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Signals in water - the deep originated CO_2 in the Peschiera-Capone acqueduct in relation to monitoring of seismic activity in central Italy

Segnali nell'acqua - la CO_2 di origine profonda nell'acquedotto del Peschiera-Capone in relazione al monitoraggio dell'attività sismica nell'Italia Centrale

Claudio Martini

Riassunto: Valutazione delle analisi effettuate sulle acque sotterranee del Lazio centrale da ACEA ATO2 SpA tra il 2001 e il 2016, secondo il modello proposto da Chiodini et al. nel 2004, che identifica nella costa tirrenica del centro- sud, due notevoli aree di rilascio della CO_2 prodotta dall'attività magmatica subcrostale: l'area TRDS (struttura di degassamento toscano-romana) e l'area CDS (struttura di degassamento campana). Ricostruzione della CO_2 prodotta dal degassamento attraverso l'analisi delle componenti del carbonio inorganico misurato nelle acque sotterranee del Lazio centrale (province di Roma e Rieti) tra il 2001 e il 2016. Rapporto causale dell'attività di degassamento del mantello nella zona TRDS con il disastroso terremoto verificatosi a l'Aquila il 6 aprile 2009. Uso della misura carbonio inorganico disciolto nelle acque sorgive dell'acquedotto del Peschiera-Capore per monitorare l'attività di degassamento nella zona TRDS, al fine di avere un segnale di allarme precoce di possibili attività sismiche in dell'Appennino centrale. Revisione e aggiornamento dei dati dopo il terremoto del 24 agosto 2016 ad Amatrice.

Abstract: *Valuation of the analysis performed on groundwater of Central Lazio by ACEA ATO2 SpA from 2001 to 2016, according to the model proposed by Chiodini et al. in 2004 that identifies in the Tyrrhenian coast of central and southern Italy, two notable releasing areas of the CO_2 produced by the sub-crustal magma activity, or two areas of natural degassing of the planet: the TRDS area (Tuscan Roman degassing structure) and the CDS area (Campanian degassing structure). Reconstruction of the CO_2 produced by degassing through the analysis of the components of inorganic carbon measured in groundwater of Central Lazio (Rome and Rieti districts) between 2001 and 2016. Causal relationship of the activity of mantle degassing in the TRDS area with the disastrous earthquake occurred at L'Aquila in April 6, 2009. Current use of the dissolved inorganic carbon measurement in the Peschiera and Capore spring waters to monitor the activity of mantle degassing in the TRDS area, in order to have an early warning signal of possible seismic activity in the Central Apennines. Revision and data updating after the earthquake in August 24, 2016 at Amatrice.*

Parole chiave: Idrogeologia del Lazio Centrale, Degassamento del mantello terrestre, Misurazione della CO_2 nelle acque sotterranee, Terremoti di L'Aquila ed Amatrice.

Keywords: *Central Lazio hydrogeology, Earth mantle degassing, CO_2 measurement in groundwater, L'Aquila and Amatrice earthquakes.*

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Introduction

Context: the geological setting of the central Appennines

The central Apenninic chain is a Neogene foldand-thrust belt that developed on ensialic crust after the Europe-Africa collision during the Alpine orogeny (Fig. 1). Four main geodynamic provinces can be recognized in the central Apennines (from east to west): 1) a deformed intra-orogenic foreland (Apulia-Adriatic) made up of several blocks that have undergone rotation in different directions and of varying degrees since the Late Cretaceous; 2) a deformed foredeep (Adriatic trough) that is widely overthrust by the Apenninic chain; 3) a thrust belt (Apennines) that developed from the Early Cenozoic to the Pleistocene; and 4) a hinterland (Tyrrhenian basin), including large volcanic centers, that is now undergoing extensional tectonics. The major thrust systems in the central Apennines strike NW-SE and dip gently towards the southwest. They include, from SW to NE: the Lepini, Simbruini, Velino-Sirente, Marsica, Morrone, Gran Sasso and Maiella thrust sheets. Additional thrusts and related folds are concealed beneath several km of Pliocene-Quaternary syn-orogenic sediments northeast of the topographic front of the range. The exposed sequences consist of thick Triassic-middle Miocene carbonate platform, slope and ramp facies (from 5 to 3 km thick). The kinematic history of thrusting in the central Apennines is recorded by Miocene through Pliocene syn-orogenic sediments in foredeeps, which

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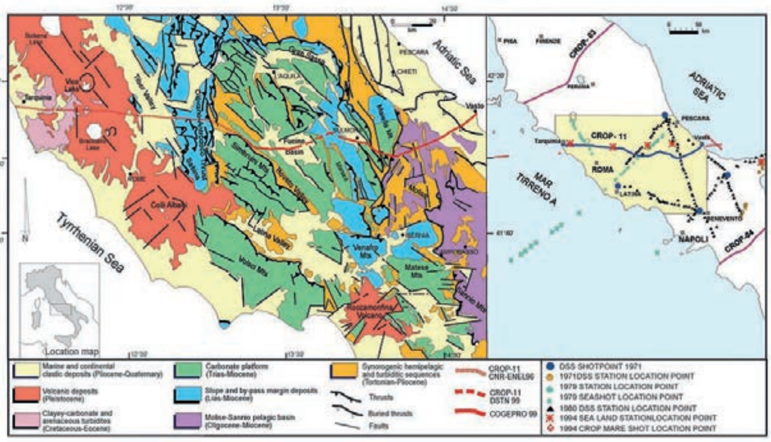

Fig. 1 - Geologic framework of Central Italy (Parotto et al. 2003).

Fig. 1 - Inquadramento geologico del centro Italia (Parotto et al. 2003).

were progressively involved in the chain towards the Adriatic foreland. Starting in the Messinian and continuing through the Early Pliocene, multi-phased deformational events formed NW-SE and NNW-SSE thrust sheets (Lepini, Simbruini, Velino-Magnola, Sirente, Marsica units). The Olevano-Antrodoco and Gran Sasso thrust systems are significant out-of sequence thrusts that truncate some of the north to northwest-striking systems. NW-SE and E-W high-angle normal fault systems, generally southwest and south-dipping, and extensional basins, of generally post-Messinian age, formed across the southwestern part of the thrust belt and are superimposed upon the compressional Neogene structure. The extensional basins were progressively filled by alluvial and lacustrine deposits. The major Pliocene-Quaternary extensional basins include Tiberino, Rieti, L'Aquila, Fucino, and Sulmona basins. The evolution of these geodynamic units suggests: the flexural retreat towards the NE of the edge of the Adriatic block, with a passive sinking of the lithosphere and associated roll-back mechanisms and the progressive eastward advance of the Apenninic chain with in-sequence and out-of-sequence faults, transport of piggy-back basins and incorporation of fore deep basins. Strike-slip faulting and rotations have severely complicated the relationships among the geodynamic units, both in the chain and in the foreland. One of the major constraints of this geodynamic context is the contrast in geophysical features, which indicates the presence of at least two distinct tectonic regions. The geological, geochemical and geophysical data of the Adriatic region (to the east) refer to an old, inactive crust having a relatively simple surface structure. The Tyrrhenian region (to the west) is characterized instead by a young, very active and thinned crust. One major problem is the involvement of the basement in the thrust tectonics. In the past, the Apenninic basement has been interpreted as not being involved in the Apennine orogeny. New evidence nowadays suggests the opposite: 1) the interpretation of the seismic data suggests that the basement was involved ("wedged Adria") in the Apenninic orogeny; 2) recent gravimetric data indicate the existence of buried steps of the basement in western areas of the Central Apennines (e.g. Latina valley); 3) the high degree of shortening of the surface units could be better explained by basement involvement. The cross-sections presented here (Fig. 2) have been reconstructed from surface (bedding, dip-domains, stratigraphic and tectonic contacts) and subsurface data. The extrapolation of surface geometry to depth has been made keeping the relationships between tectonic boundaries and bedding constant, using the poor seismic data that are available for Central Italy.

Unespected data and a new conceptual model

At the end of the 2000s, while attending to the classification of the analytical data related to drinkable water, it was noticed a curious phenomenon. Springs and wells located in distant places from each other and placed in aquifers of different nature and clearly not in contact, manifested an almost synchronous lowering of pH values. This seems to make no sense and, after verifying the accuracy of sampling and measurements we began to look for a model that could explain what was manifesting. At the half of 2009, after contacting the "Istituto Nazionale di Geofisica e Vulcanologia" (National Institute of Geophysics and Volcanology), we discovered that in 2004 a working group led by Giovanni Chiodini (Chiodini et al., 2004) has published an important essay that identifies in the central and southern Tyrrhenian coast two notable natural areas of the planet degassing, i.e. where the CO_2 produced by the sub-crustal magma activity emerges (Fig. 3 A): the TRDS area (Tuscan Roman Degassing Structure) and the CDS area (Campanian Degassing Structure). The releasing activity results at least five times greater than it was estimated in the past (Frondini et al. 2008). It has been calculated that those areas alone produce about 10% of the CO_2 released from all emerged volcanoes on planet Earth.

Beyond the margins of these areas (and especially east of the Apennines) no release of deep CO_2 has ever been detected. It's important to understand how the degassing activity is not due to the presence of volcanic areas (the more or less active) like Colli Albani and Campi Flegrei for instance, but do have a much deeper origin, coming from the mantle at depths greater than 20 km (Fig. 3 B); we can truly speak in this case of no-volcanic degassing. The causes of this phenomenon are far from being understood, but there are some interesting working hypothesis, including the so-

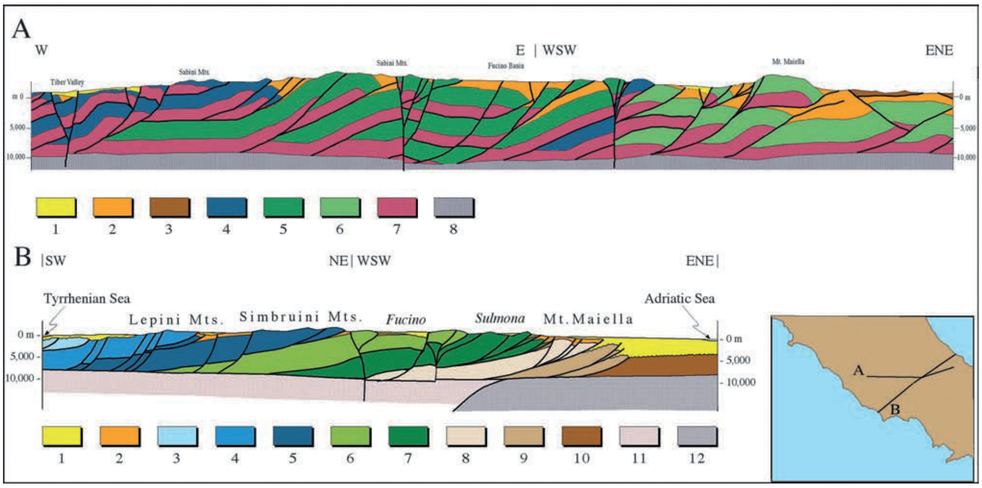

Fig. 2 - Schematic cross-sections of the central Apennine thrust belt. A 1) marine and continental deposits (Plio-Quaternary); 2) syn-orogenic deposits (Upper Tortonian-Lower Pliocene); 3) allochthonous deposits (Oligo-Miocene); 4) Umbro-Sabina and Marsica slope and by-pass marginal deposits (Lias-Miocene); 5) Latium-Abruzzi carbonate platform (Lias-Miocene); 6) Adriatic carbonate platform (Lias-Miocene); 7) Triassic carbonate platform (Trias) 8) magnetic basement. B 1) marine and continental post-orogenic sedimentary cover of the Tyrrhenian side of the Apennines and of the intramontane basins (Upper Messinian-Quaternary) and marine syn- and post-orogenic deposits of the Adriatic side of the Apennines (Lower Pliocene-Quaternary); 2) syn-orogenic deposits of the different Apennine fore-deep basins (Upper Tortonian to Lower Pliocene); 3) Mt. Circeo tectonic unit; 4) Lepini Mts. tectonic unit; 5) Ernici Mts. and Simbruini Mts. tectonic unit; 6) Marsica tectonic unit; 7) Morrone Mts. and Queglia tectonic unit; 8) Mt. Maiella tectonic unit; 9) Casoli-Bomba tectonic unit; 10) Adriatic foreland; 11) magnetic basement of the Apennine thrust belt; 12) magnetic basement of the Adriatic foreland. (Parotto et al. 2003).

Fig. 2 - Sezioni geologiche schematiche attraverso la catena appenninica dell'Italia centrale. A 1) Depositi marini e continentali (Plio-Quaternario); 2) Depositi sin-orogenici (Tortoniano sup. - Pliocene inf.); 3) Coltri Alloctone molisane (Oligo-Miocene); 4) Depositi di margine e bacinali Umbro-Sabini e della Marsica (Lias-Miocene); 5) Piattaforma Laziale-Abruzzese (Lias- Miocene); 6) Piattaforma carbonatica Adriatica (Lias-Miocene); 7) Piattaforma carbonatica Triassica (Trias); 8) Basamento magnetico. B 1) Coperture post-orogene sedimentarie marine e continentali del margine tirrenico, dei bacini intramontani e (Messiniano sup.-Quaternario) e depositi marini sin e post orogeni del margine adriatico (Pliocene inf.-Quaternario); 2) Depositi sin-orogeni dei differenti bacini di avanfossa dell'Appennino (Tortoniano- Pliocene inf.); 3) Unità tettonica del M. Circeo; 4) Unità tettonica dei M. Lepini; 5) Unità tettonica dei Simbruini-Ernici; 6) Unità tettonica Marsica; 7) Unità tettonica del M. Morrone-Queglia; 8) Unità tettonica del M. Maiella; 9) Unità tettonica di Casoli-Bomba; 10) Avampaese Adriatico; 11) Basamento magnetico della catena appenninica; 12) Basamento magnetico dell'avampaese adriatico (Parotto et al. 2003).

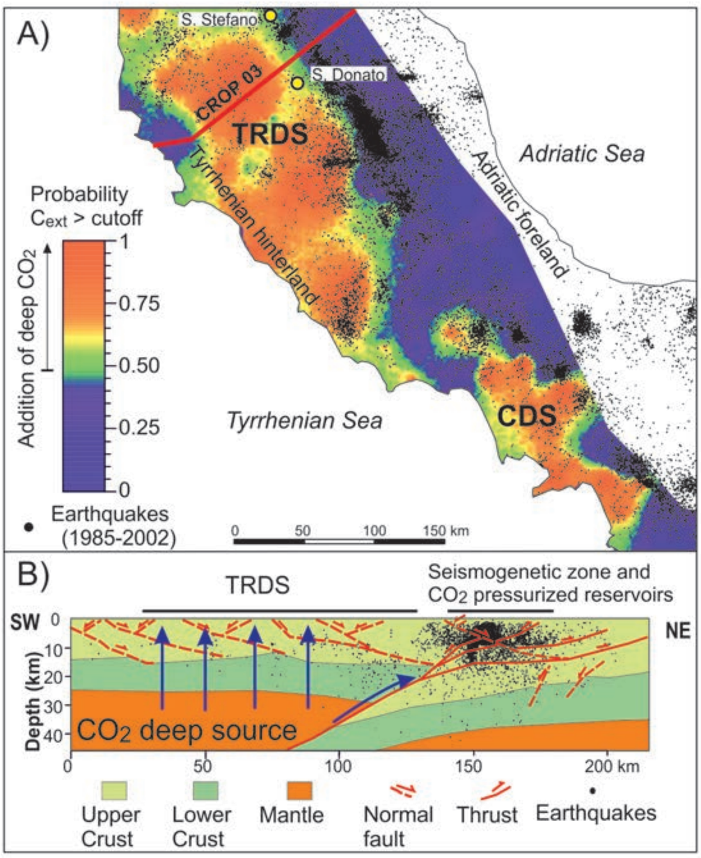

Fig. 3 -A) Degassing areas in center and southern Italy. B) CO_2 deep source and its accumulation modality under the Apennines (Chiodini et al. 2004).

Fig. 3 - A) Aree di degassamento del centro e del sud Italia. B) Modalità di accumulo della CO_2 di origine profonda sotto gli Appennini. (Chiodini et al. 2004)

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called "paradigm of asymmetric earth" from which can be assumed a relationship with the type of subduction involving the Apennines" (Carminati & Doglioni 2012). One notable consequence derived from this conceptual model is that the CO_2 sourcing from the deep tends in the TRDS area to accumulate below the Apennines, and currently it is suspected to be an important contributing cause of at least some of the major earthquakes that occur in Central Italy. Hydrogeological and seismological processes can be coupled in various ways: "*… failure of brittle rocks under deviatoric stress is usually preceded by pervasive microcrack formation. In the subsurface, this process (i.e., microfracturing) would greatly increase the surface area of the affected rock in contact with groundwater and thus allow the release of gases and dissolved ions from the rock into the groundwater, changing its chemical composition … Scenarios of this kind have led to the not unreasonable expectation that hydrological, hydrogeochemical, and related geophysical precursors may appear before the occurrence of large earthquakes … If earthquakes cause changes in hydrogeological properties and changes in fluid pressure promote seismicity, then hydrogeological and seismological processes are coupled. Triggered seismicity is one possible example of this coupling. Interaction is promoted if the state of stress is close to failure so that the small changes in stress associated with either natural hydrologic processes or hydrological responses to earthquakes can in turn influence seismicity. At least in tectonically active areas, many faults do appear to be critically stressed, consistent with earthquakes being triggered by small stress changes.*" (Manga & Wang 2007). L'Aquila had just been devastated by the 2009 earthquake, so we began to rework the dense mass of data in our possession to see if the model proposed by Chiodini could help to explain the observed data.

Materials and Methods

The ACEA ATO2 analysis database

Since 2001 all the analysis performed by the company Elabori SpA on behalf of ACEA ATO2 SpA are digitized and entered into an electronic database, queryable via a dedicated software interface (LIMS).

In order to reconstruct the amount of the deep CO2 emitted, all the analytical data relating to underground sources of drinking water supply (springs and wells) have been extracted from the database. The investigated geographic area comprises the majority of the municipalities of the Roman province (about 80%), in which are included all the major aquifers of the province itself. The great Peschiera and Capore springs, located in the province of Rieti and the Masseria del Monte well, located in Anagni (Frosinone), were also available. 282 springs and wells, for a total of 5,780 complete water analysis, has been so observed.

They has been grouped primarily by sampling frequency: 1 or 2 sample per month for the bigger ones and 1 or 2 sample per year for all of the others; and secondarily by date of first sampling:

- 2001, for all the springs and wells of the great aqueducts that feed Rome (Peschiera, Capore, Acqua Marcia, Appio Alessandrino and Nuovo Vergine), and for three wells located near Castelnuovo di Porto;
- 2002, for the Valga delle Roche spring (near Monterotondo);
- 2003-4, for all the springs and wells that feed the Simbrivio aqueduct and for all the springs and wells used in the municipalities of Ciampino and Grottaferrata;
- 2005-6, for the springs and wells of all other municipalities: Albano Laziale, Allumiere, Anguillara Sabazia, Ardea, Ariccia, Artena, Capena, Carpineto, Casape, Castel Gandolfo, Castelnuovo di Porto, Cave, Cervara Cerveteri, Ciciliano, Civitella S. Paolo, Fiano Romano, Filacciano, Formello, Frascati, Gallicano, Gavignano, Genazzano, Genzano di Roma, Jenne, Lanuvio, Lariano, Marcellina, Marino, Montelanico, Nemi, Olevano Romano, Oriolo Romano, Palestrina, Pisoniano, Poli, Ponzano Romano, Riano, Rocca Priora, S. Oreste. S. Vito Romano, Sacrofano, Sambuci, S. Gregorio da Sassola, S. Polo dei Cavalieri, Saracinesco, Segni, Subiaco, Tivoli, Tolfa, Torrita Tiberina, Trevignano Romano, Vejano, Velletri, Vicovaro, Zagarolo.

From an analytical point of view, one of the easiest way to detect the deep CO_2 is through observation of groundwater, where it dissolves easily causing alterations which can be identified. The key parameter in this regard is given by the carbon isotopic composition ($\Delta^{13}C$): the relationship between ^{12}C and ^{13}C isotopes (usually equal to 98.9%), has a characteristic signature in the one coming from the depths of the earth, where its values fall between -5 °/°° and +1 °/°° of the normal environmental value, while in the carbon derived from the interaction between rainfall and soil values fall between -24.3 °/°° and -18.5 °/°° of the normal value, and in the carbon derived from carbonate dissolution values fall between +1.55 °/°° and +2.87 °/°° of the normal value. It's just by determining the $\Delta^{13}C$ that it was possible to understand that in the TRDS and CDS areas, on average, 43.3% of the Inorganic dissolved Carbon in groundwater has a deep origin, while 33.2% is due to carbonate dissolution and 23.5% for transportation by the rains of the biological originated CO_2 contained in soils (Chiodini et al. 2004; Chiodini et al.2009; Frondini et al. 2008). Not being of course available in our database the determination of the isotopic composition of carbon, in order to obtain an as much as possible reliable estimate of the deep CO_2 releasing over time, we have proceeded in an indirect way, using the measure of Dissolved Inorganic Carbon (TDIC). Its origin in groundwater can be broken down as follows:

TDIC = Ccarb + Cext, where Cext = Cinf + Cdeep

Ccarb is the carbon derived from the dissolution of carbonates and more generally by the interaction of water with the aquifer rocks. Cinf is the carbon transported by the rains and due both to the interaction of these with the grounds crossed before being deposited in the aquifer (biological CO_2) that the atmospheric CO_2 captured by rains. Cdeep is the carbon contained in gases (mainly CO_2) that date back to the planet's surface. Then Cext is just the sum of Cinf and Cdeep, i.e. all the carbon that is not derived from the interaction of water with rocks.

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The TDIC value of each analysis was not available in the database but it was reconstructed using the hydrogeological modeling software Phreeqc Interactive 2.14.3 (Parkhurst & Appelo 1999), starting from the measured values of temperature, pH, calcium, magnesium, sodium, potassium, alkalinity, sulfates and chlorides. The patch for the calculation of TDIC in Phreeqc, starting from an Excel spreadsheet, has been written by Stefano Caliro of I.N.G.V - Naples.

Fig. 4 shows briefly the calculation process: incoming data in mg/L, TDIC values extracted in Phreeqc (yellow) and derivation of Ccarb and Cext values in mol/L.

CalcolaTDIC

	A	B	C	D	E	F	G	H	I	J	K
1	Nome	T	pH	Ca	Mg	Na	K	alcalinità	SO4	Cl	
2	23/11/2016	11.5	7.4	107	17.4	3.96	0.96	336	16	6.25	
3	23/11/2016	12	7.4	107	17.4	3.98	1.04	336	15	5.89	
4	23/11/2016	12.5	7.6	107	17.4	3.99	0.92	341	16.1	6.28	
5	23/11/2016	13.5	7.7	107	17.4	4.01	0.92	343	15.5	6.07	
6	25/11/2016	13	7.4	107	17.6	4.04	0.96	338	16.1	5.85	
7	25/11/2016	13	7.5	106	17.6	4.15	1.09	341	16.2	6.01	
8	28/11/2016	12	7.4	107	17.8	3.97	0.93	335	15	5.85	
9	29/11/2016	11	7.5	107	17.4	4.01	0.94	342	16	6.26	

Dati_originali / Foglio2 / Foglio3

speciazione

	A	B	C	D	E	F	G	H	I	J	K
1	sim	state	soln	dist_x	time	step	pH	pe	temp	C(4)	m_CO3-2
2	1	i_soln	2	-99	-99	-99	7.4	4	11.5	7.36E-03	7.49E-06
3	1	i_soln	3	-99	-99	-99	7.4	4	12	7.35E-03	7.59E-06
4	1	i_soln	4	-99	-99	-99	7.6	4	12.5	7.20E-03	1.23E-05
5	1	i_soln	5	-99	-99	-99	7.7	4	13.5	7.14E-03	1.60E-05
6	1	i_soln	6	-99	-99	-99	7.4	4	13	7.38E-03	7.85E-06
7	1	i_soln	7	-99	-99	-99	7.5	4	13	7.31E-03	9.95E-06
8	1	i_soln	8	-99	-99	-99	7.4	4	12	7.33E-03	7.57E-06
9	1	i_soln	9	-99	-99	-99	7.5	4	11	7.36E-03	9.45E-06

speciazione

3	Data di prelievo	Temperatura acqua	Concentrazione ioni idrogeno - pH	Calcio - mg/L Ca	Magnesio - mg/L Mg	Sodio	Potassio - mg/L K	Alcalinità - mg/L CaCO3	Solfati	Cloruri - mg/L Cl	TDIC mol/L	Calcio mol/L Ca	Magnesio mol/L Mg	Solfati mol/L SO4	Ccarb mol/L	Cext mol/L
4	23/11/2016	11.5	7.4	107	17.4	3.96	0.96	336	16	6.25	7.36E-03	2.67E-03	7.16E-04	1.67E-04	3.22E-03	4.14E-03
5	23/11/2016	12	7.4	107	17.4	3.98	1.04	336	15	5.89	7.35E-03	2.67E-03	7.16E-04	1.56E-04	3.23E-03	4.13E-03
6	23/11/2016	12.5	7.6	107	17.4	3.99	0.92	341	16.1	6.28	7.20E-03	2.67E-03	7.16E-04	1.68E-04	3.22E-03	3.98E-03
7	23/11/2016	13.5	7.7	107	17.4	4.01	0.92	343	15.5	6.07	7.14E-03	2.67E-03	7.16E-04	1.61E-04	3.22E-03	3.91E-03
8	25/11/2016	13	7.4	107	17.6	4.04	0.96	338	16.1	5.85	7.38E-03	2.67E-03	7.24E-04	1.68E-04	3.23E-03	4.16E-03
9	25/11/2016	13	7.5	106	17.6	4.15	1.09	341	16.2	6.01	7.31E-03	2.64E-03	7.24E-04	1.69E-04	3.20E-03	4.11E-03
10	28/11/2016	12	7.4	107	17.8	3.97	0.93	335	15	5.85	7.33E-03	2.67E-03	7.32E-04	1.56E-04	3.25E-03	4.09E-03
11	29/11/2016	11	7.5	107	17.4	4.01	0.94	342	16	6.26	7.36E-03	2.67E-03	7.16E-04	1.67E-04	3.22E-03	4.14E-03

Fig. 4 - TDIC values extraction and derivation from Ccarb and Cext values.

Fig. 4 - SValori di TDIC calcolati dai valori di Ccarb e Cext.

For carbonate aquifers, the Ccarb value has been then calculated according to the formula:

$$Ccarb = Ca + Mg - SO_4.$$

Then, by subtracting the value of Ccarb to TDIC, the value of Cext was obtained.

For volcanic aquifers it has instead assumed that Cext = TDIC.

This elaboration has been made over all of the 5,780 analyses of the database.

While not directly representing the Cdeep sought, Cext value allowed us to make some interesting observations, given that in the investigated area the relationship between Cdeep and Cinf is equal to about 2/1, and that we have detailed data on rainfall in the region.

The maximum and minimum values registered in our database for those parameters, expressed in millimoles per liter, are respectively:

- 1.1 and 37.8 for TDIC;
- 0.7 and 32.9 for Cext;
- 0.1 and 7.7 for Ccarb.

The wells and springs of Tolfa and Allumiere (71 analysis) has been not taken in account because of their very particular aquifer (acidic volcanic rocks), which presents natural TDIC values up to ten times more than any other, such as to conceal any contribution due to rainfalls and mantle degassing.

The geological literature reports that, in the TRDS area, the maximum possible value of the Cinf is equal to 4 millimoles per liter and that the probability that this value is exceeded is less than 1% (5). It can therefore reasonably be assumed that the Cext values above this threshold are entirely due to the Cdeep.

Results

Statistic analysis

An initial assessment was carried out by treating all the sources as if they were part of a single aquifer, and selecting for each the pairs of maximum TDIC, Cext, and Ccarb values as well as the pairs of minimum pH values (as CO_2 produces a weak acidification of water) in order to obtain an indicative trend of the degassing process. Two series of data have been prepared for this purpose, relating to the following two subsets of sources (Tab. 1 and Fig. 5):

1. those for which the data were available throughout from 2001 to 2009; this sample turned out to be composed of 31 different sources (12 of which relatives to carbonate aquifers) for a total of 3,347 analysis.
2. those for which were available a minimum of 8 analysis for the period 2006-2009; the sample turned out to be composed of 83 different sources (including all of the first series) for a total of 2,578 analysis.

To minimize the effect of changes in the annual and/or monthly number of samplings, the extracted values shown in the following graphs were calculated as a percentage of the maximum values (minimum values for the pH) in relation to the number of determinations made in the period.

First series

Figure 6 shows the annual values referred to Cext and pH for the first series. The geographical area covered by this selection includes the area around Rieti (Peschiera and Capore), between the Aniene valley from Subiaco to Anticoli Corrado (Acqua Marcia), Tivoli (Acquoria), Castelnuovo di Porto and the south-east area of Rome (all the springs of Appio Alessandrino and New Virgin aqueducts and the wells of Valle Martella).

The data given here has been taken from rain gauges located nearby the sources of the first series or placed in areas that have with these a hydrological relationship. Rain gauges used are located in Antrodoco, Rieti and Castelnuovo di Farfa (for Peschiera and Capore), Subiaco, Arsoli and Marano Equo (for

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Tab. 1 - Series 1 and 2 springs and wells selected for the investigation.

Tab. 1 - Serie 1 e 2 - sorgenti e pozzi selezionati per l'indagine.

Municipality	Source	Serie 1	Municipality	Source	Serie 2	Municipality	Source	Serie 2
Agosta (A. Marcia)	Miscela delle Rosoline	1	Albano	Pozzo 14	1	Rocca Priora	Doganella - Pozzo 1	31
Agosta (A. Marcia)	Sorgente Fiumetto	2	Albano	Pozzo 15	2	Rocca Priora	Doganella - Pozzo 2	32
Agosta (A. Marcia)	Sorgente Fonte di Agosta	3	Albano	Pozzo Marucci Alto	3	Rocca Priora	Doganella - Pozzo 3	33
Agosta (A. Marcia)	Sorgente Mola d'Agosta	4	Albano	Pozzo Marucci Basso	4	Rocca Priora	Doganella - Pozzo 4	34
Agosta (A. Marcia)	Sorgente Mola di Regno	5	Albano	Pozzo Paolini	5	Rocca Priora	Doganella - Pozzo 5 + 6	35
Agosta (A. Marcia)	Sorgente residue d'Agosta	6	Albano	Pozzo Parco Villa Contarini	6	Rocca Priora	Doganella - Pozzo 7	36
Agosta (A. Marcia)	Sorgente S. Lucia	7	Albano	Pozzo Totteri	7	Rocca Priora	Doganella - Pozzo 8	37
Castelnuovo di Porto	Pozzo 1 Le Terrazze	8	Anagni	Pozzo Masseria del Monte	8	Rocca Priora	Doganella - Pozzo 9	38
Castelnuovo di Porto	Pozzo 3 Le Terrazze	9	Ardea	Pescarella Pozzo 1	9	Roma	Finocchio pozzo 1	39
Monterotondo	Sorgente Valga delle Roche	10	Ardea	Pescarella Pozzo 2	10	Roma	Finocchio pozzo 2	40
Rieti	Sorgenti delle Capore	11	Ardea	Pescarella Pozzo 3	11	Roma	Finocchio pozzo 3	41
Rieti	Peschiera Sorgenti Basse	12	Ardea	Pozzo 1 Laurentina	12	Segni	Pozzo Fontanelle	42
Rieti	Peschiera Sorgenti Alte	13	Ardea	Pozzo 2 Laurentina	13	Segni	Pozzo Mola	43
Roma	Pantano Borghese - Cavallino "Felice"	14	Ardea	Pozzo 3 Laurentina	14	Subiaco	Sorgente Forma Focerale	44
Roma	Pantano Borghese - Rifolta "Bicchiere"	15	Ardea	Pozzo Costa	15	Subiaco	Sorgente Nocchitella	45
Roma	Pantano Borghese - Rifolta "Felice"	16	Carpineto	Sorgente la Fota	16	Tivoli	Sorgente Rivellese	46
Roma	Pantano Borghese-Pozzo 8	17	Castel Gandolfo	Pozzo Brandi	17	Tivoli	Sorgente Ronci	47
Roma	Pantano Borghese-Pozzo 9	18	Castel Gandolfo	Pozzo Perugini	18	Trevi nel Lazio	Nuove Sorgenti di Vallepietra	48
Roma	Pantano Borghese-Pozzo 10	19	Ciampino	Sorgente Pantanelle	19	Trevi nel Lazio	Pozzi Ceraso	49
Roma	Salone Polla 1	20	Ciampino	Pozzi Preziosa	20	Trevi nel Lazio	Sorgente Ceraso	50
Roma	Salone Polla 2	21	Ciampino	Pozzo Capri Cruciani	21	Vallepietra	Sorgente Pertuso	51
Roma	Salone Polla 3	22	Ciampino	Pozzo Sassone	22	Velletri	Pozzo 167	52
Roma	Salone Polla 4	23	Fiano Romano	Pozzo Sassete	23			
Roma	Torre Angela pozzo n°1	24	Gavignano	Pozzo Pertica	24			
Roma	Torre Angela pozzo n°2	25	Genzano	Pozzo Via Firenze	25			
Roma	Torre Angela pozzo n°3	26	Grottaferrata	Pozzo Pratone	26			
Roma	Torre Angela pozzo n°4	27	Lariano	Pozzo Colle Cagioli	27			
Tivoli	Sorgente Acquoria	28	Lariano	Pozzo Acqua di Papa	28			
Zagarolo	Valle Martella - pozzo 1	29	Lariano	Pozzo Valle Verde	29			
Zagarolo	Valle Martella - pozzo 3	30	Marino	Pozzo 3 Via Ferentum	30			
Zagarolo	Valle Martella - pozzo 4	31						

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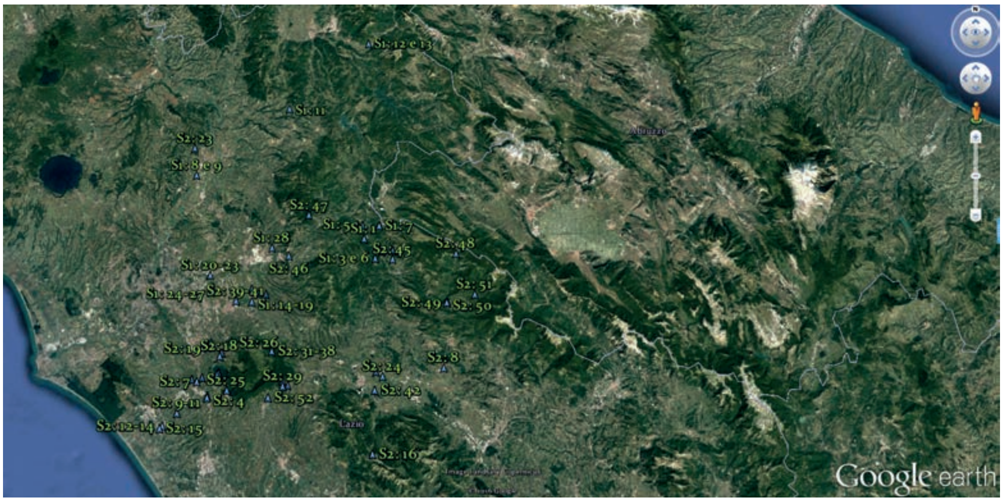

Fig 5 - Location of springs and wells selected for the investigation.

Fig 5 - Localizzazione di sorgenti e pozzi selezionati per l'indagine.

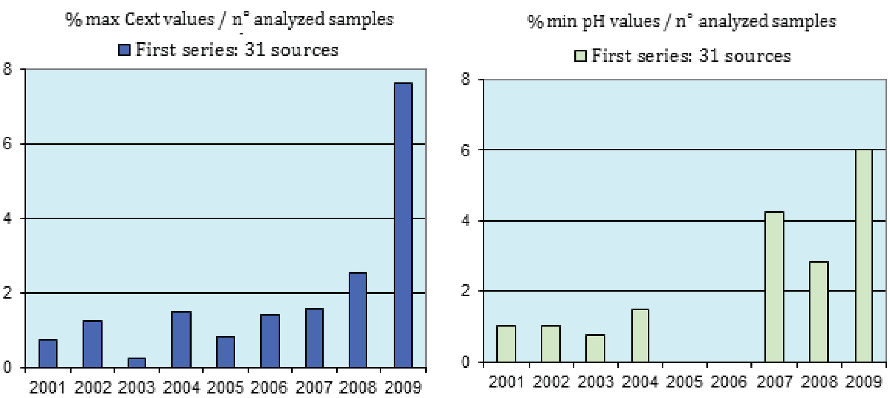

Fig. 6 - Percentage of the maximum Cext and minimum pH values compared to the total number of samples in the year. Two values for each source are considered.

Fig. 6 - Percentuale dei valori massimi di Cext e dei valori minimi di pH rispetto al numero totale di campioni nell'anno. Sono considerati due valori per ciascuna sorgente.

Acqua Marcia), Pratolungo (for Acquoria), Torrita Tiberina and Formello (for Castelnuovo di Porto), Tor Vergata, Pantano Borghese, Frascati and Zagarolo (for Rome) (source: www.arsial.it & www.idrografico.roma.it).

Starting from 2007 you can notice an increase of maximum Cext and minimum pH values, with a significant concentration in 2009. If we compare it with the trend of rains (Fig. 7), it is clear that the trend of the values of TDIC and pH cannot be explained by variations in annual rainfall.

Then, looking at the monthly detail of the 2007-2009 period (Fig. 8), we can see that the maximum Cext values will focus mainly between January and February 2009, about two months before the earthquake in L'Aquila.

The trend of the minimum pH values seems to suggest two major degassing events, respectively in November 2007 and February 2009.

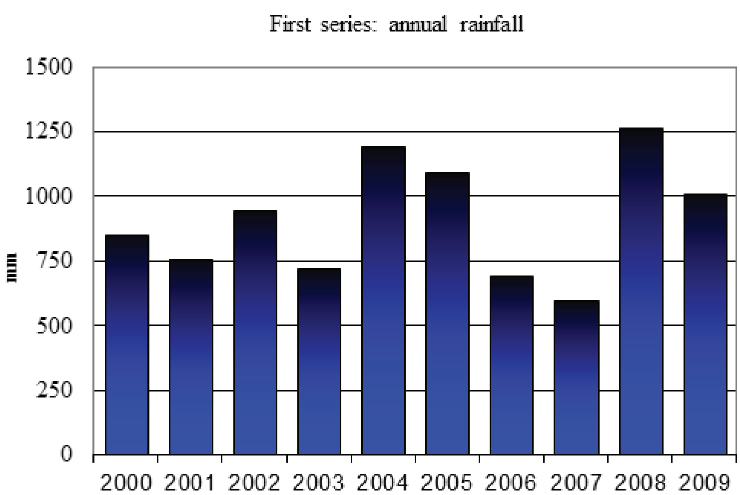

Fig. 7 - Average annual rainfall measured near the sources of the first series.

Fig. 7 - Piovosità media annua misurata presso le sorgenti della prima serie.

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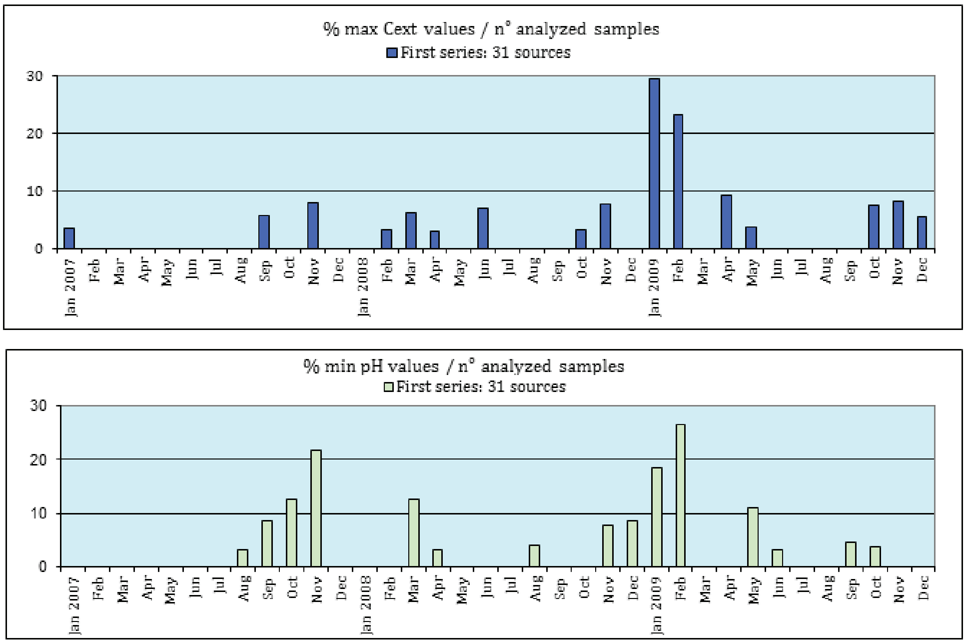

Fig. 8 - Percentage of maximum Cext and minimum pH values, compared to the total number of samples in the month (2007-2009).

Fig. 8 - Percentuale di valori massimi di Cext e di valori minimi di pH, rispetto al numero totale di campioni nel mese (2007-2009).

Second series

The same type of statistical analysis was conducted on the second series and detailed monthly from 2006 to 2009. The geographical area covered by this selection is broader and includes (in addiction to areas of the Series 1), wells and springs located in the municipalities of Albano, Anagni, Ardea, Carpineto, Castel Gandolfo, Ciampino, Fiano Romano, Gavignano, Genzano, Grottaferrata, Lariano, Marino, Rocca Priora, Segni, Subiaco, Tivoli, Trevi nel Lazio, Vallepietra, Velletri and Zagarolo. 33 of the 83 analyzed sources are by carbonate aquifers so here it was possible to examine the trend of Ccarb (Fig. 9).

The observations made about the first series are confirmed, and moreover can be noticed a second peak in the maximum Cext values, to a lesser extent, between September and November 2007, synchronous with the first overall decrease in pH values.

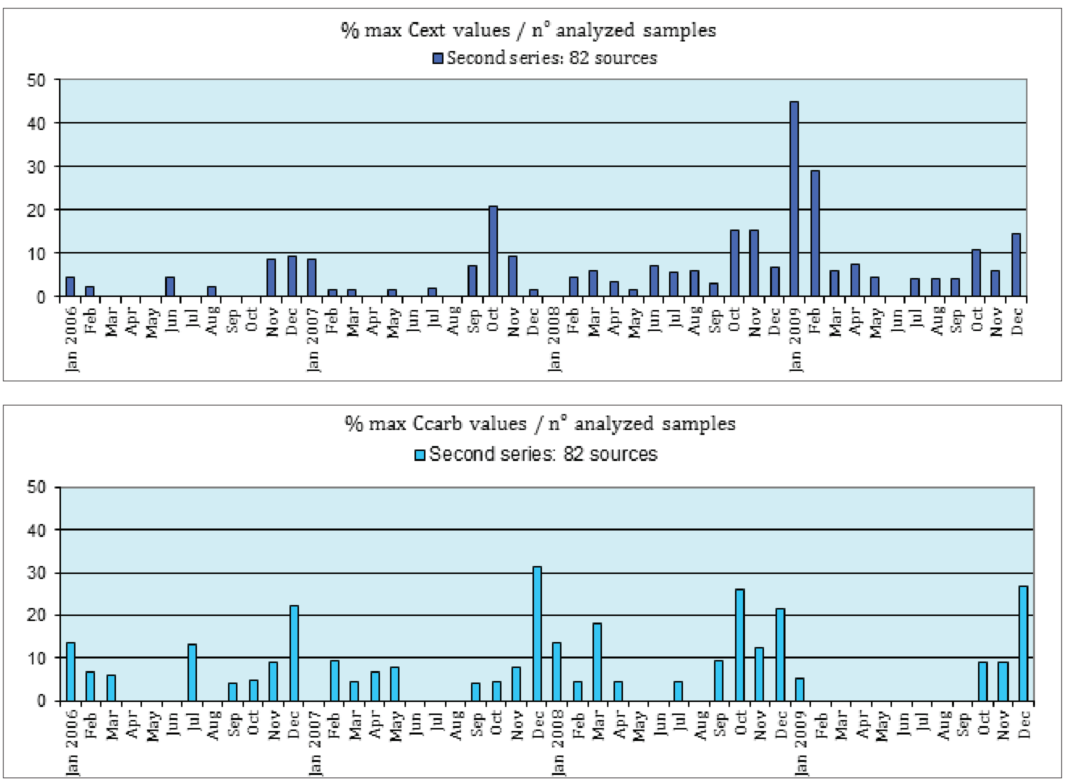

Fig. 9 - Percentage of the maximum Cext and Ccarb values and minimum pH values compared to total number of samples in the month (2006 - 2009).

Fig. 9 - Percentuale dei massimi valori di Cext e Ccarb e dei valori minimi di pH rispetto al numero totale di campioni nel corso del mese (2006-2009).

The trend of the maximum Ccarb values relative to the 33 carbonatic sources follows in reverse (as expected) that of rainfall: for example, the peak in December 2007 shown in figure 9 can be explained with the exceptional drought of the second half of 2007. Account must be taken in this type of evaluation: the timing of aquifer recharge in relation to rainfall vary greatly, from a few hours (i.e. Vallepietra Springs) up to 6 months (i.e Peschiera Springs), and for most of the minor sources are not known.

The trend in average rainfall, monthly reported in detail in Fig. 10, was obtained by adding to the rain gauges of the first series those of Trevi nel Lazio, Neroli, Civitella San Paolo, Roma Termini, Ardea and Velletri (source: www.arsial.it & www.idrografico.roma.it).

TDIC Tend in single sources

Let us now observe, in single sources, the trend of Cext values (coupled with Ccarb values when sources are from carbonate aquifers), remembering that values greater than 4.0 E-03 (4 millimoles per liter) necessarily correlate with the activity of degassing in the TRDS area. For this purpose we have selected all those sources for which we have series of continuous data (or with a few breaks in the series) since at least 2006.

Out of 47 sources found to be suitable for this purpose, as many as 35 (over 70%) record, over a period of at least fifty days before the earthquake in L'Aquila, a very high value of Cext, never previously observed during the whole period for which analytical data are available. This phenomenon occurs both in volcanic than in calcareous aquifers. The peak values it usually takes between the end of 2008 and the first half of February 2009. In the following graphs (Fig. 11) are shown 10 of the most noticeable cases, including the great springs of Peschiera, Capore and Acqua Marcia. For Acqua Marcia, all the individual sources that compose the aqueduct have been treated here as a unit. For each day of sampling it has been selected the one with the greater Cext value (the Ccarb is not reported). The single sources with the maximum Cext values recorded at the beginning of 2009 are the Rosoline and the Mola di Regno.

Discussion

Data thus collected and processed seem to indicate that the mantle degassing in the TRDS area has reached a very high level between the end of 2008 and the beginning of 2009, and that probably this level has a causal relationship with the disastrous earthquake occurred at L'Aquila the 6th of April 2009.

The main objection about this interpretation calls into question the exceptional rainfall occurred in December 2008, which was preceded by two very wet months, although within the norm (Fig. 10). Could the peak values refer to a higher than normal contribution of Cinf, the carbon of biological origin transported by rain (being Cext the sum of Cinf and Cdeep)? No, for at least two reasons. Firstly, because similar rainy periods, such as the October-December 2005 quarter, did not give rise to similar signals while on the contrary the dry periods as the autumn of 2007 showed them, and secondly because the signals are almost synchronous in sources that have a refilling time significantly different (for example,

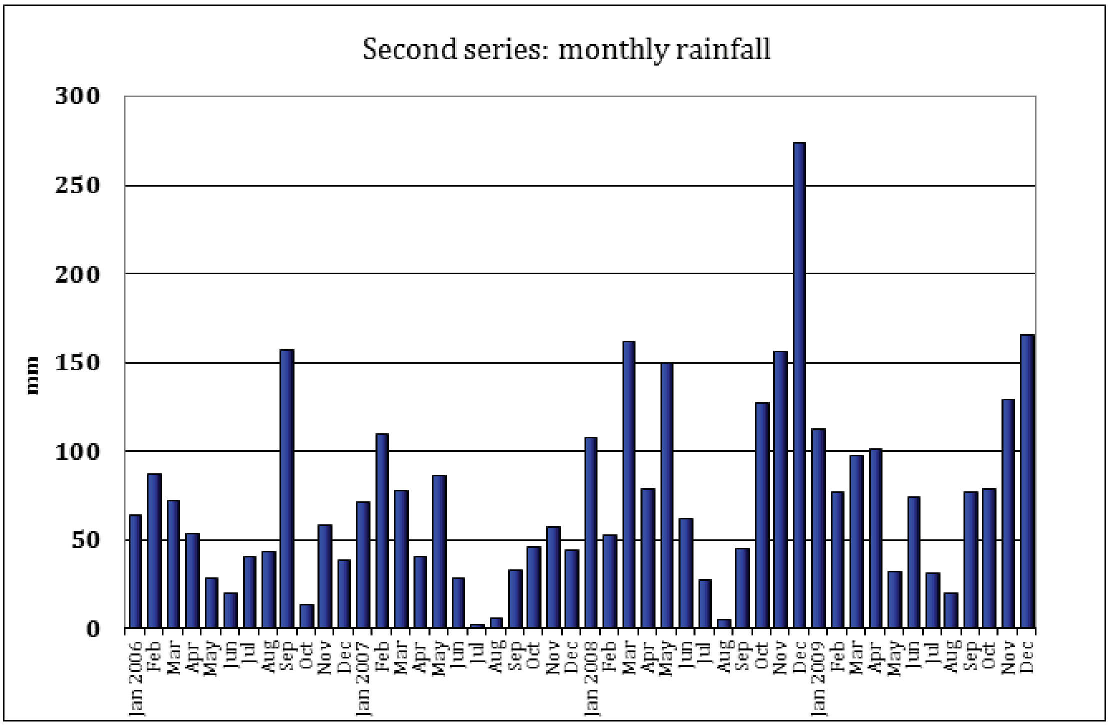

Fig. 10 - Average monthly rainfall detected near the sources of the second series.

Fig. 10 - Piovosità media mensile rilevata in prossimità delle sorgenti della seconda serie.

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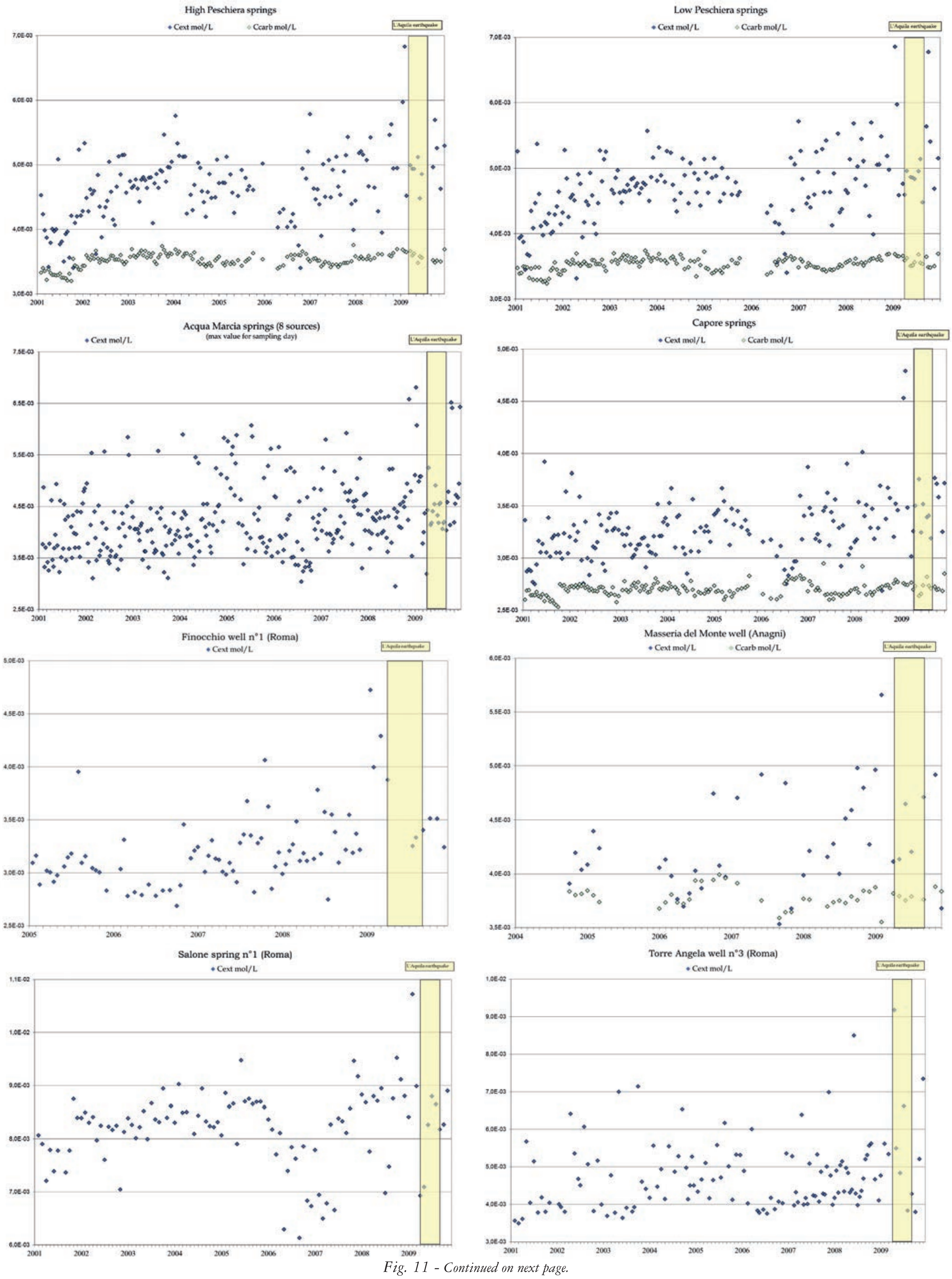

Fig. 11 - Continued on next page.

Fig. 11 - Segue nella pagina successiva

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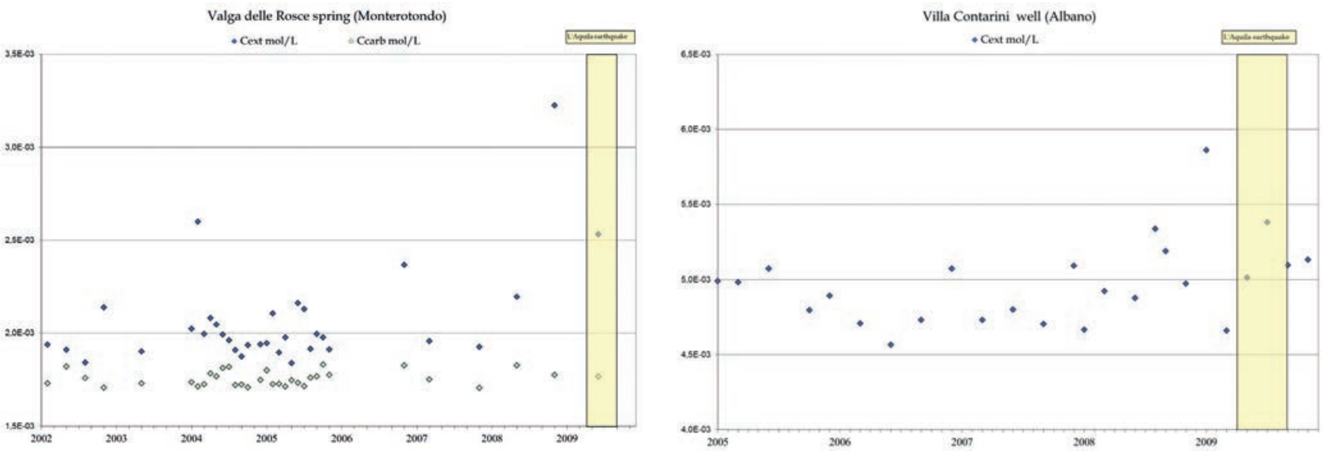

Fig. 11 - Ten of the most noticeable cases of a degassing peak signal just before the L'Aquila earthquake.

Fig. 11 - Dieci dei casi più evidenti di un segnale di picco del degassamento precedenti di poco il terremoto dell'Aquila.

between Peschiera and Acqua Marcia there is a difference of three months and in any case the rains in December could not have reached the aquifer of Peschiera in January-February). Moreover, other studies have reported an unusual CO_2 level in air or water in the near of L'Aquila before the seismic series, (Adinolfi et al. 2011; Bonfanti et al. 2012; La Vigna 2013; La Vigna et al. 2013; Petracchini et al. 2015; Quattrocchi et al. 2012; Voltattorni et al. 2012) and a similar correlation has been proved to exist in other context (Hainzl and Ogata 2006; Heinicke et al. 2011; Perez et al. 2008; Pierotti et al., 2013).

Conclusions

What can we tell about the possibility of a constant measurement of dissolved inorganic carbon in the spring waters to monitor the activity of mantle degassing in the TRDS area, in order to have an early warning signal of possible seismic activity in the central Apennines?

From the technical point of view the installation of automatic semi-continuous analysers of the carbon isotopic composition in remote areas still presents problems of calibration and maintenance that make it less suitable for long-term monitoring because of the transportation costs of specialized personnel (similarly the frequent transport of samples in a central laboratory equipped for the measure would have a high cost).

The automatic semi-continuous determination of the TDIC in a big carbonatic aquifer would be less expensive in equipment and much less onerous from an organizational point of view. The components Ccarb and Cext, when lacking the contemporary determination of Ca, Mg and SO_4, would not be separable from the value obtained, however we have seen how the oscillations of the components Ccarb and Cinf have here a small influence on the value of TDCI, which on the contrary is very influenced by fluctuations in Cdeep.

The Peschiera springs, being a very large aquifer with a long and known recharge time and located in a key position, are the ideal place for the installation of an automatic (isotopic or TDCI) analyser able to monitor the TRDS degassing activity. Here the value of Ccarb appears to be particularly stable over time (see the relative graphs) and we have now the possibility to use the values recorded before the L'Aquila earthquake to calibrate a warning threshold, in the first approximation around the value of 10 millimoles per liter. This value is obviously not absolute, but closely related to the source in question. Looking at the full scale of the graphs relative to single sources is easy to understand how each source possesses a specific range of TDIC values.

Fig. 12 shows the trend of TDIC in the high Peschiera springs. Actually, ACEA ATO2 perform a monthly monitoring, relative to the normal potable controls. By using a field analyser we could turn instead to a daily (or even hourly) monitoring, which could be integrated with the sensor network of seismic activity and with the satellite monitoring, in order to improve the ability to pre-alert authorities and population.

At the moment this has not yet be done, but there is a further possibility and it has already been made operational. The idea is that to monitor TDIC and Cext in the Peschiera-Capore mixture that is distributed in the municipality of Rome and whose analytical data are available almost daily. Surprisingly, despite mixing (which is very stable in time; in the 2006-2015 period, the mixing ratio between the Peschiera and the Capore springs was, respectively, of 64% and 36%, with a maximum offset of +/ - 1.5%), a mild treatment with sodium hypochlorite, the passage in penstocks for hydropower generation and a long-distance water supply, the information on the content of inorganic carbon appears to be preserved.

Fig. 13 shows the trend of TDIC from 2008 through August 2010 in all drinking fountains and water centres of Rome and surroundings that provide the Peschiera-Capore mixture, while Fig. 14 shows the maximum values of Cext (and the relative Ccarb values) for each sampling day. A focus on the daily detail allows us to conclude that the degassing activity reached its maximum around February the 12, 2009, a date

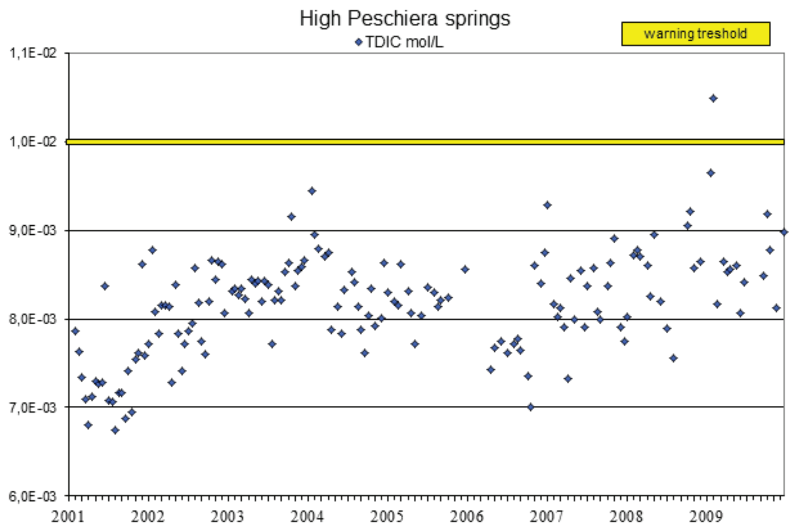

Fig. 12 - The trend of TDIC in the high springs of Peschiera and the superimposed warning threshold.

Fig. 12 - Andamento del TDIC nelle sorgenti alte del Peschiera e soglia di allarme impostata.

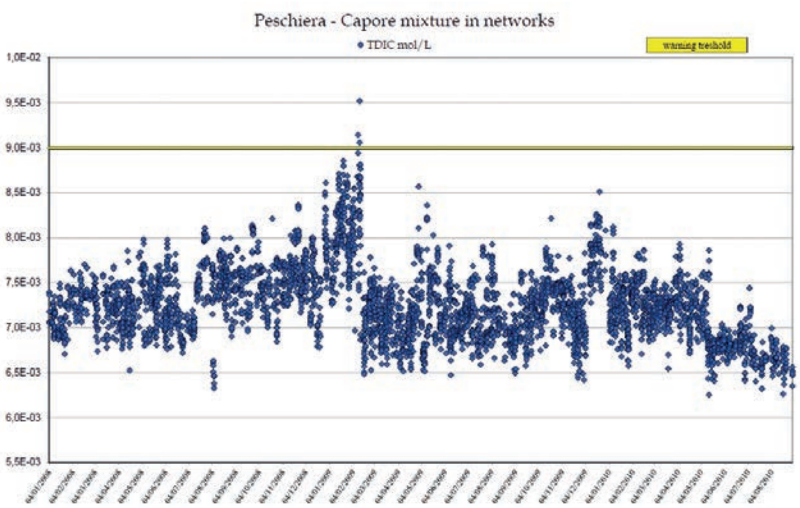

Fig. 13 - The trend of TDIC in all sampling points that provide the Peschiera-Capore mixture.

Fig. 13 - Andamento del TDIC in tutti i punti di prelievo di rete che contengono la miscela Peschiera-Capore.

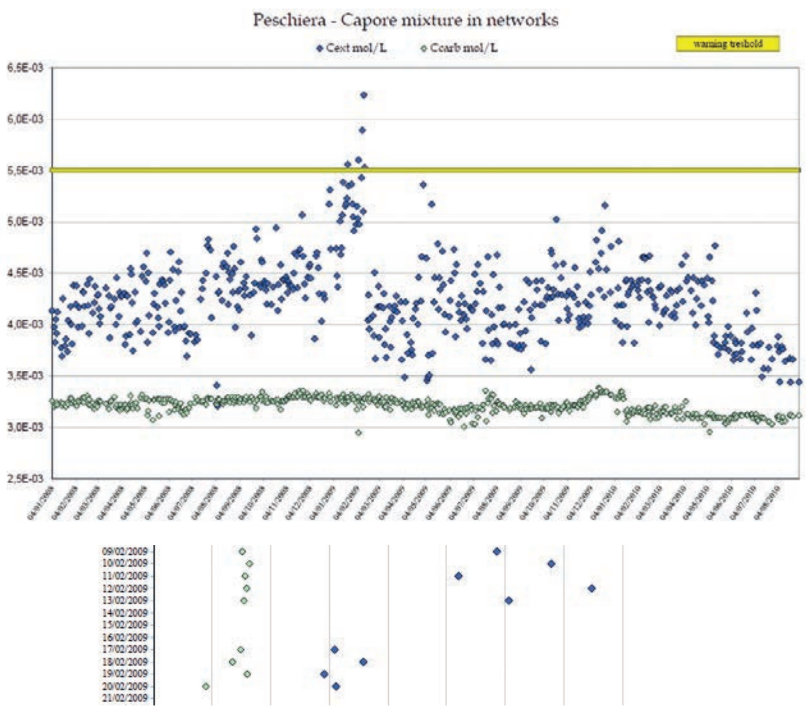

Fig. 14 - Maximum values per day of Cext in all the sampling points that provide the Peschiera-Capore mixture, and a focus on the degassing peak.

Fig. 14 - Valori massimi giornalieri di Cext in tutti i punti di prelievo di rete che contengono la miscela Peschiera-Capore, e ingrandimento delle date con i valori del picco di degassamento.

after which there is a sudden and sharp drop in TDIC values. Here also, the value of the warning threshold is obviously arbitrary and it is based on what was recorded before the painful event of L'Aquila.

A last note has to be made in relation to the earthquake in August 24, 2016 at Amatrice and to the following seismic series recorded in the central Apennines and not yet concluded at the moment (end of November 2016). No signals of an improved degassing activity has been recorded neither before nor during this seismic event (not even the high and low Peschiera, the Capore and the Salone springs have recorded unusual values). Last two graphs (Fig. 15 and 16) show the complete historical trends in the Peschiera-Capore mixture, updated to the moment (starting from 2006). Of course the correlation between degassing and earthquakes in the TRDS area is a weak one and many more factors must be considered before to assert a causal relationship, however the signal in water that preceded L'Aquila cannot be ignored.

The TDIC and Cext monitoring will continue, as it is an integrant part of the Water Quality Monitor, a system of classification and evaluation of all the analytical data ACEA ATO2 has developed over the last 10 years and that was recently awarded with the CEEP CSR Label 2016 (www.ceep.eu).

The complete analytic database related to this work, as well as all future developments, is available to the scientific community on request.

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Dedicated to the memory of my father.

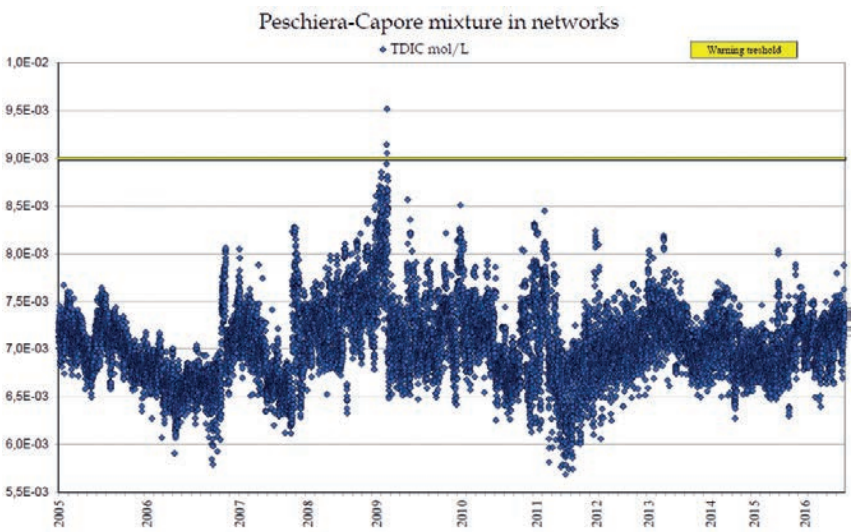

Fig. 15 - 2005/2016 trend of TDIC in all sampling points that provide the Peschiera-Capore mixture.

Fig. 15 - Andamento 2005-2016 del TDIC in tutti i punti di prelievo di rete che contengono la miscela Peschiera-Capore.

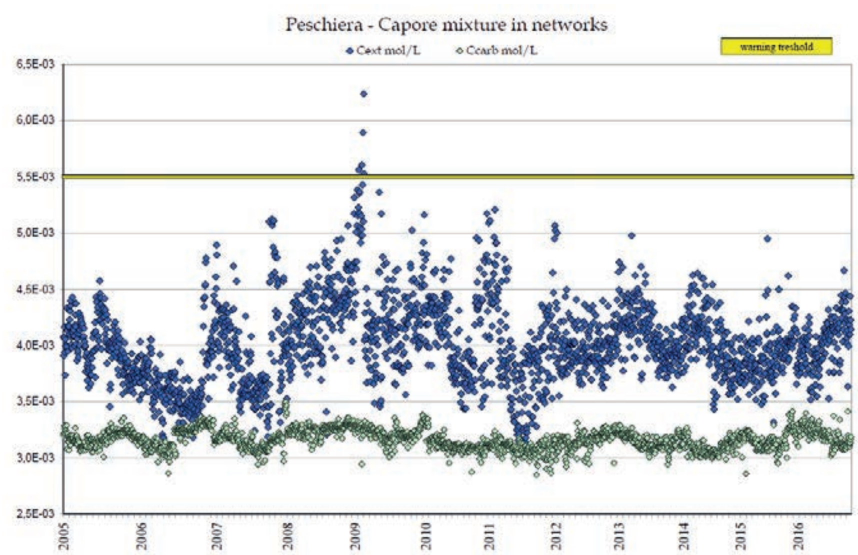

Fig. 16 - 2005/2016 maximum values per day of Cext in all the sampling points that provide the Peschiera-Capore mixture.

Fig. 16 - Andamento 2005-2016 del Cext in tutti i punti di prelievo di rete che contengono la miscela Peschiera-Capore.

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