

PAPER • OPEN ACCESS

Lithological Influence and Human Impact On the Hydrochemistry of an Apennine Watershed (Southern Italy)

To cite this article: Nicolò Colombani *et al* 2016 *IOP Conf. Ser.: Earth Environ. Sci.* **44** 022020

View the [article online](#) for updates and enhancements.

Related content

- [Effect of lithological heterogeneity of bitumen sandstones on SAGD reservoir development](#)
E A Korolev, S A Usmanov, D S Nikolaev et al.
- [Feature level fusion for enhanced geological mapping of ophiolite complex using ASTER and Landsat TM data](#)
M Pournamdari and M Hashim
- [Lithological Discrimination Based on the Inversion of Roughness in Hami Area, Xinjiang](#)
Ni Zhuoya, Huo Hongyuan, Gan Fuping et al.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Lithological Influence and Human Impact On the Hydrochemistry of an Apennine Watershed (Southern Italy)

Nicolò Colombani ¹, Emilio Cuoco ², Gianluigi Busico ², Thomas Darrah ³, Micòl Mastrocicco ², Dario Tedesco ²

¹ IRPI, National Research Council, Via Amendola 122, 70126 Bari, IT

² DISTABIF, Second University of Naples, Via Vivaldi 43, 81100 Caserta, IT

³ School of Earth Sciences, Ohio State University, 125 South Oval Mall, 43210 Columbus (OH), USA

E-mail address: n.colombani@ba.irpi.cnr.it

Abstract. This study focuses on chemical and physical parameters of the Calore Catchment (Italy), to identify the sources of surface and groundwater mineralization. The study also evaluates water quality variations due to potential anthropogenic contamination. The proposed approach is a suitable screening tool to gain information on upland catchment characterized by complex hydrogeological and structural settings.

1. Introduction

Riverbed seepage and spring discharge have a major influence on the hydrology and hydrochemistry of streams [1], however the temporal and spatial variability of groundwater influence on watercourses in upland catchments is seldom studied. So far, most studies have focused mainly on hydrochemical and hydrogeological surveys on surface waters; adding springs and seeps sampling allows assessing water sources in geologically complex catchments and speculating on the mechanisms of groundwater–surface water interactions [2]. The most important mechanisms that naturally control the water chemistry in upland catchments are [3]: the composition and amount of the atmospheric precipitation, the evaporation and fractional crystallization, and the extent of water interactions with the bedrocks and the soils. The hydrogeochemical signature of ground and surface waters could be identified using the concentrations of the major ions and their ratios [4]. In this study, physical and chemical data of springs and streams are used to assess to which extent these parameters can trace the sources of surface waters, and whether their alteration due to anthropogenic contamination may hamper the identification of these sources.

2. Site description

The Calore River Catchment (CRC), located in the Southern Apennine, covers 3058 km² with a mainly mountainous morphology (Figure 1). The Calore River flows for 108 km, from its headwaters (1660 m a.s.l.) to the confluence with the Volturno River (55 m a.s.l.) and has an average annual discharge of 32 m³/s, with large seasonal variations.



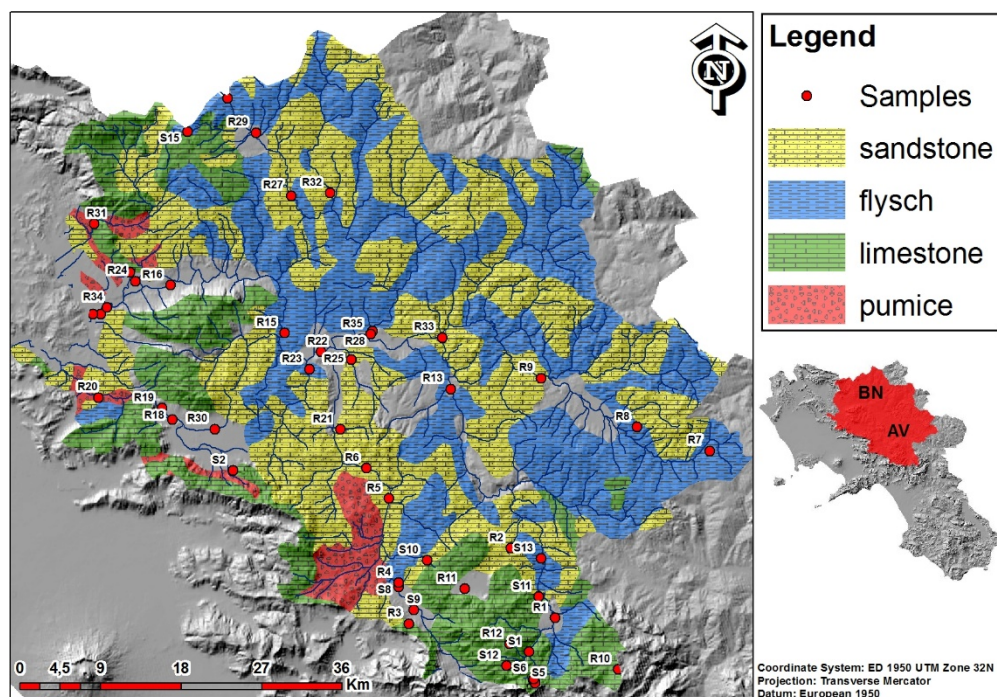


Figure 1. Geolithological sketch of the CRC and distribution of the sampling points. Labels from S1 to S16 represent springs' samples while from R1 to R36 represent rivers' samples.

The Southern Apennine chain is a fold-and-thrust orogeny comprising marine stratigraphic units and continental margin successions made of platform carbonates and pelagic deposits, covered by Neogene terrigenous sequences and late Miocene to Quaternary clastic deposits. In the late Miocene, the Southern Apennines were deformed by tectonic phases and rotational movements linked to a large back-arc extension with the formation of peri-Tyrrhenian grabens, accompanied by volcanic activity since the mid-late Pleistocene [5]. The resulting NW-SE, NE-SW and E-W extensional faults control the distribution of the alluvial basins [6]. In the CRC, the Mesozoic limestones of the Apennine platform outcrop in the Taburno, Camposauro and Matese Mountains. The Cenozoic flyschoid materials are widely exposed especially in the valleys of the northern Benevento Province and in the eastern Avellino Province.

The Upper Miocene–Pliocene sandstone frequently occurs at the top of all these successions. The Upper Pleistocene pyroclastic deposits outcrop in the southwestern CRC. Figure 1 shows the distribution and extension of the main geolithological units of the CRC: limestone (38.6%), sandstone (21%), flysch (17%) and volcanic deposits (5.4%). It is worth to note that the karst massifs give origin to most of the springs feeding the Calore River.

3. Materials and methods

The study relies on samples collected during summer low flow (SLF) and winter peak flow (WPF) from 2008 to 2014. 282 samples were collected (Figure 1): 166 for the SLF and 116 for the WPF. 56 samples pertain to springs and 226 to the Calore River. In-situ parameters (EC, pH, temperature and Eh) were measured at each sampling location. Major ions were determined following the international standard methods [7, 8].

4. Results and discussion

Samples from SLF and WPF have a median pH of 7.8 and 7.9, respectively. The median value of EC is 526 $\mu\text{S}/\text{cm}$ for SLF and 475 $\mu\text{S}/\text{cm}$ for WPF. The lowest EC (107 $\mu\text{S}/\text{cm}$) was recorded for the volcanic

samples, since they are little mineralized flowing on vitrified rocks; while the highest EC (903 $\mu\text{S}/\text{cm}$) recorded within the alluvial sediment of the Benevento plain, may be due to external contamination sources [9]. The most abundant cation is Ca^{2+} both in SLF and WPF (median 74.6 and 66.6 mg/L, respectively), followed by Na^+ (28.8 and 22.1 mg/L, respectively), K^+ (11.5 and 10.1 mg/L, respectively) and Mg^{2+} (9.5 and 9.3 mg/L, respectively). The most abundant anion is HCO_3^- both in SLF and WPF (median 250 and 252 mg/L, respectively), followed by SO_4^{2-} (38.5 and 27.4 mg/L, respectively), Cl^- (30.3 and 20.5 mg/L, respectively) and NO_3^- (11.2 and 7.6 mg/L, respectively). Water samples fall in the field of water-rock interaction both at SLF and WPF (Figure 2). The SLF cluster indicates the predominance of Na^+ , K^+ and Cl^- over Ca^{2+} and HCO_3^- both for surface waters and springs, especially for the flysch samples; while samples pertaining to the limestone reservoirs show a large Ca^{2+} and HCO_3^- content. Information about the weathering processes (carbonate vs silicate) are also given by Figure 3.

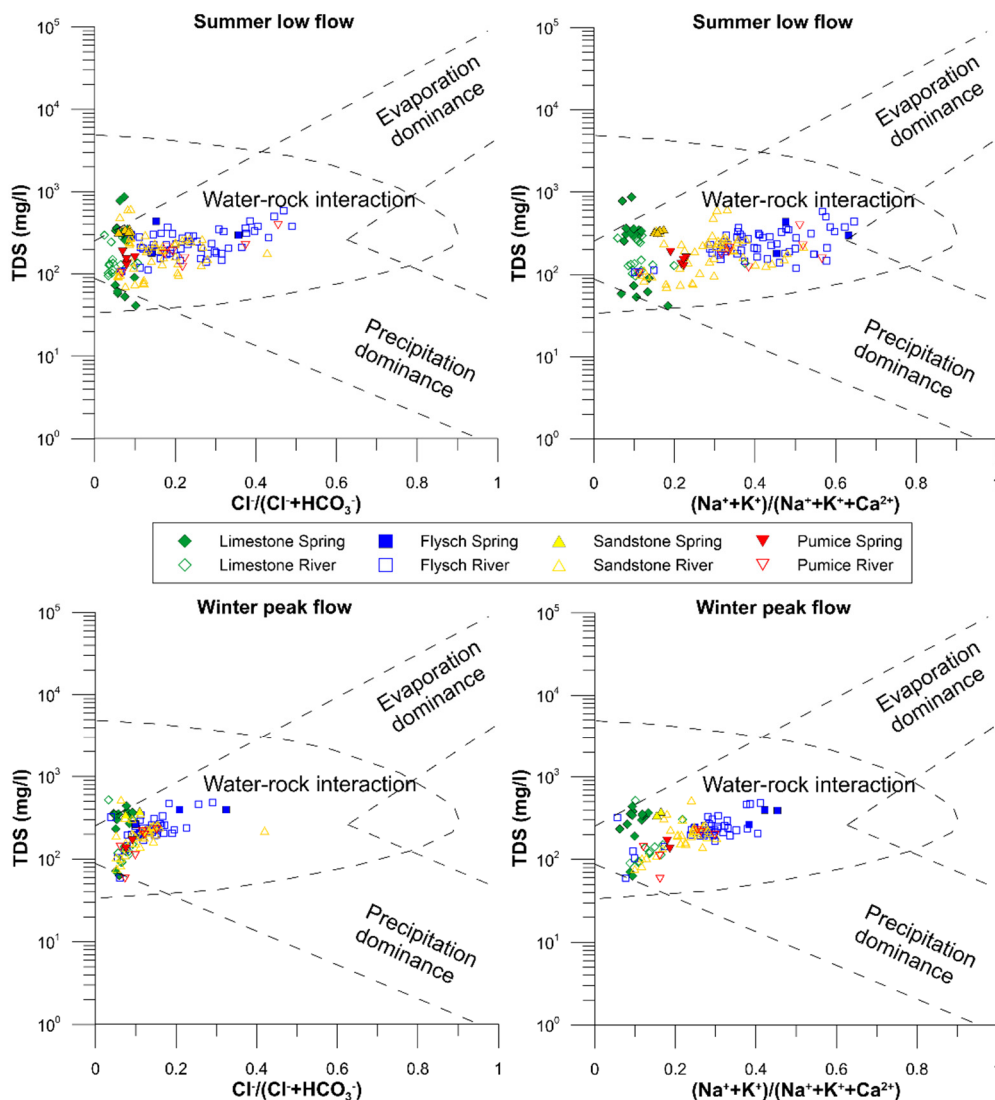


Figure 2. Gibbs diagrams at SLF and WPF. Filled symbols represent springs outcropping on different geological units and open symbols represent surface waters

Most samples lie below the 1:1 aequiline of ($\text{Mg}^{2+} + \text{Ca}^{2+}$) vs ($\text{SO}_4^{2-} + \text{HCO}_3^-$) suggesting a significant contribution of silicate weathering due to the induced HCO_3^- imbalance from hydrolysis reactions. However, some samples fall along or above the aequiline suggesting the contribution from the main

sedimentary formations weathering too. Together with water-rock interaction, anthropogenic inputs play an important role in the geochemistry of the CRC. Figure 4 shows the abundance of NO_3^- vs NH_4^+ both during SLF and WPF. NH_4^+ concentrations are low for all springs' samples and for the limestone and pumice river's samples, both at SLF and WPF. On the other hand, NH_4^+ concentrations are higher for the sandstone and flysch river's samples. In the SLF, flysch samples display NH_4^+ concentrations as high as 0.89 meq/l in the river samples collected in the Benevento plain.

Since springs' samples are collected at considerable altitudes, they are scarcely affected by anthropogenic contamination as well as the samples collected from the rivers flowing on limestone and pumice units that are outcropping in the most elevated part of the CRC. Conversely, samples collected from the rivers flowing on the flysch and alluvial deposits of the Benevento plain are affected by anthropic activities, namely urban sewage or agricultural practices. Since the rivers' samples collected during the WPF were in oxic conditions, with Eh always above 380 mV, the NH_4^+ concentration, like imputable to sewage effluent, were probably partially transformed into NO_3^- (Figure 4), due to nitrification reactions promoted by high oxygen availability. This behaviour was less evident in the SLF when Eh was around 160 mV.

High NO_3^- concentrations are also recorded in areas of the CRC other than the Benevento plain but always at low elevation, confirming a possible contribution of farming and agricultural activities. Thus, in the lower alluvial plain of the CRC, both water-rock interaction and anthropogenic pollution play an important role in governing water geochemistry. Conversely, at higher altitudes the principal mechanism of surface water mineralization is by far water-rock interaction. To distinguish among anthropic and geogenic contribution to water geochemistry, the molar ratios of selected major ions may be used. For the CRC, the most striking molar ratios are $\text{Mg}^{2+}/\text{Ca}^{2+}$ and $(\text{Mg}^{2+}+\text{Ca}^{2+})/(\text{Na}^++\text{K}^+)$ (Figure 5). In the CRC, despite the anthropogenic influence, it is possible to delineate each end-member and the evolution of waters originating from the parent rock and flowing through different lithology's.

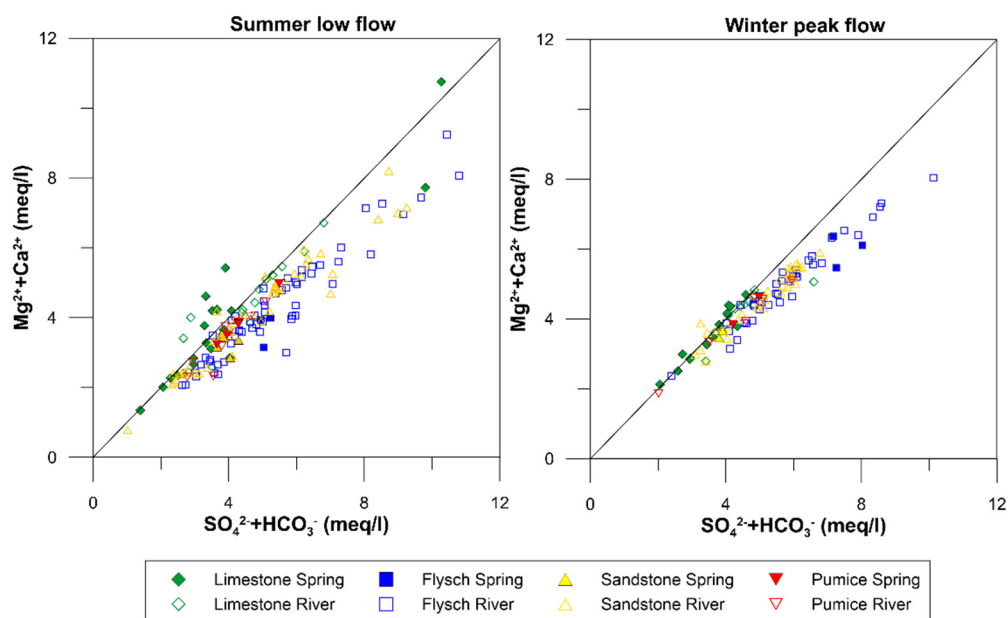


Figure 3. $(\text{Mg}^{2+}+\text{Ca}^{2+})$ vs $(\text{SO}_4^{2-}+\text{HCO}_3^-)$ at SLF and WPF. Filled symbols represent springs outcropping on different geological units and open symbols represent surface waters

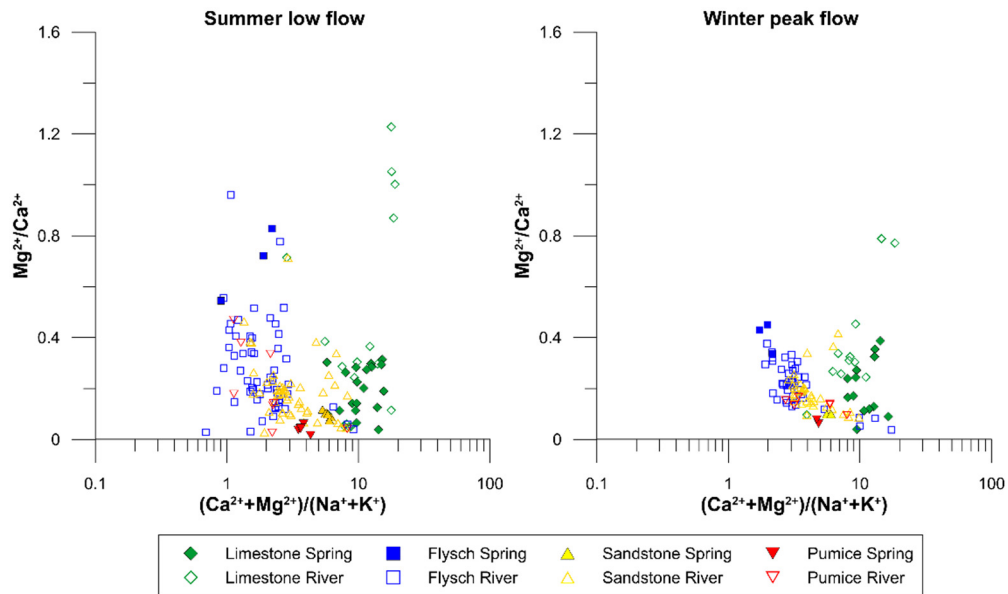


Figure 4. Mg^{2+}/Ca^{2+} vs $(Mg^{2+}+Ca^{2+})/(Na^{+}+K^{+})$ at SLF and WPF. Filled symbols represent springs outcropping on different geological units and open symbols represent surface waters

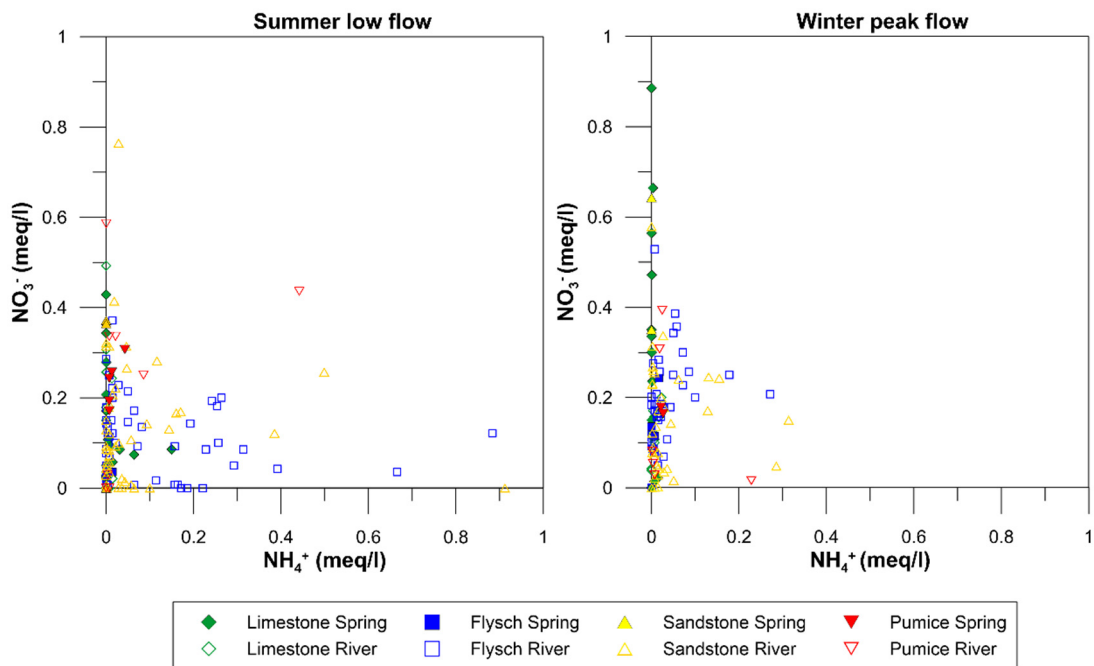


Figure 5. Binary plot of NO_3^- vs NH_4^+ at SLF and WPF. Filled symbols represent springs outcropping on different geological units and open symbols represent surface waters

This is especially true for the SLF, where the flysch end-member has the lowest $(Ca^{2+}+Mg^{2+})/(Na^{+}+K^{+})$ and the highest Mg^{2+}/Ca^{2+} , which progressively decreases in the rivers' samples at decreasing altitude, showing the same values of some sandstone rivers' samples, suggesting a mixing along the river course. Even the limestone end-member is clearly identified by the highest $(Ca^{2+}+Mg^{2+})/(Na^{+}+K^{+})$, with a variable Mg^{2+}/Ca^{2+} , with values of 1.23 at SLF, suggesting the presence of dolomitic rock.

5. Conclusions

Water chemistry in the CRC is variable and complex: contrasts in geology explain the main differences in stream chemistry, while deviations from the main hydrogeochemical signatures are due to anthropogenic activities. At SLF, the identification of the end-members is easy and the distinction of their evolution is also possible. Under WPF, subsurface flow alters the Calore River chemistry, but the differentiation of the parental waters is still possible. This study demonstrates that a simple geochemical assessment, based on easy-to-sample streams and springs and on cost-effective methods could be an adequate tool to gain a sound insight into river catchment geochemistry helping distinguishing among sources of surface and ground waters, especially in upland catchment characterized by complex geologic and structural settings.

References

- [1] Soulsby C, Tetzlaff D, van den Bedem N, Malcolm IA, Bacon PJ, Youngson AF. Inferring groundwater influences on surface water in montane catchments from hydrochemical surveys of springs and streamwaters. *J Hydrol* 2007; 333:199-213
- [2] Caulfield J, Chelliah M, Comte J-C, Cassidy R, Flynn R. Integrating petrography, mineralogy and hydrochemistry to constrain the influence and distribution of groundwater contributions to baseflow in poorly productive aquifers: Insights from Gortinlieve catchment, Co. Donegal, NW Ireland. *Sci Tot Environ* 2004; 500-501:224-234
- [3] Gibbs RJ. Mechanism controlling world water chemistry. *Sci* 1070; 170:1088-1090
- [4] Zhu GF, Li ZZ, Su YH, Ma JZ, Zhang YY. Hydrogeochemical and isotope evidence of groundwater and recharge in Minqin Basin, Northwest China. *J Hydrol* 2007; 333:239-251
- [5] De Vivo B, Rolandi G, Gans PB, Calvert A, Bohrson WA, Spera FJ, Belkin HE. New constraints on the pyroclastic eruptive history of the Campanian volcanic Plain (Italy). *Miner Petrol* 2001;73:47-65
- [6] Di Bucci D, Massa B, Tornaghi M, Zuppetta A. Structural setting of the Southern Apennine fold-and-thrust belt (Italy) at hypocentral depth: The Calore Valley case history. *J Geodyn* 2006; 42:175-193
- [7] ASTM D4327-11. Standard Test Method for Anions in Water by Suppressed Ion Chromatography. ASTM International, West Conshohocken, PA, 2011
- [8] ASTM D6919-09. Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography. ASTM International, West Conshohocken, PA, 2009
- [9] Cuoco E, Darrah TH, Buono G, Verrengia G, De Francesco S, Eymold WK, Tedesco D. Inorganic contaminants from diffuse pollution in shallow groundwater of the Campanian Plain (Southern Italy). Implications for geochemical survey. *Environ Monit Assess* 2015; 187(2):46