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MARIACARMELA BELGIORNO (*), PAOLA MARIANELLI (*), GIUSEPPE PASQUINI (*), ALESSANDRO SBRANA (*)

A CONTRIBUTION TO THE STUDY OF A PISA ALLUVIAL PLAIN SECTOR FOR LOW TEMPERATURE GEOTHERMAL ASSESSMENT

Abstract - *A contribution to the study of a Pisa alluvial plain sector for low temperature geothermal assessment.* The target of this work is to evaluate the possible feeding of the east sector of the Pisa plain hydrogeological system by the Monte Pisano meteoric waters, using a geochemical and geological approach. The study was made considering the Calci basin and the area of the sedimentary plain adjacent at the Calci fan, where spring and well waters have been sampled and analyzed. The analyses of the major and minor elements of the well waters have confirmed a common origin with the springs above the Calci major alluvial fan, showing the same geochemical fingerprint. The isotopic analyses (δD - $\delta^{18}O$) allowed to compute the average altitude of infiltration of the waters. The altitudes obtained for the groundwaters sampled close to the alluvial fan are comparable with the average altitude of the Monte Pisano, confirming the hypothesis of the feeding of this aquifer sector by the Calci alluvial fan. The meteoric waters infiltrate through the debris-alluvial bodies that cover the south-western side of the Monte Pisano slopes reaching the aquifers at the foot of the hills. A possible water contribution to the feeding of about $5 \cdot 10^6$ m³/yr has been estimated from the hydrologic budget of the drainage basin above the Calci alluvial fan.

Key words - Hydrogeochemistry, stable isotopes, low-temperature geothermal energy, Monte Pisano, Calci, Tuscany, Italy

Riassunto - *Un contributo allo studio di un settore della piana alluvionale di Pisa ai fini di una valutazione geotermica a bassa temperatura.* Lo scopo di questo lavoro è quello di valutare una possibile alimentazione del settore orientale del sistema idrogeologico della Piana di Pisa dalle acque meteoriche del Monte Pisano, attraverso un approccio geochemico e isotopico. Lo studio è stato effettuato considerando il bacino di Calci e l'area della piana di Pisa adiacente alla conoide alluvionale di Calci, dove acque sorgive e di falda sono state campionate e successivamente analizzate. Le analisi degli elementi maggiori e minori delle acque di falda hanno confermato l'origine comune tra le acque sorgive, al di sopra della conoide di Calci, e le acque di falda, mostrando una stessa impronta geochemica. Le analisi isotopiche (δD - $\delta^{18}O$) hanno permesso la determinazione della quota media di infiltrazione delle acque. Le quote ottenute per le acque di falda campionate nei pressi della conoide di Calci risultano comparabili con le quote medie di infiltrazione del Monte Pisano, confermando l'ipotesi dell'alimentazione di questo settore dell'aquifero dalla conoide alluvionale. Le acque meteoriche si infiltrano attraverso i corpi detritici e alluvionali che coprono il lato sud-occidentale del Monte Pisano, raggiungendo in questo modo l'aquifero alle pendici dell'altura. È stato stimato dal bilancio idrologico del bacino idrografico di Calci un possibile contributo di circa $5 \cdot 10^6$ m³/anno di acqua.

Parole chiave - idrogeochimica, isotopi stabili, geotermia a bassa temperatura, Monte Pisano, Calci, Toscana

INTRODUCTION

The use of shallow low temperature geothermal energy represents today one of the most promising way to reduce the emissions of carbon dioxide and other greenhouse gases, which are one of the main causes of the climate changes. In order to use this technology, the quantitative knowledge of the geothermal-hydrogeological characteristics of the aquifers is necessary. The data presented in this work are part of the assessment of the low temperature geothermal potential existing in the subsoil of the Pisa alluvial plain. In particular water springs inside the Calci basin (Tuscany Region, Central Italy) and wells at the transition between the Calci alluvial fan and the nearby alluvial plain has been sampled (Fig. 1) to study the possible role of meteoric waters in the recharge of the Pisa hydrogeological system, dominated by a Confined multilayer aquifer (Baldacci *et al.*, 1994). The study area is the southern portion of the wider Plio-Pleistocene extensional basin (Viareggio basin) located in the northern Tyrrhenian side of Tuscany (Pascucci *et al.*, 2005). The shallow sediments (up to 200 m of depth) are represented by an interlayering of fine and coarse sediments, sands and gravels, separated by clays and silts, formed following the transgressive-regressive events occurred in the area from the Upper Miocene (Aguzzi *et al.*, 2007, Sarti, 2012., Amorosi *et al.*, 2009; Sarti *et al.*, 2015). According to Baldacci *et al.* (1994) the sands and the local gravel hosting the confined aquifers could be intercalated to the debris and alluvial bodies of the Calci fan (Fig. 2), allowing the meteoric water, which infiltrate through the Monte Pisano hillslope alluvial fan, to feed this sector of the aquifer.

ANALYTICAL PROCEDURES AND RESULTS

Water pH and temperature have been determined in the field using a multiparameter probe and a thermocouple thermometer. The analyses of the major and minor elements have been determined by ion

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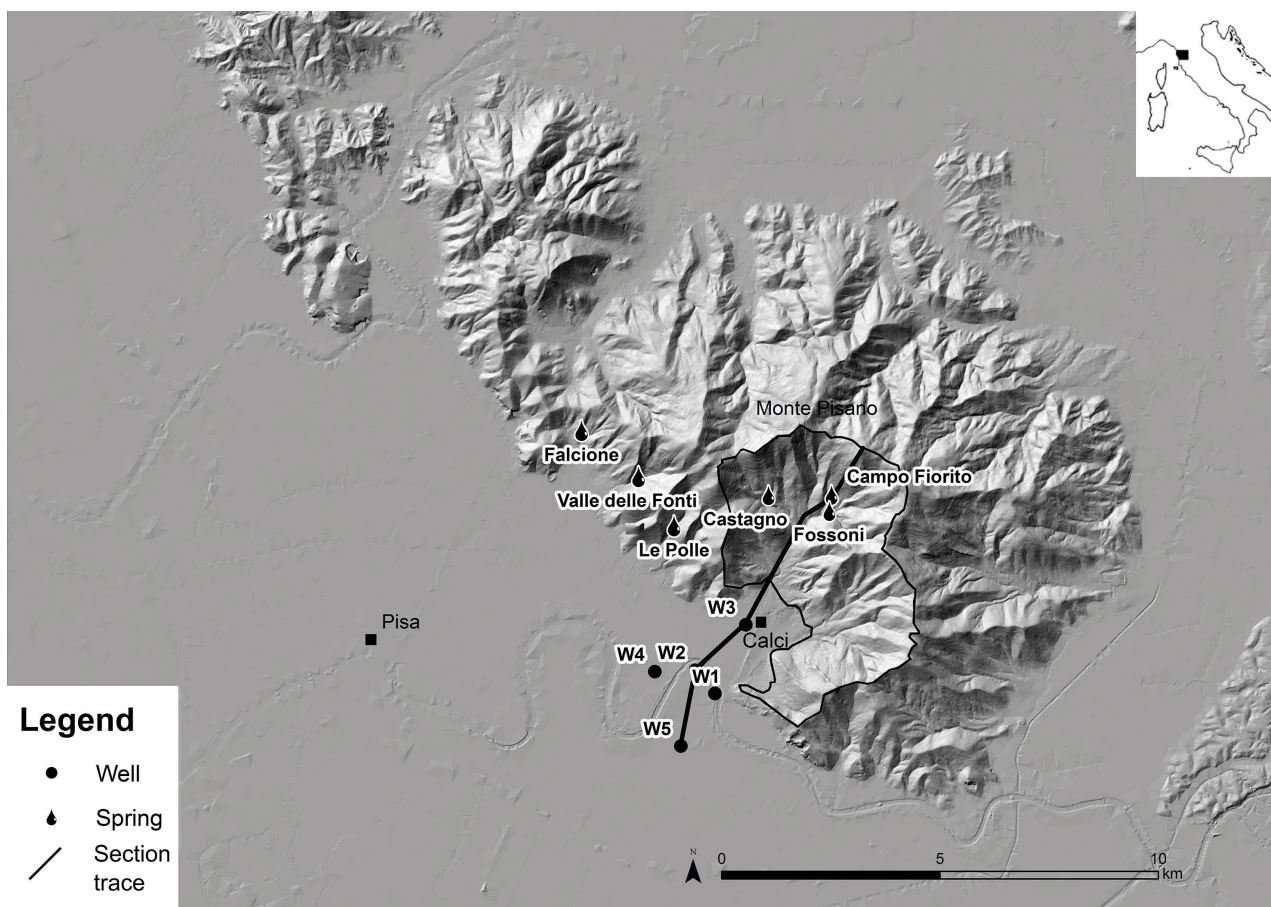


Fig. 1 - Digital Terrain Model (DTM) of the study area. In the figure are reported the sampling points of the Monte Pisano springs and of the groundwaters from wells, the Calci drainage basin, defined using a topographic contouring, and the scheme trace reported in Fig. 2.

chromatograph (IC) and visible light spectrophotometer. The isotopic analyses have been performed through CRDS (Cavity Ring Down Spectroscopy) technology, using a Picarro L2120-i laser spectroscope, present in the CEGlab (laboratory of the Excellence Centre for geothermal energy in Larderello).

The chemical analyses of the water samples are reported in Tab. 1. All the spring waters, except for Castagno, are low-mineralized, while the well waters show a higher mineralization, with the TDS values ranging from 188,8 to 396,3 mg/l. The pH of the samples ranges from weakly acid to slightly alkaline (5,8-7,6).

The Cl⁻ in the water springs ranges from 19,2 mg/l to 25,7 mg/l, while the wells sampled have higher chloride content, reaching 66,6 mg/l.

The isotopic values (δD - $\delta^{18}O$) of samples are reported in Tab. 2 and plotted in Fig. 3.

All the samples fall near the Central Italy Local Meteoric Water Line (Longinelli and Selmo, 2003), described by the equation:

$$\delta D = 7,047\delta^{18}O + 5,608$$

and the generic Italian Meteoric Water Line (Giustini *et al.*, 2016), described by the equation:

$$\delta D = 8.32\delta^{18}O + 15.37$$

The spring water values range from 6,8‰ to 6,3‰ for the $\delta^{18}O$ and from 38,1‰ to 39,9‰ for the δD , while the well waters values are isotopically more homogeneous, ranging from 6,3‰ to 6,6‰ for the $\delta^{18}O$ and from 36,7‰ to 37,8‰ for the δD .

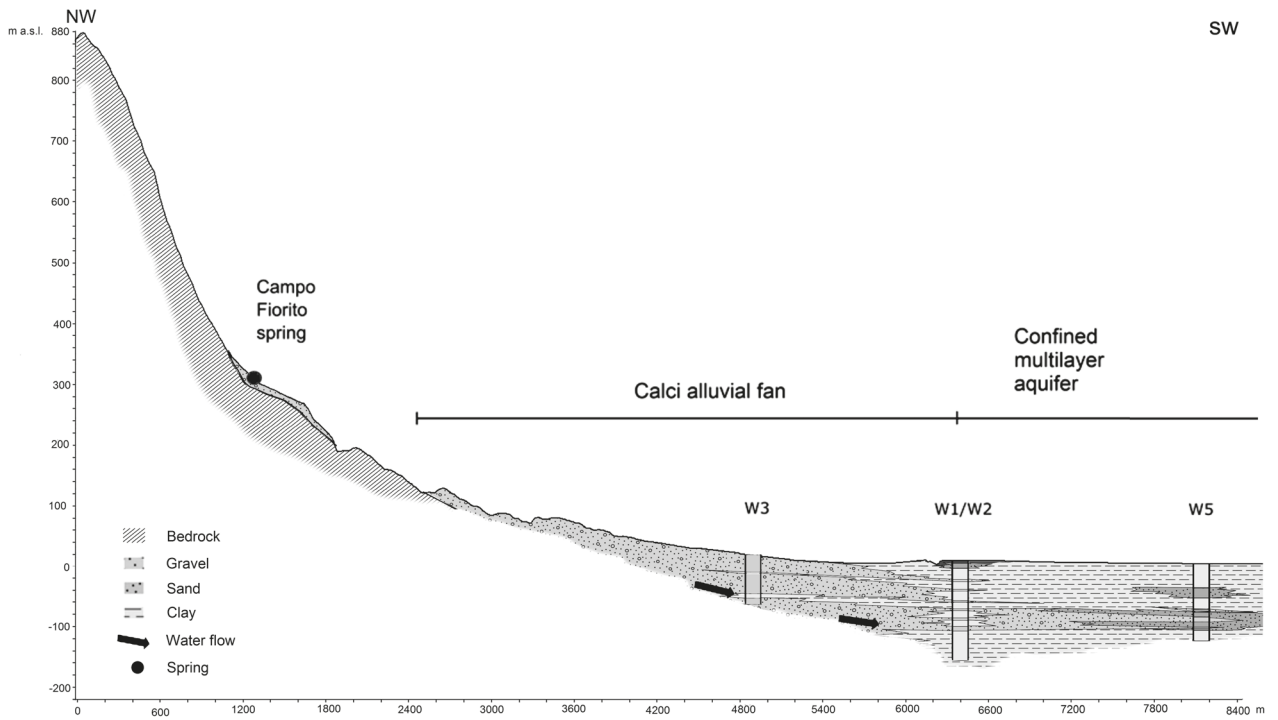


Fig. 2 - Scheme of water circulation through the Calci alluvial fan and the aquifer.

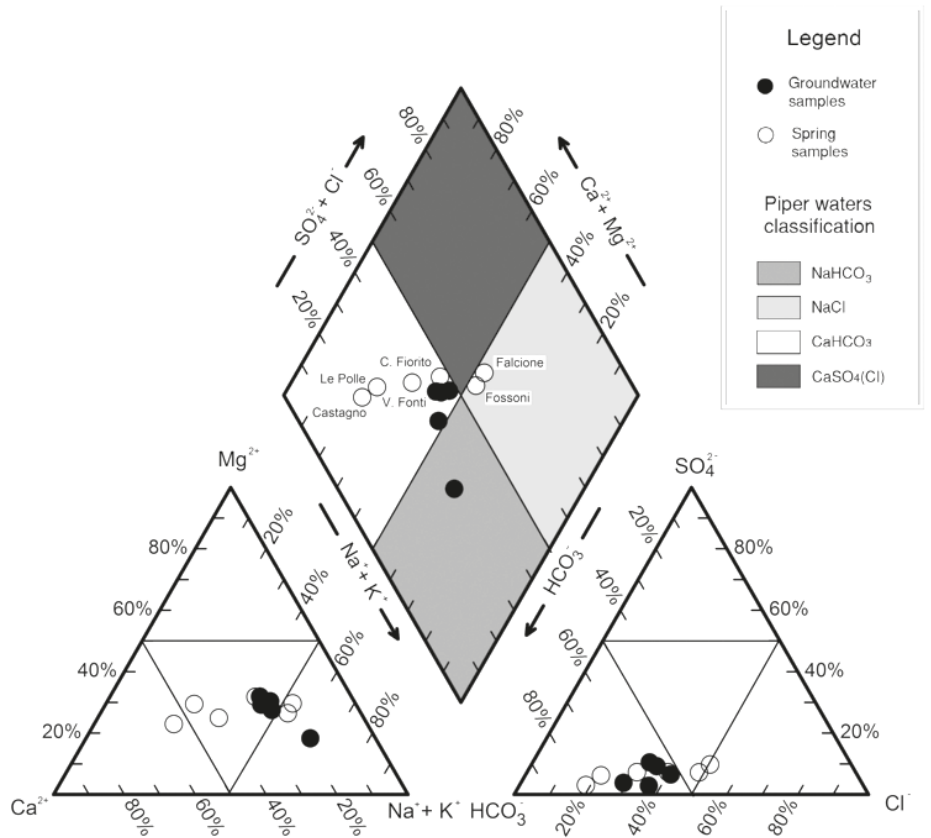


Fig. 3 - Isotopic composition (δD - $\delta^{18}O$) of the springs and of the groundwaters sampled. IMWL: Italian Meteoric Water Line (Giustini *et al.*, 2016); LMWL: Local Meteoric Water Line of the Central Italy (Longinelli and Selmo, 2003).

Tab. 1 - Chemical data (expressed in mg/l) of the samples.

Locality	VALLE DELLE FONTI										
	FALCIONE SPRING	CAMPO FIORITO SPRING	CASTAGNO SPRING	FOSSONI SPRING	LE POLLE SPRING	AGNANO SPRING	W1 GROUNDWATER	W2 GROUNDWATER	W3 GROUNDWATER	W4 GROUNDWATER	W5 GROUNDWATER
T(°C)	15	17,3	14,4	14,3	13,5	14,4	20	16,3	15,7	17,5	17,9
pH	5,8	6	7,1	5,9	7,6	6,9	6,4	6,4	6,2	6,3	6,6
TDS	98,4	107,8	301,5	86,7	182,3	152,6	396,3	188,8	269,1	260,2	302,5
Ca ²⁺	7	4	103,6	4,5	19,8	15,6	28,9	11,1	17,1	15,2	12,7
Na ⁺	11,8	13,4	14,8	13,1	12,2	14,7	53,4	24	31,1	33,1	49,5
Mg ²⁺	5	4,1	8,3	3,5	7,8	5,8	19,2	8,6	12,8	10,3	7,7
K ⁺	0,5	0,4	0,8	0,4	0,5	0,6	2	1,3	2	1,4	1,4
SiO ₂	16,4	16,2	15,8	7,2	9,1	9,4	15,1	15,4	14,6	25,4	33,4
HCO ₃ ⁻	31,7	43,9	109,8	26,8	104,9	75,6	177,2	70,8	112,7	117,1	147,6
Cl ⁻	19,2	20,2	25,7	19,8	22	22,1	66,6	32,1	38,3	41,1	37
SO ₄ ²⁻	4,7	4,1	14,4	5,2	7,1	7	8,2	6,9	16,5	4,3	6,6
Mn ²⁺	0,9	0,8	0,8	1,7	1,1	0,6	0,7	1	1,9	0,5	1,8

Tab. 2 - Isotopic data (δD and δ¹⁸O).

	VALLE DELLE FONTI										
	FALCIONE SPRING	C. FIORITO SPRING	CASTAGNO SPRING	FOSSONI SPRING	LE POLLE SPRING	AGNANO SPRING	W1 GROUNDWATER	W2 GROUNDWATER	W3 GROUNDWATER	W4 GROUNDWATER	W5 GROUNDWATER
δ ¹⁸ O	-6,2	-6,8	-6,8	-6,5	-6,5	-6,6	-6,4	-6,6	-6,5	-6,4	-6,3
δD	-36,9	-39,6	-39,5	-38,3	-38,5	-38,8	-37,7	-37,8	-37,2	-37,5	-36,7

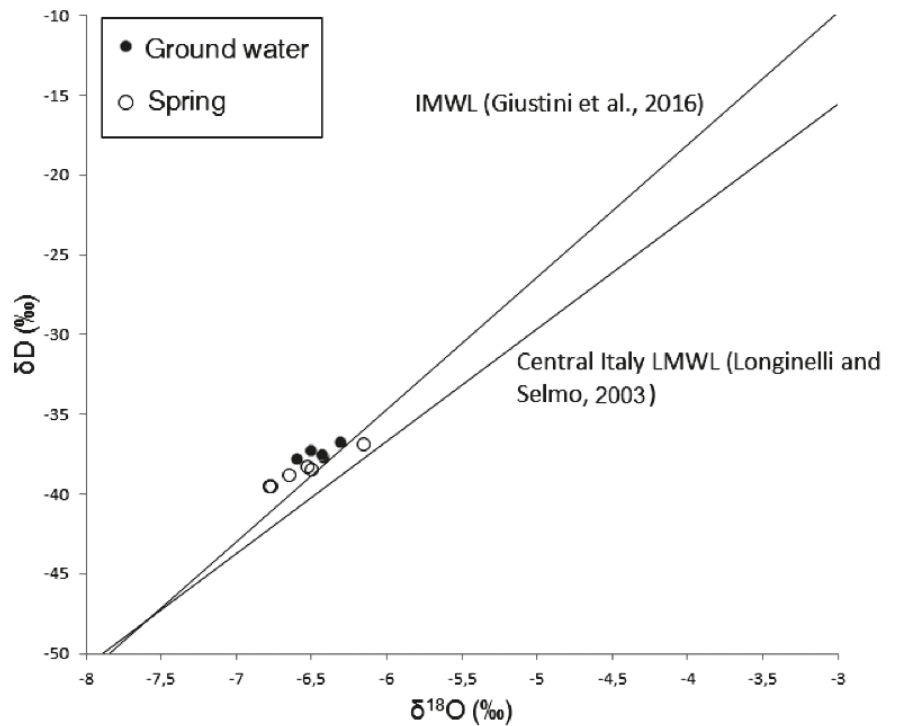


Fig. 4 - Piper diagram for spring and well groundwater samples.

DISCUSSION

In the Piper diagram (Fig. 4) the proportions of the major cations and anions are presented. The spring waters range from sodium-chloride to calcium-bicarbonate waters, while the well water samples fall between the calcium-bicarbonate and the sodium-bicarbonate fields, showing a homogeneous composition except for the sample W5 that has a slightly higher content of Na^+ and K^+ . The Shoeller-Berkaloff diagram (Fig. 5) highlights very similar trends between the groundwater samples, in particular with the Campo Fiorito pattern, confirming the same fingerprint between Campo Fiorito and Fossoni springs and the well groundwaters. The sample W5, whose location is more peripheral than the other samples, shows a higher concentration of Na^+ and K^+ . This could be caused by ionic-exchange reactions (“freshening”), (e.g. Appelo, 1994) between the Ca^{2+} ions, contained in the calcium-bicarbonate waters, and the sodium hosted in the alluvial sediments saturated with Na^+ coming from saline intrusions (Cerrina Feroni *et al.*, 2010).

The variability in the $\delta^{18}\text{O}$ and δD could be caused by the “altitude effect”, which influences the oxygen and hydrogen composition of precipitations. In order to evaluate the rainwater average altitude of precipitation (H) it has been applied the following relation:

$$H = \frac{\delta^{18}\text{O}_{(\text{sample})} - \delta^{18}\text{O}_{(\text{Pisa})}}{-0,0023}$$

The difference between the measured isotopic values ($\delta^{18}\text{O}_{\text{sample}}$) and the average value of $\delta^{18}\text{O}$ of the Pisa rain water ($\delta^{18}\text{O}_{\text{Pisa}}$), Giani and Panichi (2003), has been divided by the Northern Italian mean gradient (-0,23‰/100m, Giustini *et al.*, 2016). Results are shown in Tab. 3.

Castagno and Campo Fiorito springs show the highest infiltration altitude, while Falcione has the lowest value, according to the infiltration altitude of the springs drainage basins.

The values obtained for the groundwater samples range from 444 m (W5) and 568 m (W2). This results are comparable to the altitude of the drainage basin above the Calci alluvial fan, that ranges from 100 to 918 m. This result is in agreement with the hypothesis (Baldacci *et al.*, 1994) of the aquifers recharge by meteoric waters, infiltrating on the Monte Pisano reliefs.

These findings have been complemented by the hydrologic budget of the drainage basin above the Calci alluvial fan. The hydrologic budget was performed using the topographic contouring of the drainage basin and does not consider eventual external contributions related to the stratigraphic-structural conditions. Data

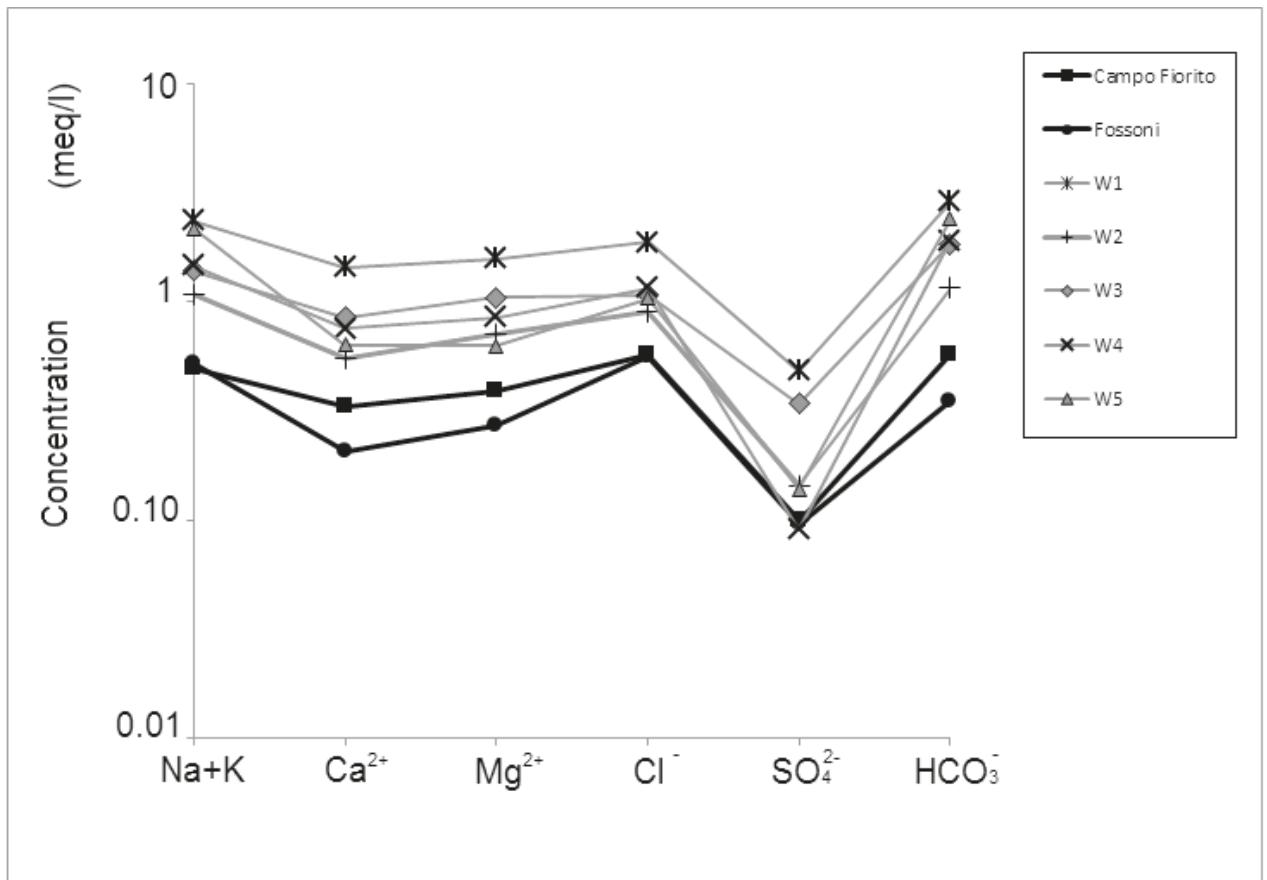


Fig. 5 - Schoeller-Berkaloff diagram.

Tab. 3 - Infiltration altitude computed for the spring and the well waters (see text).

	ELEVATION (M A.S.L.)
Castagno	665
Fossoni	557
Campo Fiorito	634
Falcione	374
Le Polle	523
Valle delle Fonti	587
W1	492
W2	568
W3	526
W4	493
W5	444

from 2001 to 2011 of three pluviometric stations, managed by SIR (Servizio Idrologico Regionale) have been used (<http://www.sir.toscana.it/>): Monte Serra (918 m a.s.l.), Asciano Pisano (95 m a.s.l.), and San Giovanni alla Vena (8 m a.s.l.); while two SIR thermometric stations have been used for the temperature: Pisa Agraria (6 m a.s.l.) and Monte Serra (918 m a.s.l.). Data show an average rainfall of about 1000 mm/yr and an average temperature of 14°C. The evapotranspiration, found with the Turc formula (Celico, 1986), is about 630 mm.

Since the surface runoff data are not available, it has been used the Kennessey method, that allow to determinate the runoff coefficient (Ck), basing on physiographic and climatic parameters (Bauducco *et al.*, 1994, Ghiglieri *et al.*, 2014).

The effective infiltration *I_e*, has been estimated utilizing the hydrologic budget of the Calci basin, corrected for evapotranspiration and runoff. The result is about 5*10⁶ m³/yr.

CONCLUSIONS

The chemical and isotopic analyses of the Monte Pisano springs and well waters close to the Calci fan allow to perform the following considerations:

- The spring waters show a low mineralization and range from sodium-chloride to calcium-bicarbonate compositions. The amounts of Cl⁻ is probably ascribed to the effect of the marine aerosol, that influence the composition of rainwaters infiltrating through the debris cover of the Monte Pisano;
- The well groundwaters show a chemical composition comparable with those of the springs above the Calci alluvial fan;
- The isotopic analyses allow to determinate the average infiltration altitude, applying the Northern Italian mean gradient (Giustini *et al.*, 2016). The results suggest that the waters infiltrate at altitudes compatible with the mean altitude of the drainage basin above the Calci fan;
- The data confirm the hypothesis of Baldacci *et al.* (1994): the confined aquifers in the plain are at least partially recharged by the meteoric waters infiltrating in the alluvial fan of the Monte Pisano, in addition to the contribution from the permeable formations of the Cerbaie and Pisan hills and the carbonate formations at the North of the plain.

A possible water contribution of about $5 \cdot 10^6$ m³/yr has been estimated to the feeding of the aquifers hosted in the subsoil of alluvial plain in correspondence of the Calci basin.

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