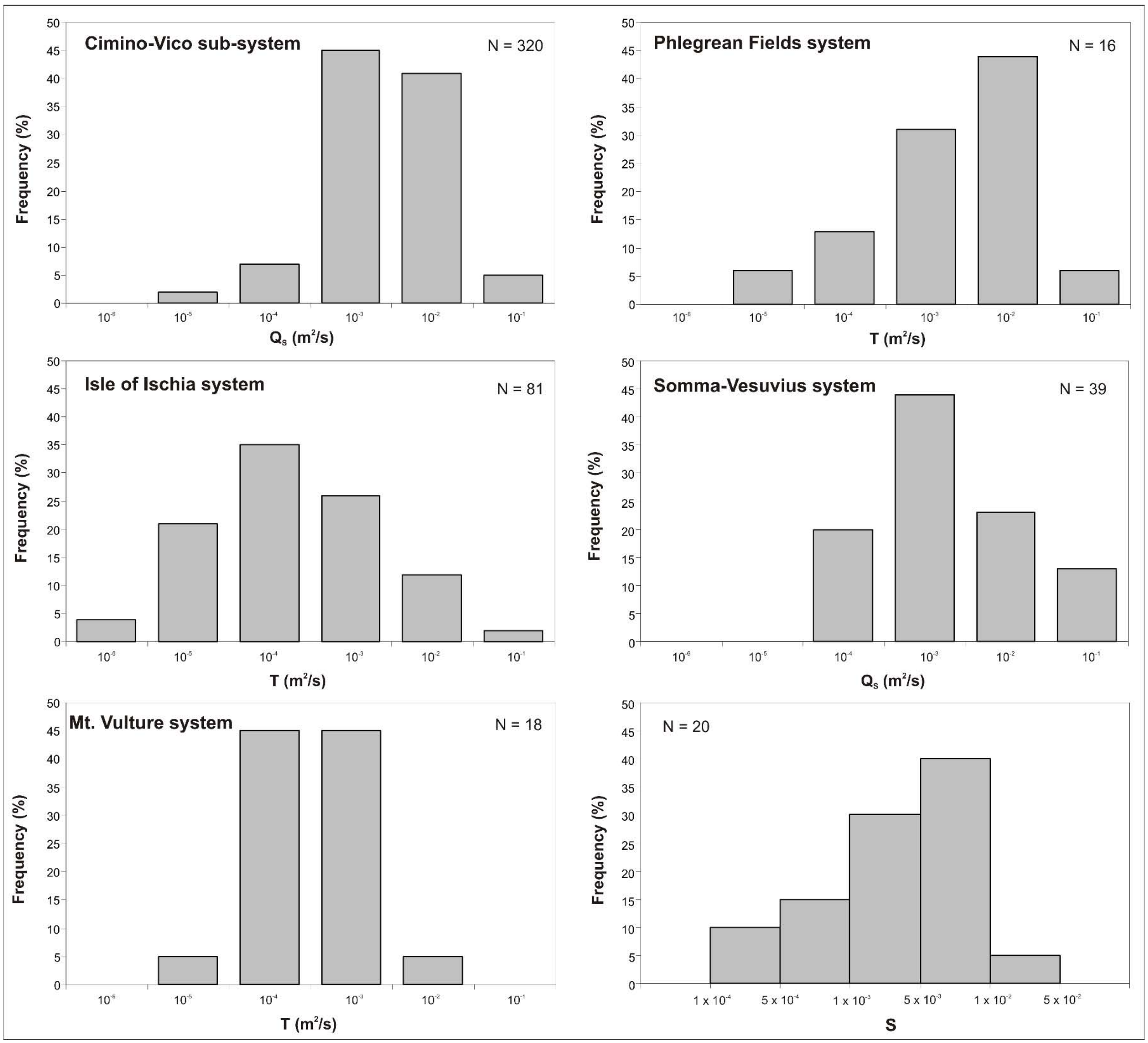

Fig. 2: *Frequency plots of the specific capacity (Q_S) or transmissivity (T) for some aquifer systems and of the storativity (S) for all available pumping tests (N – number of tests).*

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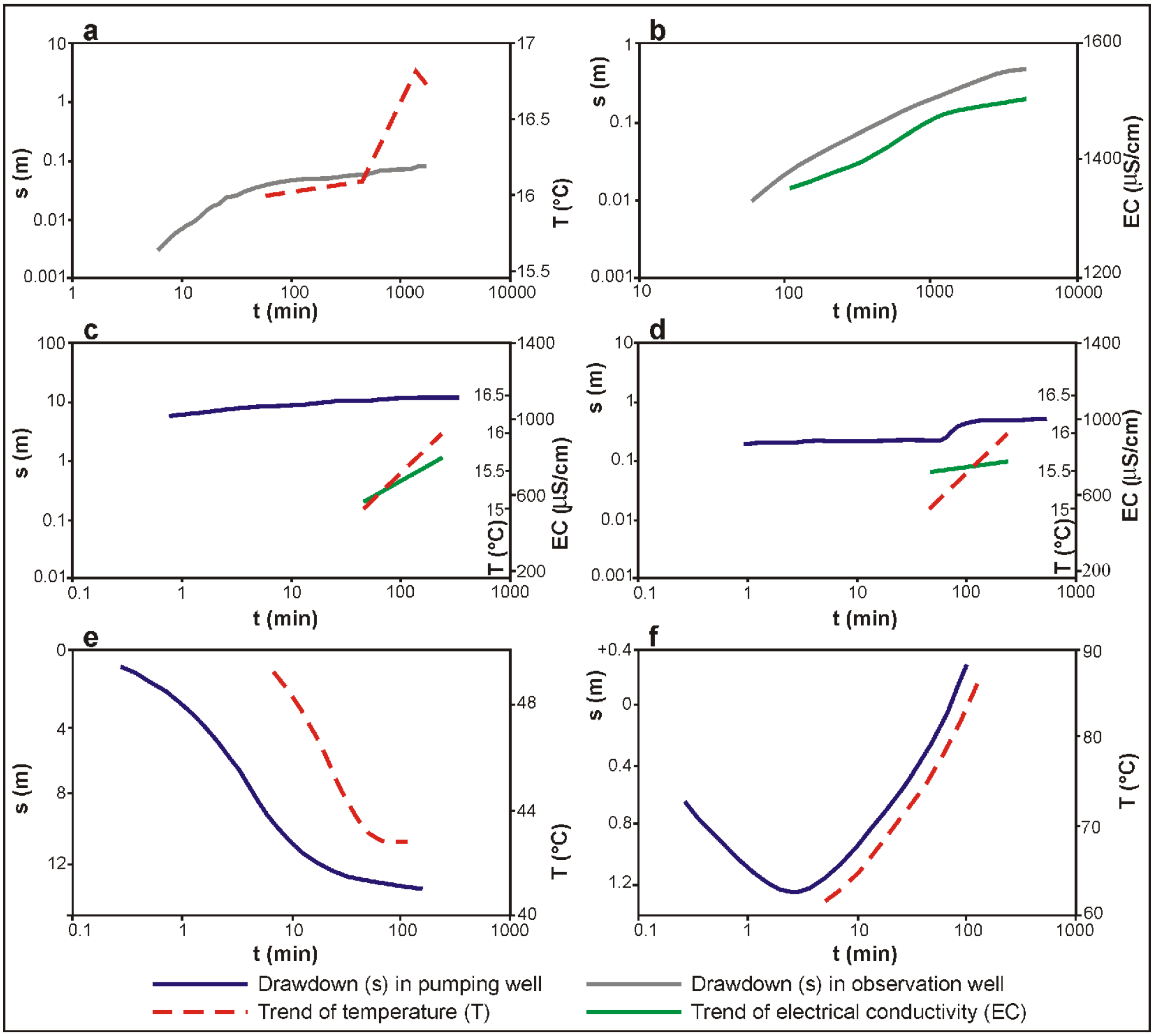

Fig. 3: *Trends of drawdown (s), water temperature (T) and electrical conductivity (EC) during some pumping tests: a) shallow well close to the hydrothermal area of Viterbo in the Cimino-Vico sub-system; b) well of the Mount Vulture system; c) and d) wells of the Phlegrean Fields system; e) shallow well close to the coast of the Isle of Ischia system; f) deep well close to faulted zone of the Isle of Ischia system.*

This scenario occurs especially in the Isle of Ischia system, where the heterogeneity of the aquifers is confirmed by the wider range of transmissivity resulting from the pumping tests (Fig. 2).

Lower As contents characterize the Roccamonfina, Somma-Vesuvius, and Etna systems, which have in common a reduced hydrothermal activity and waters of the bicarbonate type (Tab. 4 and 2). Nevertheless, these systems differ in their content of As inferred from the rocks, being higher for the potassic volcanites of Somma-Vesuvius and Roccamonfina than for the alkali basalts of Etna (Aiuppa et al., 2003). Hydrogeologically, the Somma-Vesuvius and Etna systems are characterized by an extended and yielding basal aquifer, the absence of perched aquifers, and the highest values of specific capacity and/or transmissivity, which indicate an active groundwater flow (Tab. 1 and Fig. 2). Additionally, the Roccamonfina system is characterized by an extended and yielding basal aquifer; and from the limited data on hydraulic parameters of the aquifer, it seems to have a significant specific discharge.

In the other systems, the As contents in the groundwater are intermediate between the previous extreme cases.

For the Cimino-Vico-Sabatino system, differences have been found between the Cimino-Vico and Sabatino sub-systems (Tab. 4). Higher mean values and a wider range characterize the first sub-system, where numerous thermal waters emerge related to the local hydrostratigraphical and volcano-tectonic setting. The same Cimino-Vico sub-system is characterized by a significant hydraulic heterogeneity of the aquifers, a specific capacity generally lower than that of the Somma-Vesuvius system (Fig. 2) and a significant vertical division of groundwater circulation (Tab. 1). These hydrogeological features together with the more active hydrothermal activity seem to be responsible for the wider range of As content.

For the Albani Hills system, the available data of As content in the groundwater do not significantly represent the whole aquifer system, but the low As content found seems to be consistent with the reduced hydrothermal activity only near the more recent volcano-tectonic structures (Tab. 1, 2 and 4).

The Mount Vulture system, though characterized by intermediate values of As, is characterized by a reduced dispersion of the parameter compared with the other systems. In this case, the presence of an extended and yielding basal aquifer, the absence of perched aquifers, the absence of hydrothermal activity, and the lower and reduced range of transmissivity values must be borne in mind when comparing the Mount Vulture system with the Somma-Vesuvius system (Tab. 1, 2 and 4 and Fig. 2).

For the Vulsini system, from the few data where the type of sampled sources was specified, higher values have again been found in the waters of springs and wells close to the more recent volcano-tectonic structures.

From the comparison of As content in the groundwater and hydrogeological characteristics of the volcanoes under examination, in addition to what is well known about the influence of the hydrothermal activity, rock mineralogy and water chemistry (for example, Ballantyne and Moore, 1998; Smedley and Kinniburgh, 2002; Webster and Nordstrom 2003; Aiuppa et al., 2003; 2006), it is evident that there is a great variability of As within the single system and among the different systems. This variability is correlated with (i) the local hydrostratigraphy and structural setting and (ii) the extent of groundwater circulation in the volcanites and the groundwater flow velocity.

In the active hydrothermal areas, hydrostratigraphy and the recent volcano-tectonic structure control the uprising of deep fluids, which represent a localized or diffuse source of As in the groundwater of the basal aquifer of the volcanites. This phenomenon typically occurs in the Phlegrean Fields and Isle of Ischia systems (and in the other systems where thermal waters emerge), it is highlighted from the well-known correlation between As content and water temperature (for example, Aiuppa et al., 2003; 2006; Angelone et al., 2009).

The extended basal groundwater circulation and higher flow velocities in the volcanites do not allow for the preservation of high As concentration, as any As released is flushed away or diluted, according to Smedley and Kinniburgh (2002). This scenario is typically found in the Somma-Vesuvius, Etna and Roccamonfina systems, which are also characterized by limited hydrothermal activity.

In the other cases, the variability of As content in the groundwater within the single system can be related to the previously cited processes interacting together in aquifers that are more heterogeneous, as typically occurs in the Cimino-Vico sub-system. In the more heterogeneous aquifer systems, the local hydrogeological conditions affect the As concentration in groundwater and, therefore, the range of values found. The observed phenomenon of the increase of water salinity and temperature during the pumping tests from wells close to volcano-tectonic structures or located in hydrogeologically complex areas (Fig. 3) can be interpreted as the increased uprising of deep fluids with higher As content. Therefore, the distance from a well to fractures and faults and the local hydraulic characteristics of the aquifer can influence the As content in the tapped waters. In other cases, where overlapped aquifers exist, the depth and length of the circuits can influence the As content in tapped waters; for example, the spring and well waters of the perched aquifers of the Cimino-Vico sub-system show lower As concentrations (Angelone et al., 2009) (Fig. 4a).

The local hydraulic diffusivity of the aquifer (i.e., the ratio of transmissivity and storativity) has a great influence on As content in groundwater tapped from wells falling in more heterogeneous aquifer systems. Where high values of hydraulic diffusivity result, a well close to a fractured and faulted zone can easily capture the localized source of As (Fig. 4b); where low values of hydraulic diffusivity result, a well falling within an area having a complex hydrostratigraphy and hydrochemical vertical zonation can induce the up-coning of deep waters with higher As content as a consequence of the development of a deeper pumping cone (Fig. 4c).

The systems of the Latium Region appear to need a reassessment of the groundwater management approach in view of the heterogeneity of the aquifers, the significant hydrothermal activity and the massive use of groundwater for drinking water supply (Tab. 3).

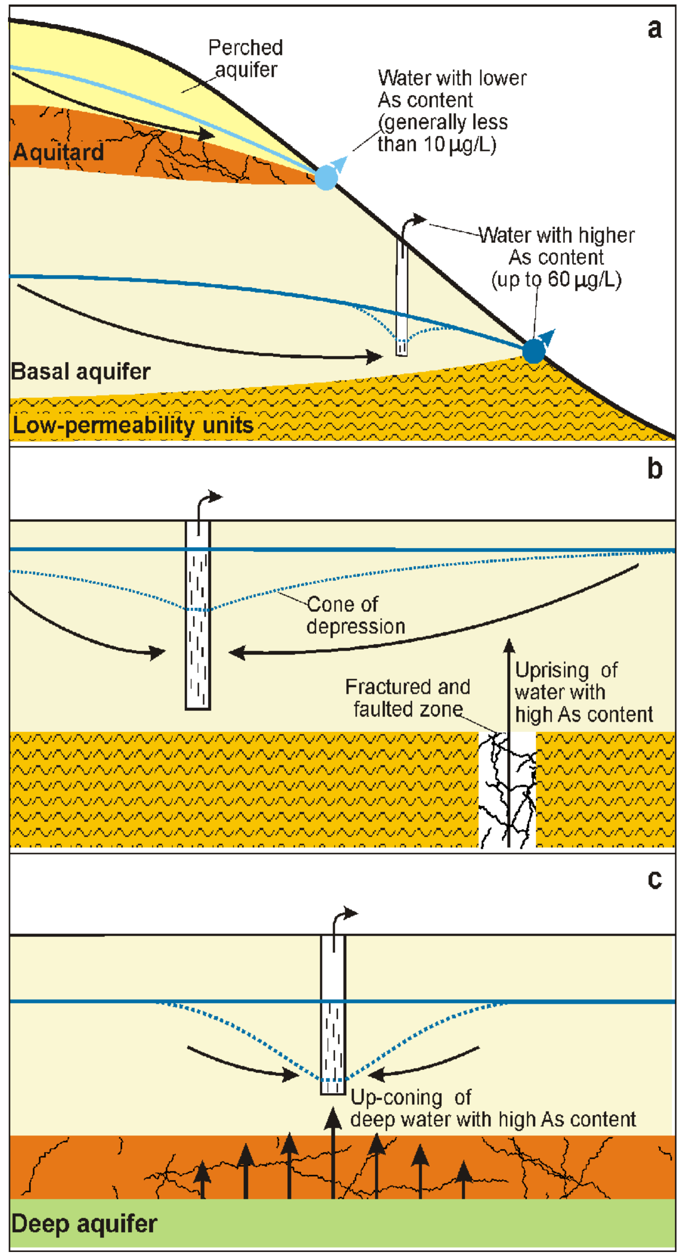

Fig. 4: *Schematic cross-sections showing: a) the influence of the depth and length of the circuits on the As content in groundwater with reference to the Cimino-Vico sub-system; b) the possible impact of pumping from a well close to a fractured and faulted zone, when the volcanic aquifer is characterized by high values of hydraulic diffusivity; c) the possible impact of pumping from a well falling within an area having a complex hydrostratigraphy and hydrochemical vertical zonation, when the volcanic aquifer is characterized by low values of hydraulic diffusivity.*

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Conclusion

The As content in the groundwater of the volcanic areas of central and southern Italy covers a wide range of values and often exceeds the limit of 10 µg/L. In addition to well-known relations among the content of geogenic contaminant in groundwater and volcanic rock composition, water chemistry and hydrothermal activity, the results show that the As distribution is controlled by the hydrogeological features and hydraulic parameters of the volcanic aquifers. Relatively low As concentrations are found when the flow is relatively fast in a basal aquifer less influenced by the uprising of deep fluids. When the groundwater circulation is more fractioned, the aquifers are hydraulically heterogeneous, and the vertical discontinuities permit interactions between the basal aquifer and the deep fluids, the As concentration in the groundwater has a wider range, frequently exceeding a value of 50 µg/L.

Based on these results, a new approach concerning the location of wells and their pumping method should be developed to improve groundwater management in consideration of the impact of tapped water on human health. For this purpose, it must be considered that the more vulnerable zones within these volcanic aquifers are related to the nature of the substrata of the volcanites, the volcano-tectonic structures and the hydrothermal areas. It should always be verified that the pumping effects on the horizontal and vertical flow contain mixing between the relatively shallow and deeper groundwater circuits, particularly where the groundwater circulation is more fractioned. An integrated approach that includes the hydrogeological and hydrochemical zonations seems to be a valuable method for determining groundwater resources for drinking water not only in the examined volcanic aquifers, but in many others contaminated environments where a correlation between contaminant and geology exists.

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