Chemical variations in time in a context of climate variability: examples in different hydrogeological settings

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AIM OF THE STUDY

Rainfall and temperature variability causes changes in groundwater recharge that can also influence groundwater quality by different processes.

The aim of this study is the analysis of the **hydrogeochemical variations over time due to meteorological variability** in two different study areas in Italy.

STUDY AREAS

Two study areas in Italy:

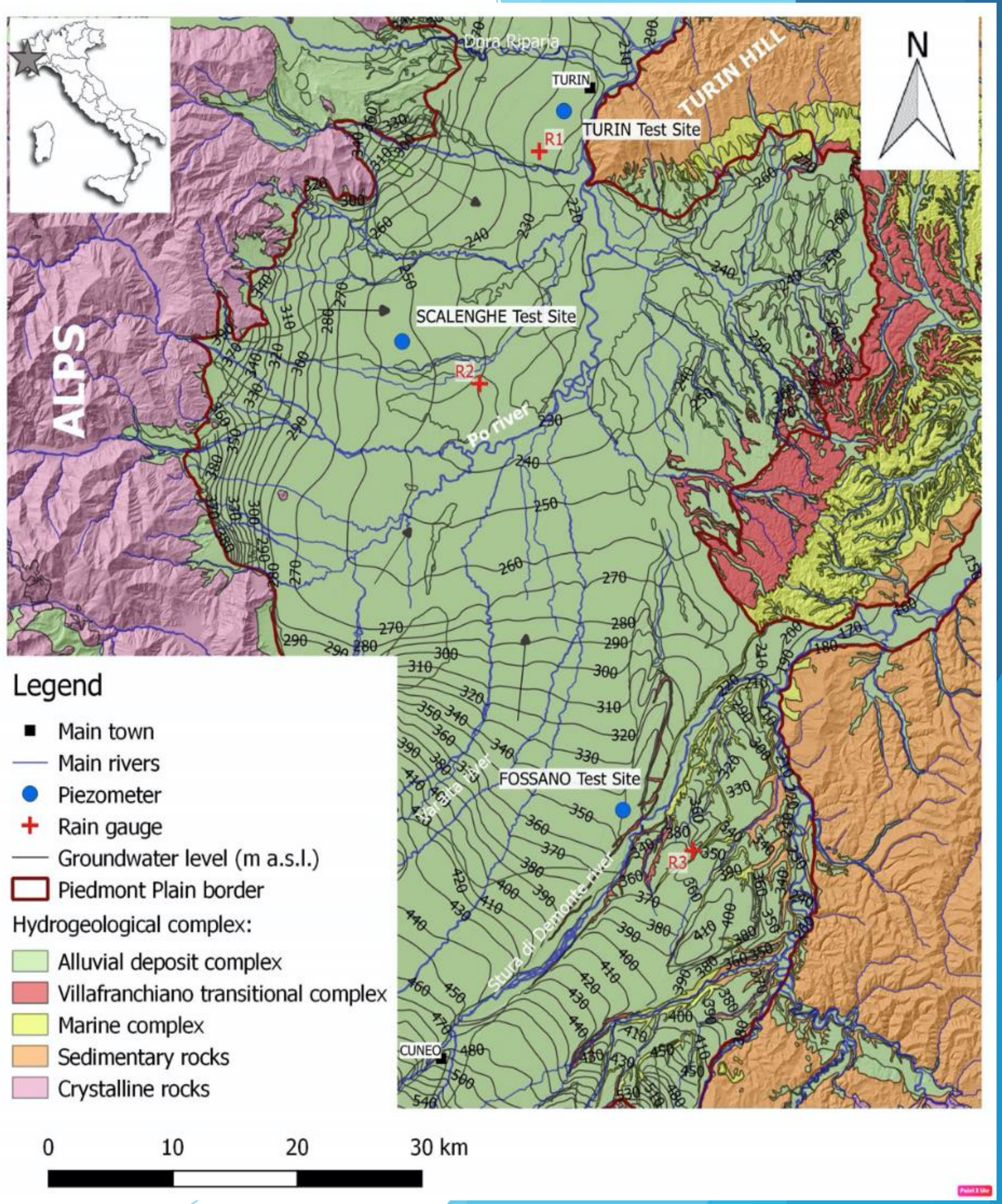
- an alluvial aquifer in the Piedmont Po plain
- an alluvial-pyroclastic aquifer in the Campanian plain

The examined plains show groundwater with natural quality not satisfying the European drinking water standards, or anthropogenic contamination.

STUDY AREA IN PIEDMONT PLAIN (NW ITALY)

Three test sites were selected in the Piedmont plain. Two sites were chosen because a diffuse nitrate contamination in shallow GW, due to intensive agricultural and livestock activities (**Fossano and Scalenghe test sites**).

The **Turin test site** is characterized by a point-source contamination by chromium VI by in the shallow aquifer, due to the presence of past industrial activities.

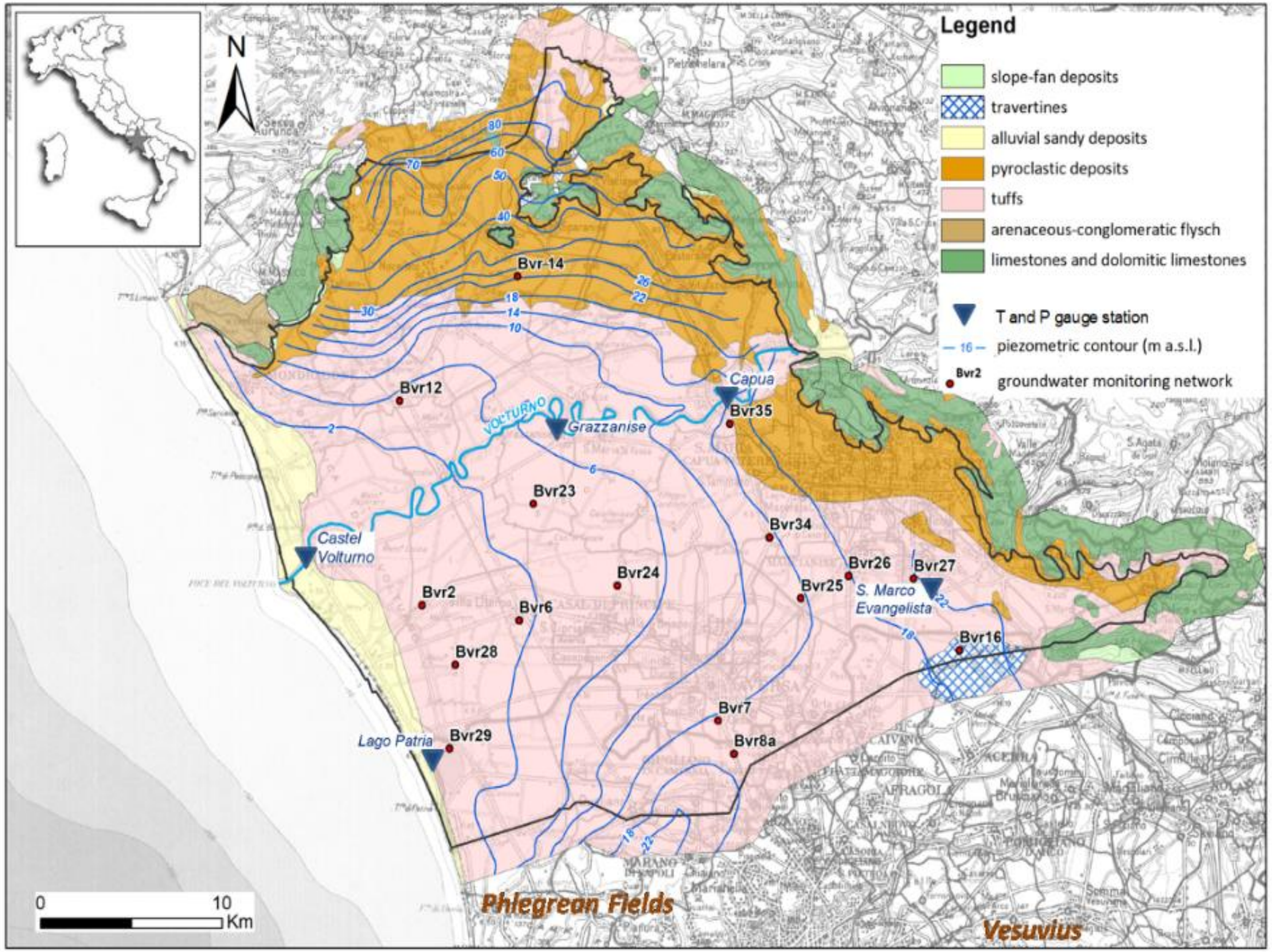


STUDY AREA IN "VOLTURNO-REGI LAGNI" PLAIN (S ITALY)

The study area is a large coastal plain, with porous aquifers containing waters high in As and F, due to the closeness of volcanic active areas (Phlegrean Fields and Vesuvius).

The presence of reducing environments brings high values of other two ions of natural origin: Fe and Mn.

Finally, a widespread nitrate contamination is present, prevalently due to manure spreading and/or sewage leaking.



METHODS

The trend analysis procedure was applied to the temporal dataset of available chemical data spatially significative for the considered areas. The Mann–Kendall method allowed the evaluation the statistical significance of the trends of the ions and of the climatological data.

The cross-correlation was used for demonstrating the concordance between ions, temperature, precipitation, and groundwater levels.

All these methods were used in order to clarify the relation between the annual/monthly recharge and the concentration of the chemical compounds in GW.

RESULTS

The Piedmont plain

Good correlation between groundwater levels and precipitation.

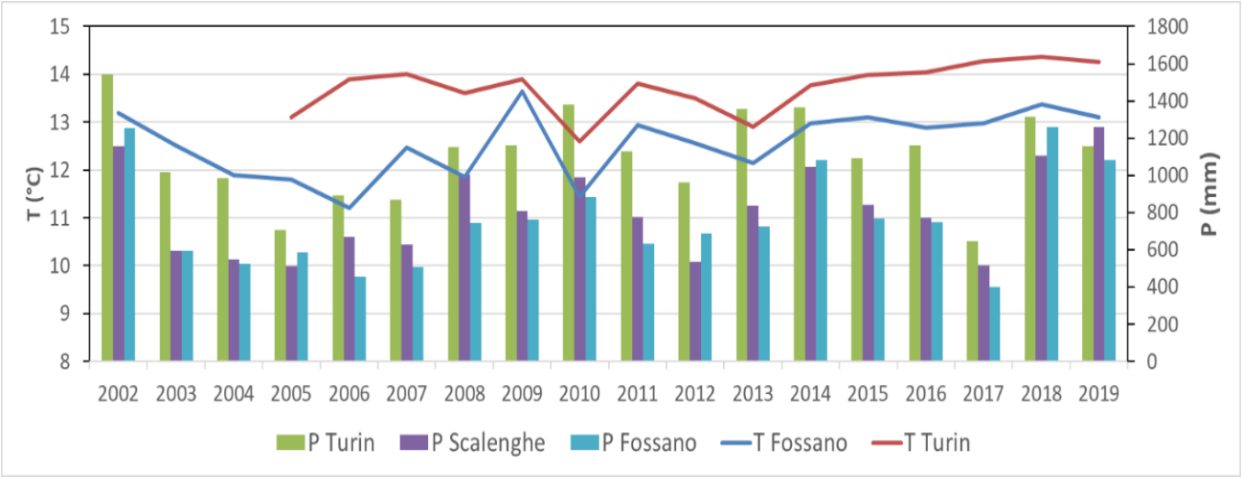


Figure. Piedmont plain. Yearly rainfall in mm and yearly average temperature in °C from 2002 to 2019.

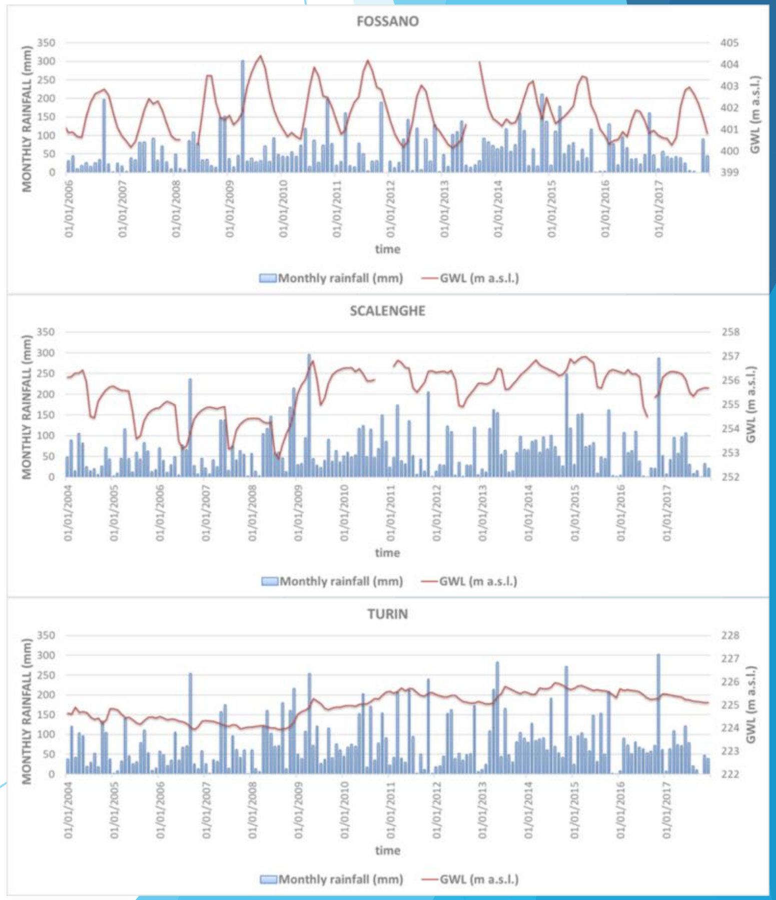


Figure. Piedmont plain. Comparison between the average monthly water table level and monthly rainfall in correspondence with the three test sites from 2004–2006 and 2017.

Chemical analyses

Piezometers	Number of Data Points	Nitrate (mg/L)					Chloride (mg/L)					Chromium VI (µg/L)				
		Min	Max	Medn	σ	γ	Min	Max	Medn	σ	γ	Min	Max	Medn	σ	γ
Fossano	29	20.0	64.2	30.8	12.2	1.3	5.9	20.7	10.6	4.2	0.6	-	-	-	-	--
Scalenghe	30	37.6	70.4	52.3	8.3	0.1	11.9	21.3	16.9	2.6	−0.1	-	-	-	-	-
Turin	54	-	-	-	-	-	-	-	-	-	-	15.5	129.0	49.5	30.2	0.4

Table. Piedmont plain. Summary statistics (from 2009–2019 for chromium VI and 2014–2018 for nitrate and chloride) for groundwater (GW) chemical parameters (nitrate and chloride in mg/L; chromium VI in µg/L); the location of the wells is in Figure 1. Medn = median; σ = standard deviation; γ = skewness; - = data not available.

Piezometer	Period	Chlorides (mg/L)	Nitrates (mg/L)	CrVI (µg/L)
Fossano	2004–2018	No trend	No trend	-
Scalenghe	2004–2019	Increasing	No trend	-
Torino	2009–2019	-	-	No trend

Table. Piedmont plain. Results of Mann–Kendall trend test analysis of GW chemical parameters. Level of confidence 95%. - = data not available.

The analysis in Piedmont plain highlighted a **low correlation between ion concentrations (chromium VI, chloride, and nitrate) and temperature.** The correlation between **ion contents and GW levels or rainfall**, on the contrary, showed **different degree of concordance**, depending on the analyzed test site.

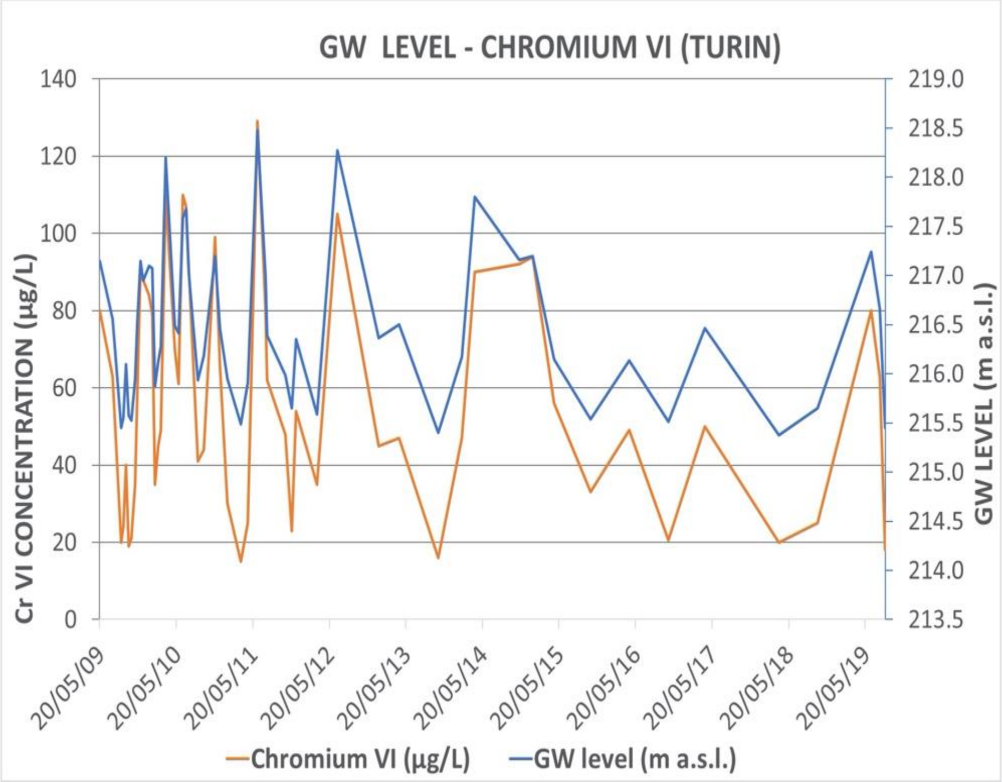


Figure. Piedmont plain. Time series of chromium VI concentration and GW level in Turin test site from 2009 to 2019 .

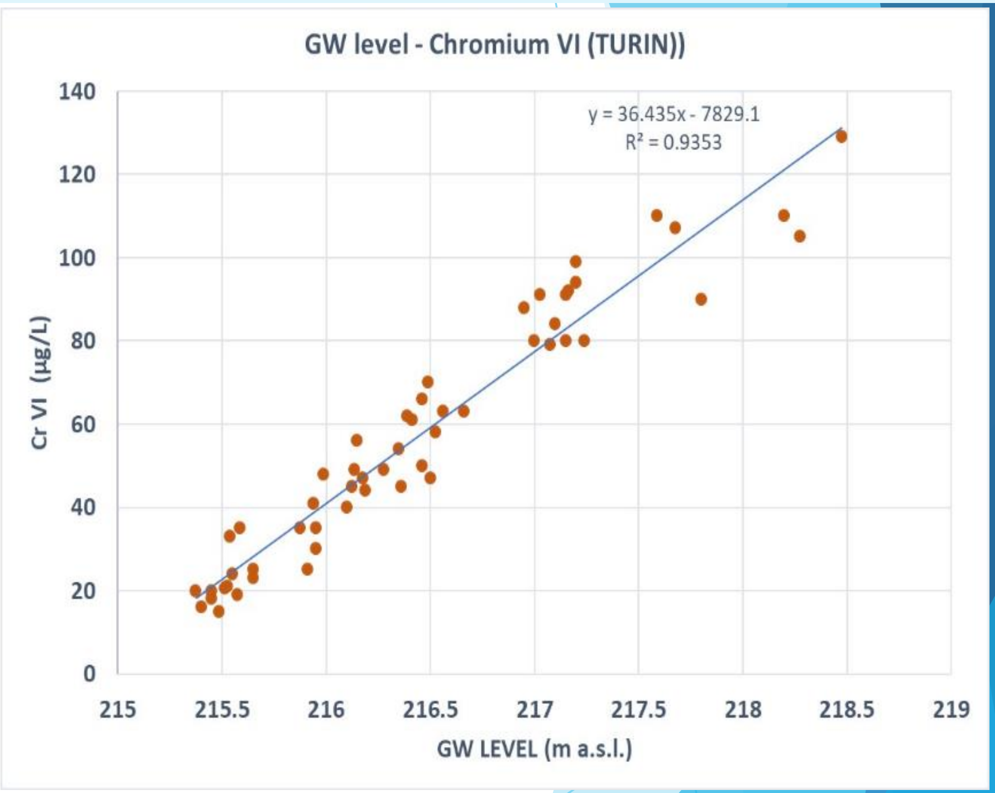


Figure. Piedmont plain. Chromium VI concentrations vs. GW level in Turin test site.

In the Turin test site, the correlation between **chromium VI in the shallow aquifer and GW levels** was clearly identified.

In Fossano test site, **a weak common trend between GW level and analyzed chemicals** was found.
In Scalenghe test site **chloride and nitrate concentrations show a similar trend** over time compared to the GW level

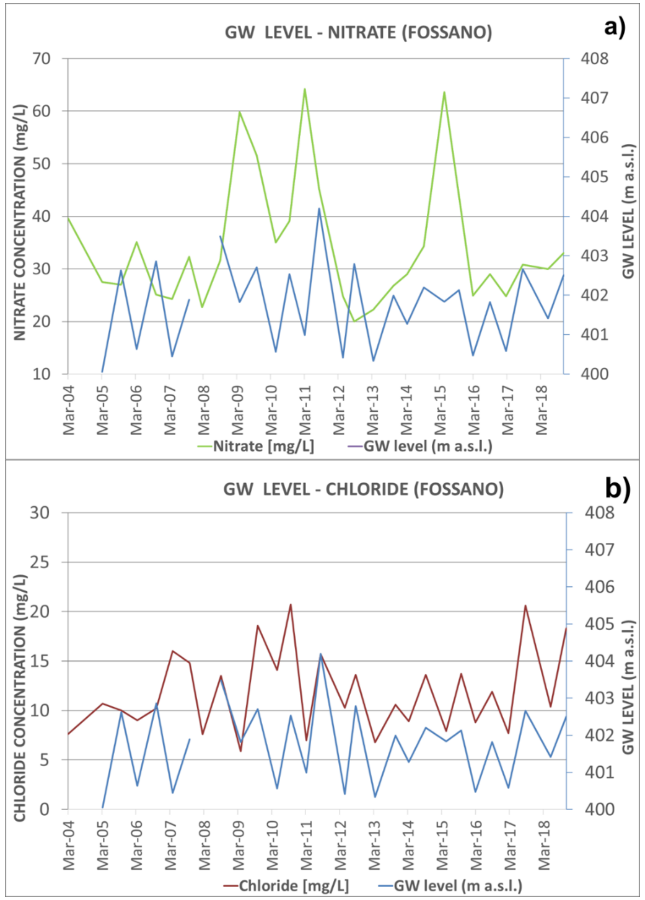


Figure. Piedmont plain. Time series of nitrate (a) and chloride (b) concentration and monthly GW level in Fossano test site from 2004 to 2018.

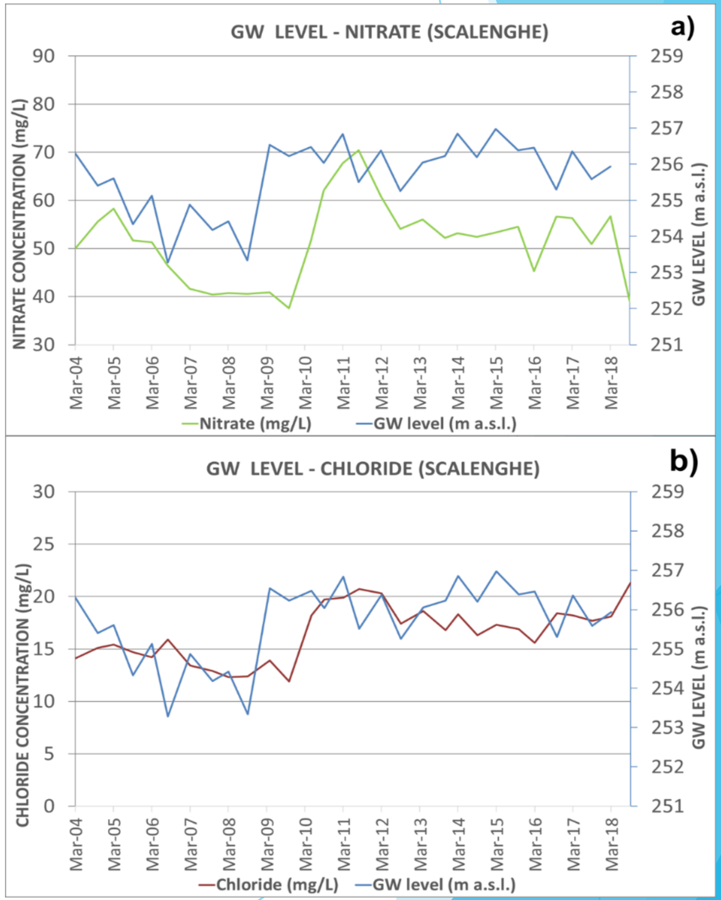


Figure. Piedmont plain. Time series of nitrate (a) and chloride (b) concentration and monthly GW level in Scalenghe test site from 2004 to 2018 .

The cross-correlation analysis showed an excellent correlation between GW levels and chromium VI considering a lag of 0 months, and a good correlation between yearly rainfall and chromium VI considering a temporal lag of 1 month.

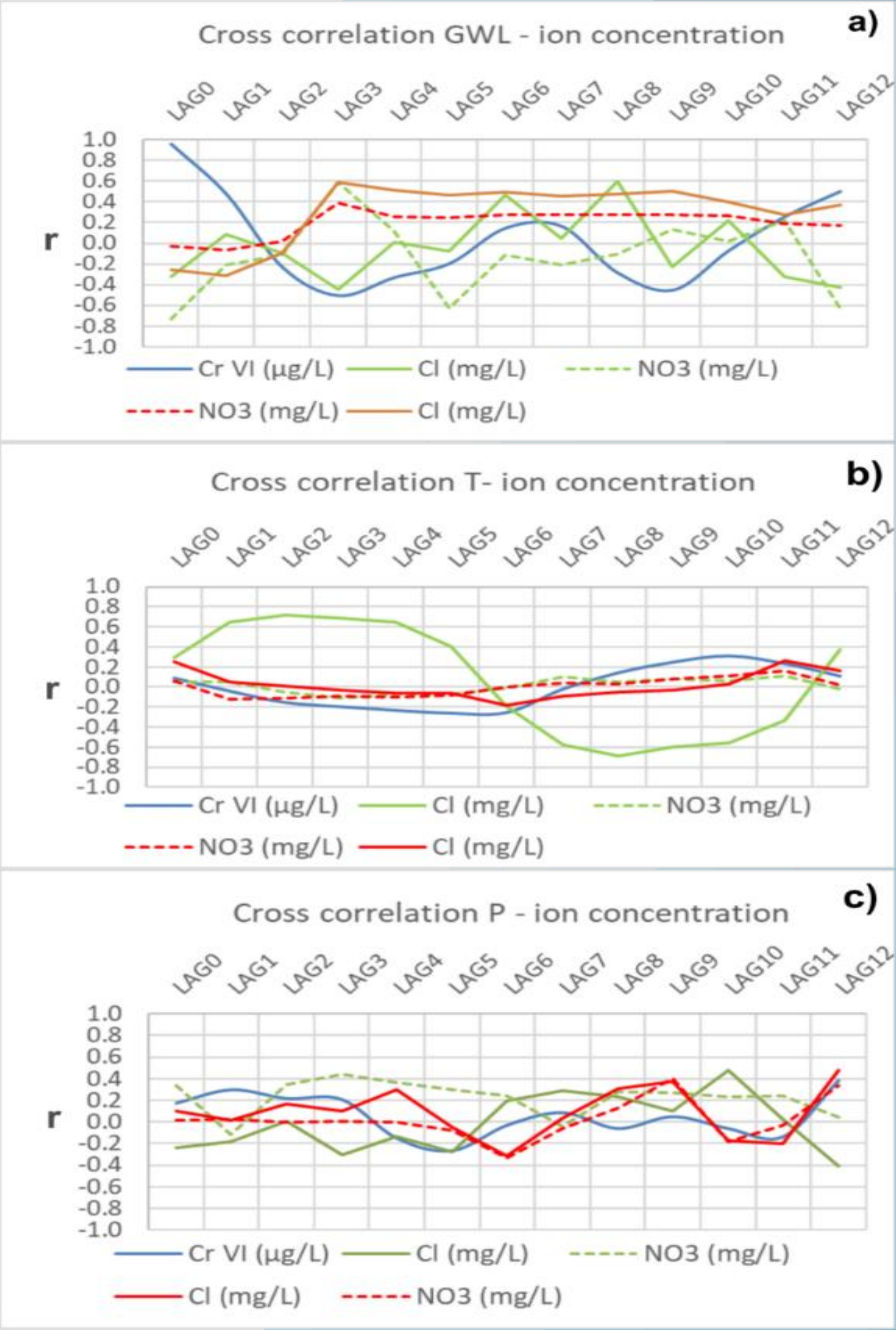
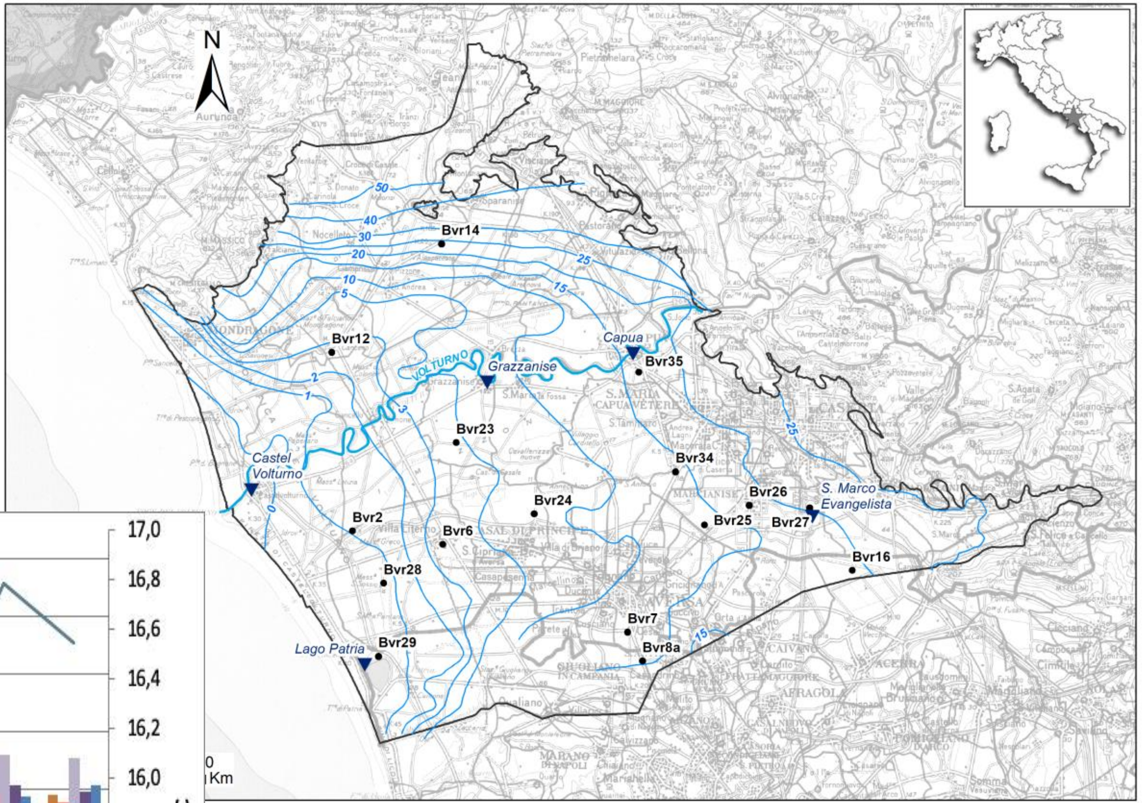
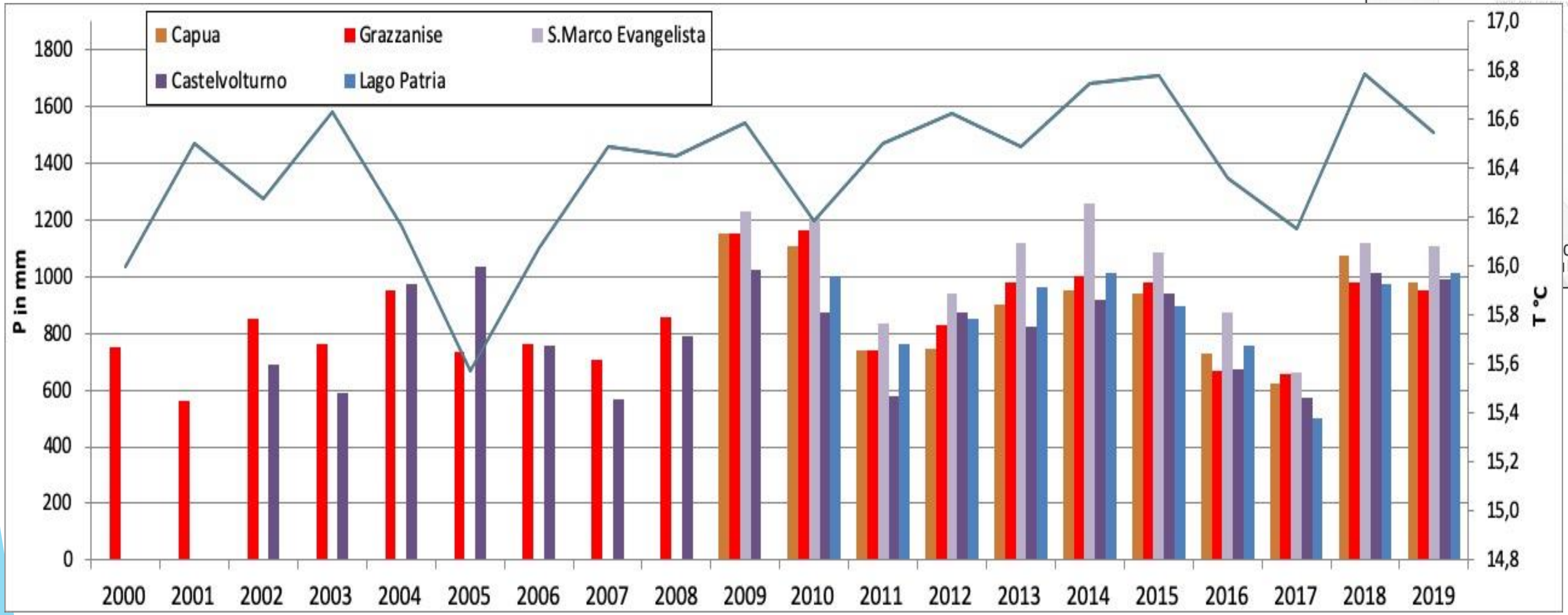


Figure. Piedmont plain. Cross-correlation between ion concentrations and GW levels (a), monthly temperature (b), and monthly rainfall (c). (blue = Turin test site; green = Fossano test site; red = Scalenghe test site).

The “Volturno-Regi Lagni” plain





Volturno-Regi Lagni” plain. The 2000–2019 yearly rainfall in mm in the gauge stations (blue triangles in the figure) and yearly average temperature in °C in Grazzanise station.

Chemical analyses of the“Volturno-Regi Lagni” plain

Sampling well	Number of data point	Fluoride (µg/L)					Arsenic (µg/L)					Iron (µg/L)					Manganese (µg/L)					Nitrate (mg/L)				
Bvr-		Min	Max	Medn	σ	γ	Min	Max	Medn	σ	γ	Min	Max	Medn	σ	γ	Min	Max	Medn	σ	γ	Min	Max	Medn	σ	γ
2	24-26	230	1740	1036	356.2	-0.1	0.8	51.0	25.6	14.1	-0.2	2	7914	982	2321	1.2	0.7	5760	3887	1854	-0.9	0.3	127.5	2.4	35.1	2.3
6	24-26	687	1829	1310	321.9	-0.3	2.0	8.3	5.0	1.7	0.1	2.5	280	10	59.1	3.3	0.1	14.7	2.5	4.2	1.7	38	115	55	21.7	1.2
7	22-25	957	2000	1500	211.2	-0.2	3.5	9.7	6.2	1.5	0.1	2.5	202	10	48.4	3.2	0.0	5.0	0.6	1.5	1.1	9.8	103	56.5	20.2	0.2
8a	15	100	1800	1500	403.7	-2.4	1.3	8.7	5.3	1.8	-0.4	10	186.6	10	56.8	1.8	0.8	65.7	7.7	16.5	2.7	11.5	102	51.6	28.3	-0.2
12	14-16	2.1	1901	1339	538.7	-1.4	0.3	4.5	1.0	1.0	2.8	5	348	5	116	1.7	0.5	52.0	1.8	13.5	3.6	11	30.2	12	4.7	3.5
14	14-15	1.0	1430	940	393.6	-0.5	5.0	31.0	18.3	7.7	-0.0	35	2720	922	840.3	0.7	120.9	742	241	145.8	3.0	0	79	2	24.8	2.4
16	18-22	716	1600	1200	261.2	-0.3	0.2	11.6	4.4	3.1	0.7	10	2072	162	529.7	2.1	1.3	889	137	230.5	1.8	11	130.3	47.8	36.1	0.9
23	19-26	0.8	4203	919	846.0	3.3	2.7	75.8	21.0	17.9	1.1	5	8971	464	3065	-0.3	0.7	1516	834	398.2	-0.5	0	250	0.7	52.2	4.0
24	16	426	1770	1215	265.3	-1.3	1.0	6.1	4.05	1.2	-0.9	2.5	179	22.2	56.8	1.8	0	11	2	2.9	1.5	40	73.6	45.5	8.0	2.4
25	25-27	128	3250	1322	577.0	1.2	0.5	25	8.8	1.4	1.6	5	3016	1425	933.1	-0.2	0.5	2645	416	482.5	3.9	0.09	154	2.8	35.3	3.0
26	22-25	1100	5710	1305	883.9	4.8	0.5	8.9	6.15	2.2	-1.4	5	197	10	64.9	1.9	0.11	58	1.8	12.2	4.3	0.8	112	72	29.5	-0.5
27	24-26	581	2000	1318	269.0	-0.5	1.0	11.0	8.0	2.6	-1.2	2.5	317	10	84.9	2.2	5.6	138.1	17.5	41.1	1.8	2	79.1	46	19.1	-0.4
28	23-25	260	1523	1206	362.4	-1.2	0.8	7.2	4.4	1.6	-0.6	5	710	10	148.2	3.8	0.5	2173	45	545	2.1	28.6	97	44	18.39	0.8
29	18-20	331	3592	2220	883.3	-0.4	1.6	34.0	7.55	7.6	1.9	2.5	155	10	46.67	2.16	2.5	17000	7970	4625	-0.1	0.8	106	2.01	24.47	4.0
34	20-26	776	1577	1271	228.4	-0.6	2.0	7.5	5.4	1.4	-0.7	0	404	5	93.13	3.34	0	91	0.95	22.97	3.1	39.3	121	86.9	19.73	-0.5
35	18-23	1.3	2027	1054	419.1	-0.2	0.5	62.5	8.8	12.7	4.0	0	9100	53.7	1993	4.20	0.08	325	146	106.3	0.3	12	89.3	31.5	13.61	2.97

Summary statistics in 2003–2019 for GW chemical parameters; In red values exceeding the standard; Medn = median; σ = standard deviation; γ = skewness.

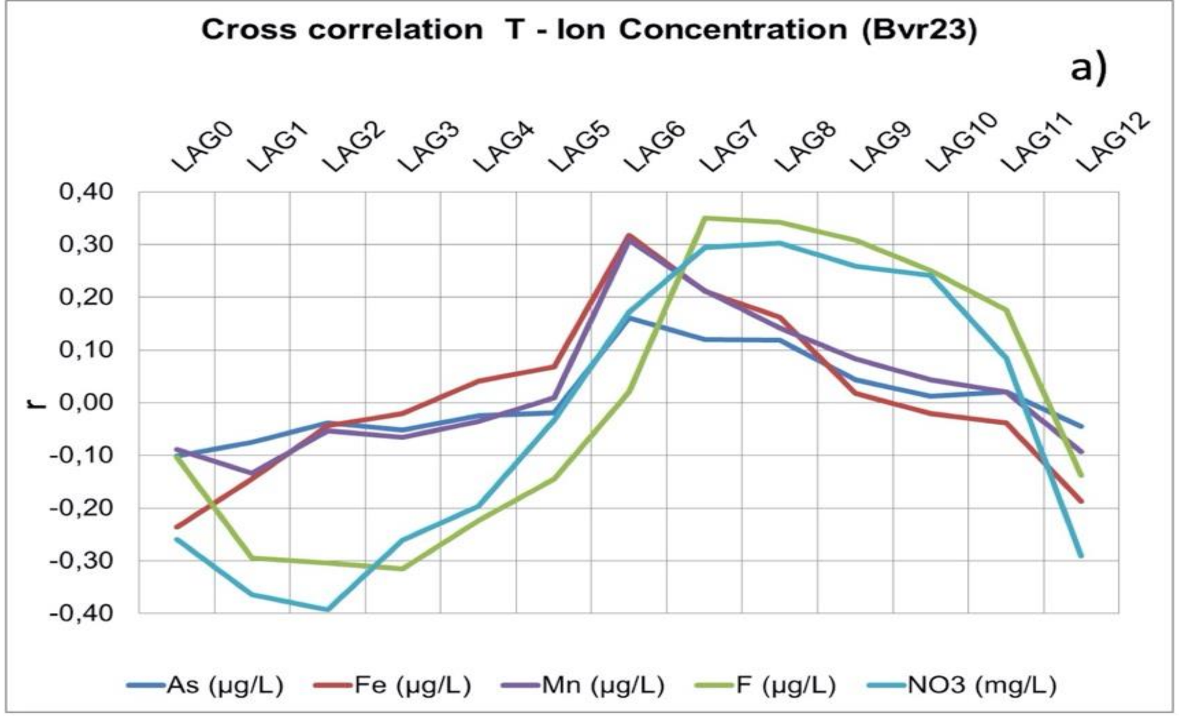
In the **Volturno-Regi Lagni plain** the variability of the precipitation and, especially, of the air temperature is very low. Climatological data demonstrates a **low concordance of temperature and precipitation with the examined ions of geogenic origin** (arsenic, fluoride, iron, and manganese) **and of anthropogenic origin** (nitrate). **F is very stable and NO_3 is randomly variable**, being affected by other factors of anthropogenic origin.

Well	Period	As (μg/L)	Fe (μg/L)	F (μg/L)	Mn (μg/L)	NO_3 (mg/L)
Bvr 2	2003–2015		increasing		increasing	decreasing
Bvr 6	2002–2015	increasing	decreasing		decreasing	
Bvr 7	2002–2019	increasing	decreasing			increasing
Bvr 12	2012–2019			increasing		
Bvr 14	2004–2019	decreasing	decreasing			
Bvr 16	2012–2019	decreasing	decreasing			
Bvr 23	2002–2019					increasing
Bvr 24	2003–2019				decreasing	
Bvr 26	2003–2013		decreasing		decreasing	
Bvr 27	2003–2019		decreasing		decreasing	
Bvr 28	2003–2019		decreasing		decreasing	increasing
Bvr 29	2003–2019					decreasing
Bvr 34	2002–2014		decreasing		decreasing	
Bvr 35	2002-2019				increasing	decreasing

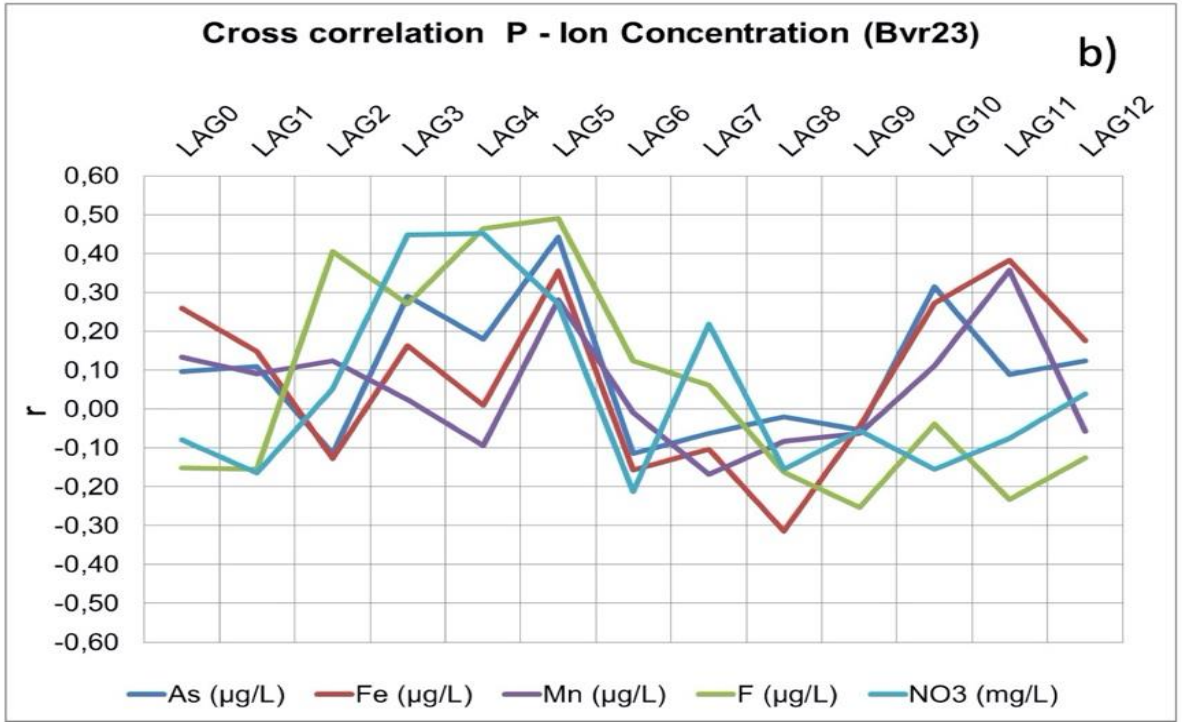
"Volturno-Regi Lagni" plain. Results of Mann–Kendall trend test analysis of GW chemical parameters.

The trend is absent for fluoride, while it is prevalently decreasing for iron and manganese. The trend of iron and manganese is generally concordant (70%) and discordant with the trends of other ions

“Volturno-Regi Lagni” plain

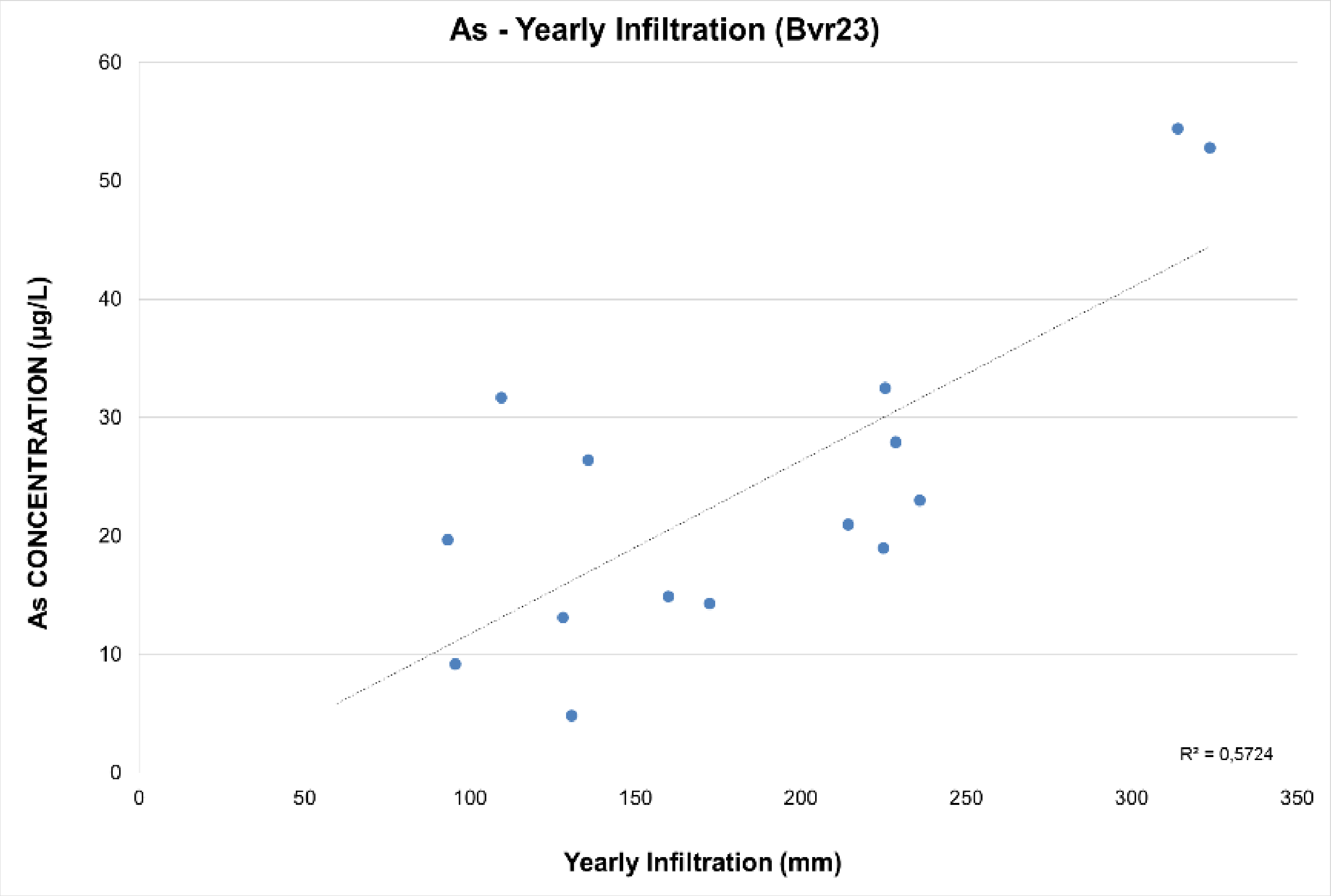


The cross-correlation between **temperature and ion concentrations** shows that the correlation is better for **iron and manganese** considering a temporal lag of 6 months.



The cross-correlation analysis shows a better correlation between **rainfall and ion concentrations** than temperature and ion concentrations. The best correlation is considering a temporal lag of 5 months for **arsenic and fluoride**. The better correlation is always the positive one.

“Volturno-Regi Lagni” plain



The positive correlation between arsenic concentrations and yearly infiltration is fairly good (r = 0.572).

Conclusions

- The study highlighted that **ions in GW are generally strictly related to climatological data**.
- The dependency degree is variable, based on the **typology of contaminant** and the **aquifer features**. In general, ions in **shallow unconfined aquifers** (e.g., in the Piedmont plain) are highly correlated to the fluctuation of climate variables. In contrast, **semiconfined or confined aquifers** (e.g., in the Volturno-Regi Lagni plain) react with a higher delay to these variations….**but they react**
- The excellent correlation between GW level and chromium VI in the unconfined aquifers confirms the possible activation of a severe impact, concerning the **degradation of GW quality during important infiltration events**. The forecast of an increasing rainfall intensity suggests a growing occurrence of this impact in future, with severe consequences for GW quality.
- **Multiple environmental change drivers** can obliterate the dependency between meteorological data and chemicals (especially nitrates).
- **Identifying climate variability effects on GW quality is extremely challenging, and long-term monitoring efforts are required to understand climate-related spatiotemporal trends in GW quality.**

The complete description of the study can be found in Lasagna et al. (2020)

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Meteorological Variability and Groundwater Quality: Examples in Different Hydrogeological Settings

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Abstract: Rainfall and temperature variability causes changes in groundwater recharge that can also influence groundwater quality by different processes. The aim of this study is the analysis of the hydrogeochemical variations over time due to meteorological variability in two different study areas in Italy: an alluvial aquifer in the Piedmont Po plain and an alluvial-pyroclastic aquifer in the