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PRESERVATION OF DRINKING WATER: EXAMPLES AND APPLICATIONS OF NEW TECHNOLOGIES FOR THE QUALITY AND QUANTITATIVE MONITORING OF THE RESOURCE.



September 5-8, 2022 Brasov, Romania



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"We forget that the water cycle and the life cycle are one."



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~ Jacques Yves Cousteau

Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption

What is drinking water?

water intended for human consumption means:

- all water, either in its original state or after treatment, intended for drinking, cooking, food preparation or other domestic purposes in both public and private premises, regardless of its origin and whether it is supplied from a distribution network, supplied from a tanker or put into bottles or containers, including spring waters;
- all water used in any food business for the manufacture, processing, preservation or marketing of products or substances intended for human consumption

pH - HYDROGEN ION CONCENTRATION

It is a quantity that indicates how aggressive, acid (pH below 7) or basic (pH above 7) a water is. Recommended value between 6.5 and 9.5.

EC - CONDUCTIVITY

HARDNESS

COLOUR, ODOUR, **TASTE, AND TURBIDITY**

Acceptable to consumers and no abnormal change



It is the ability of a solution to conduct electricity and is measured in Siemens micro units per centimeter (µScm-1) at a temperature of 20°C. Recommended value of 2.500 µScm-1.

It is closely related to the presence of calcium and magnesium ions in solution. The most commonly used unit of measurement is the French Degree (°F), which corresponds to 10 mg/l of calcium carbonate. Recommended value between 15 and 50°F.

What is drinking water?

Ammonium	ιο μ 9 /1	its occu process
Arsenic	10 μg/Ι	It is an its occu process
Chloride	250 mg/l	The chi form of (CaCl2) conduc
Sulphate	250 mg/l	They oc reason
Nitrate	50 mg/l	They an of natu nitroge activitio

Ammonium

Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption



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It is an element present in rocks, minerals and soil, and urrence in water is mainly due to natural ses of dissolution from minerals and rocks.

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loride ion is widely distributed in nature in the sodium (NaCI), potassium (KCI) and calcium salts. Chloride increases the electrical tivity of water.

ccur naturally in numerous minerals and for that can also be found in drinking water.

re compounds present in water either as a result ral phenomena (decomposition cycle of nous substances) or as a consequence of human es.

Why drinking water is important?

When a community gets access to safe water, some of the benefits are:



The improvement Water Supply Quality, Sanitation, and Hygiene



Increase the Amount of Healthy Food Available





Improve Poor Communities









Better School Attendance

> Gender Equality

Reduce Conflict

Global water crisis facts



Despite improvements in recent years, water scarcity affects more than 40% of people. This situation is projected to rise as temperatures do. By 2050, it is projected that at least one in four people will suffer recurring water shortages.

Protecting and restoring water-related ecosystems is essential!

884 million

people still lacked even basic drinking water

billion

people are affected by water stress 80

percent

of countries have developed or have set up an integrated water resources management





70 percent

of the world's wetlands have been destroyed in the last century

Goal targets to 2030



- achieve universal and equitable access to safe and affordable drinking water for all
- improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials
- implement integrated water resources management at all levels
- protect and restore water-related ecosystems, including mountains, forests, wetlands, rivers, aquifers and lakes





The Valseriana case study (Northern Italy)

- Water chemical-physical monitoring and resident time dating of groundwater
- New index-based approach to assess the vulnerability of karst springs
 - Estimation of the effects of Climate Change on springs discharge until 2100

An interesting example regarding the application of new techniques for preserving water resource from both a quantitative and qualitative point of view is the one carried out in the 2018-2019 biennium on the Nossana and Ponte del Costone springs.







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- The springs are located in Northern Italy, in the Central Pre-Alps within the Province of Bergamo, Lombardy Region
- Nossana catchment: 80 km2
- Ponte del Costone catchment: 10 km2
- High differences in altitude. Nossana: from 447 m a.s.l. to 2512 m a.s.l. Ponte del Costone: from 427 m a.s.l. to 1161 m a.s.l.





- The whole environment is dominated by calcareousdolomitic carbonate series
- The Nossana aquifer is set in the Calcare di Esino formation (Ladin -Carnic age)
- The water system of Ponte del **Costone** is formed by 13 springs distributed in about 1 km along the Serio river and it has the **Dolomia Principale Formation** (Noric age) as reservoir rock
- The average precipitation is close to 2000 mm/year with peaks of about 3000 mm/year (Ceriani et al., 2000)







Credits: Eco di Bergamo





From Vigna & Banzato, 2015

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• The springs are managed by the public company UniAcque S.p.A. and feed more than 315,000 people • Characterized by a dominant drainage system Nossana spring discharge 0.5 - 18 m3s-1

Nossana spring







- The Ponte del Costone cumulative discharge 0.15 - 0.45 m3s-1
- System with dispersive circulation
- Three main groups distribuited along Serio river: Galleria del Costone, Merlo, and Bosco (from South to North)

Ponte del Costone springs

Water chemical-physical monitoring



1 - SAMPLING CAMPAIGN (MAY 2018 - JULY 2019)

34 sampling points were set up. 23 points are related to natural spring waters, 4 points to surface waters, 2 points to wells , 3 points to waters from karst caves, and 2 points to the Val del Riso mine



3 - HYDROCHEMICAL CHARACTERIZATION

- Through the use of PHREEQC (Parkhurst & Appelo, 2013), pCO2 and Saturation Indices were calculated with respect to calcite (SIc) and dolomite (SId)
- Using Instant Clue software (Nolte et al., 2018), a Hierarchical Cluster analysis was performed considering major cations (Ca2+, Mg2+, K+, and Na+), major anions (HCO3-, CI-, NO3-, and SO42-), alkalinity (CaCO3), temperature, CO2 partial pressure, SIc and SId, and electrical conductivity [µS/cm]



4 - FLOW DYNAMICS FEATURES WITHIN THE WATER SYSTEMS

Through comparison of the results of chemical and isotopic analysis, a hypothesis was proposed about how the flow dynamics within the two water systems work



2 - HYDROCHEMICAL AND ISOTOPIC ANALYSIS

• Chemical analyses were performed at UniAcque S.p.A. laboratories via ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS) • Stable isotopes analyses (180, 2H, and 13C) were performed in the laboratory of the Université d'Avignon et des Pays de Vaucluse (France) using an isotope ratio mass spectrometer (IRMS).

• the 3H/3He analyses have been commissioned to the laboratories of the Institute of Environmental Physics and Oceanography at the University of Bremen (Germany) (Sültenfuß et al., 2009).

Hierarchical clustering analysis



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Mg ²⁺	Na⁺	K⁺	HCO ₃ -	CI-	NO ₃ -	SO4 ²⁻
9.0	0.6	0.3	150.2	1.0	3.9	3.6
19.9	4.9	1.3	240.6	9.4	5.1	48.9
9.6	1.6	0.8	207.7	2.8	5.4	7.8

Isotopic features and **Resident time estimation**

• Study area Meteoric Water Line:

 $\delta^{2}H = 7.71^{18}O + 9.40$

 Deuterium enrichment given by re-evaporation due to effect of secondary valleys (Riso Valley)





• 10 years for Nossana, 30 years for Ponte del Costone • For the main springs cyclical renewal of the resource is not clear

\cdot \cdot \cdot						
	Sai	mpling 2015	Sampling 2019			
Spring name	Age (years)	Recharge year	Age (years)	Recharge year		
Camplano	1.50	2014	0.96	2018		
Valle Rogno	8.10	2007	5.24	2014		
Nossana	7.90	2008	13.10	2006		
Costone 2	29.30	1986	32.48	1987		





• Tritium decays by emitting electrons (β -) into Helium-3, so it can be used for dating. (half-life of 12.32 y, total decay in 246 y)



the study area, and by the altitude.

- springs of about 30 years
- comparison.



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• The chemical composition of the waters reflects the carbonate context and is completely controlled by the spatial distribution of the different geological formations, by the different degree of susceptibility to karst dissolution of the rocks that characterize

• It was estimated the age of the reserve (or residence time) for Nossana of about 10 years, while for the Ponte del Costone

• For these main springs, the cyclical renewal of the resource is not evident; rather, the water reserve ages in the 2015 - 2018

Vulnerability assessment of karst aquifers

DEFINIZIONE DI VULNERABILITà

AT

- (Northern Italy);
- method;
- through isotopic data.

Geological data

The geological, geomorphological, and elevation data of the area were obtained from the Geoportale della Regione Lombardia (Regione Lombardia, 2020)

Karst network development

For the development of the karst network and the evaluation of the propensity to karstification of the area, the work of FSLo (2011) was

The meteorological data were obtained from the open-data section of the Environmental Regional Agency (ARPA Lombardia, 2020)



 define an integrative methodology that represent the conditions of intrinsic vulnerability of the middle Valseriana

 delineate an approach that does not require a lot of data and expensive investigations available in order to make it applicable in mountain contexts: COPA+K

GOALS

validate this new proposed approach

Meteorological data

Isotopic data

The stable isotope data (δ 180 and δ 2H) related to the waters of Nossana and Ponte del Costone springs and Serio river



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CONCENTRATION OF **FLOW**





PRECIPITATION



ASSOCIATION BETWEEN MAIN DISCONTINUITIES AND THEIR DISTANCE **TO SPRING**



KARST NETWORK DEVELOPMENT

COPA+K method $C \times O \times P \times A + K$

A factor

Association between discontinuities and their distance to spring





Distances to spring



Buffer 200 m around main discontinuities



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Factors

- a) Digital Elevation Model
- b) Concentration of flow
- c) Overlaying layers
- d) Precipitation
- e) Association between discontinuities and their distance to spring
- f) Karst network development



35.6% to 23.6%

CONSIDERING THE MOST VULNERABLE CLASSES (VH AND H), THE VALUES MOVE FROM 35.6% (COP) TO 23.6% (COPA+K) OVER THE WHOLE STUDY AREA.

The COPA+K method allows the identification of more restricted areas than COP.



THE PERCENTAGE DIFFERENCE INCREASED BY 12.3%, EMPHASIZING THE GREATER SUSCEPTIBILITY OF THE **NOSSANA SYSTEM**

COPA+K made possible to better differentiate the areas of greatest vulnerability in the two considered catchments



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Validation map process

• From the relationship given by the local isotopic line, it was possible to estimate the mean elevation of recharge areas of the Nossana and Ponte del Costone springs;

Nossana spring --> 1776 m a.s.l. Costone spring average --> 1561 m a.s.l.





- precipitation distribution maps;
- isotopic correlation.



 Mean annual precipitation data from 10 ARPA meteorological stations were interpolated to obtain a gridded (50x50 m) altitudedependent precipitation distribution --> TPS and IDW;

• The elevation values of the high vulnerability areas and related precipitation amounts were extrapolated from the DTM and the

• After performing a weighted average, the mean elevations of the high vulnerability areas were obtained for the Nossana and Ponte del Costone catchments to be compared with the results of

Applying the weighted average for the TPS and IDW interpolation methods, the values are within the range of elevation estimated by isotopic correlation (±106 m).





water A

 δ 180 value of a hypothetical recharge water A at the 1000 m elevation by exploiting local isotopic correlation



The demonstration of this mixing encourages the hypothesis of the validation of the map, given the excellent result obtained for the Nossana catchment.



Validation map process

- The COPA+K approach allowed determining more precise areas compared to COP (most vulnerable areas from 35.6% to 23.6%);
- COPA+K method underlined the different responses of the two considered water systems (percentage difference from 5.2% for COP to 17.5% for COPA+K approach);
- The COPA+K vulnerability map was validated by correlating δ 180 values and precipitation altitude through a local isotopic correlation from reference data;
- A commingling of the Ponte del Costone springs with the waters of the Serio river has been demonstrated;
- The COPA+K has been shown to be an excellent method for the entire karst environment of the Pre-Alpine belt due to its easy applicability --> NO lot of data and NO considerable computational effort.





Projections of Future Discharges under Climate Change

- Daily discharge of Nossana spring from 1998 to 2017 (UniAcque S.p.A);
- Daily precipitation and temperature from 1998 to 2017 (ARPA Lombardia);
- Temperature and precipitation data from 9 RCMs runs including 3 IPCC different scenarios based on greenhouse gasses emission*.

*Coordinated Regional Climate Downscaling Experiment (CORDEX) - www.euro-cordex.net



 Quantification of the expected changes in precipitation and temperature in the study area (reference period 1998-2017) Calibration and validation of a hydrological lumped parameter model based on observed data Recognition of possible limits in the future utilization

of the spring as a drinking supply (2021-2100)



From AR5 - IPPC, 2014.



For this research, scenarios related to RCP 2.6 (low), RCP 4.5 (medium), and RCP 8.5 (high degree of greenhouse gas emissions) were considered.

> The IPCC (Intergovernmental Panel on Climate Change) analyzed 4 potential future scenarios that depend on policy-makers' decisions to reduce greenhouse gas emissions.

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Considered scenarios



Method

RCP 2.6 --> 3 models RCP 4.5 --> 3 models RCP 8.5 --> 3 models

pl 2021-2040 **p2** 2041-2060 **p3** 2061-2080 p4 2081-2100

Warning threholds: Q 1.32 mc/s for winter Q 1.52 mc/s for summer

Reference period 1998-2017



	Precipitation			Tmin			Tmax		
Model	NSE	MAE (mm)	%MAE	NSE	MAE (°C)	%MAE	NSE	MAE (°C)	%MAE
Mod_1 RCP 2.6	0.79	12.35	10.71	0.96	1.10	17.69	0.97	1.18	7.09
Mod_1 RCP 4.5	0.66	14.97	12.97	0.97	1.00	17.19	0.97	1.08	6.48
Mod_1 RCP 8.5	0.76	12.71	11.20	0.97	1.00	15.96	0.98	0.90	5.43
Mod_2 RCP 2.6	0.31	19.81	17.16	0.97	0.90	14.20	0.97	0.99	5.95
Mod_2 RCP 4.5	0.52	17.44	15.12	0.97	1.00	16.13	0.96	1.27	7.65
Mod_2 RCP 8.5	0.31	22.90	19.85	0.97	0.90	15.42	0.96	1.28	7.66
Mod_3 RCP 2.6	0.23	20.53	17.79	0.97	1.00	15.96	0.96	1.19	7.14
Mod_3 RCP 4.5	0.37	17.17	14.88	0.98	0.80	12.79	0.97	0.99	5.95
Mod_3 RCP 8.5	0.52	17.78	15.41	0.98	0.80	12.69	0.97	0.98	5.88



Precipitation --> NSE > 0.0; MAE < 20% Temperature --> NSE > 0.8; MAE < 20%

Step 1 - Climate model evaluation

Step 2 - Statistical downscaling



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Performed using Change Farctors and Weather simulator (RainSim V3.0 -Burton et al., 2008)

- Not all models agree regarding mean annual precipitation trends in different periods
- General summer precipitation decrease (Jul-Sep) and autumn increase (Oct-Nov) for all periods
- Temperature increases up to ≈ 5 °C (RCP 8.5 – p4)

Step 3 - Hydrologic Model Calibration



Daily rainfall-runoff performed with GR4J model (Génie Rural Journalier with 4 parameters - Perrin et al., 2003), extended with the **CemaNeige snow** accounting routine (Valéry et al., 2014)

Random generation of 10,000 model parameter sets Model spin-up: 1998-1999 **Calibration: 2000-2008** Validation: 2009-2017 Criteria 1: KGE > 0.70; INSE > 0.5 Criteria 2: number of days and consecutive with discharge below warning thresholds

- 10 parameter sets
- thresholds
- threshold best indicator



Underestimation number of days below warning

Maximum number of days below the warning

Step 4 - Future discharges

- threshold 36 extra days
- threshold 64 extra days.





• Variation of recharge periods

Jul

Aug Sep Oct Nov

- Variation of annual cycle trend
- Decrease in mean discharge



• Longest period below the 1.32 m3/s warning • Longest period below the 1.52 m3/s warning



- Mean temperature will likely increase throughout the rest of the XXI century, from 0.7 °C in 2021–2040 (RCP4.5, Mod_2) to 5.8 °C in 2081–2100 (RCP8.5, Mod_1)
- No clear trend for precipitation, changes in mean annual rainfall varies between -18.5% (2041-2060, RCP4.5, Mod_2) and 15.1% (2041-2060, RCP8.5, Mod_2)
- Pronounced decrease of precipitation is expected in the summer period after 2060
- Mean discharges are generally projected to decrease in comparison to observed flow
- After 2060, the length of the periods with discharge lower than the warning thresholds is expected to increase. These periods could last up to 64 days (86%) longer than in 1998–2017

Additional water resources might be needed to satisfy the population water demand in the Nossana Spring area, especially after 2060





Take home message

Nossana and Ponte del Costone can be simplified with hierarchical models (Asante et al., 2018, White, 2002):

- Piston effect controlled by the amount of precipitation
- Diffuse infiltration in very different timing due to the different response to karst dissolution of the encasing rocks



demonstrated the importance of groundwater monitoring and water systems.

The applied studies in the Valsieriana has characterization in order to gain a deeper understanding of the internal dynamics of

The future perspectives are to: repeat the use of these techniques to detect the actual qualitative-quantitative variations in the water resource

 Start investigating new additional water resources to meet water demand after 2060, as demonstrated by hydrological modeling.

 expand the investigation to neighboring catchments to understand the real potential of all spring water resources in the region



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Thank you for attention!



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Citrini, A., Camera, C., & Beretta, G. P. (2020). Nossana spring (northern Italy) under climate change: Projections of future discharge rates and water availability. Water, 12(2), 387.

Citrini, A., Camera, C. A., Alborghetti, F., & Beretta, G. P. (2021). Karst groundwater vulnerability assessment: application of an integrative indexbased approach to main catchments of middle Valseriana springs (Northern Italy). Environmental Earth Sciences, 80(17), 1–20.



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References

Asante, J., Dotson, S., Hart, E., & Kreamer, D. K. (2018). Water circulation in karst systems: Comparing physicochemical and environmental isotopic data interpretation. Environmental Earth Sciences, 77(11), 421. https://doi.org/10.1007/s12665-018-7596-y

Burton, A.; Kilsby, C.; Fowler, H.; Cowpertwait, P.; O'Connell, P. RainSim: A spatial-temporal stochastic rainfall modelling system. Environ. Model. Softw. 2008, 23, 1356–1369. Castro, M. C., Goblet, P., Ledoux, E., Violette, S., & de Marsily, G. (1998). Noble gases as natural tracers of water circulation in the Paris Basin: 2. Calibration of a groundwater flow model using noble gas isotope data. Water Resources Research, 34(10), 2467–2483. https://doi.org/10.1029/98WR01957

Ceriani, M., Carelli, M., Agnelli, U., Bodio, N., Colombo, S., Lauzi, S., & Martelli, M. (2000). Carta delle precipitazioni medie, massime e minime annue del territorio alpino della Regione Lombardia (registrate nel periodo 1891 – 1990). Professione geologo, 10, 12-27

Desa, U. N. (2016). Transforming our world: The 2030 agenda for sustainable development

Dettori, M., Arghittu, A., Deiana, G., Castiglia, P., & Azara, A. (2022). The revised European Directive 2020/2184 on the quality of water intended for human consumption. A step forward in risk assessment, consumer safety and informative communication. Environmental Research, 209, 112773.

Doerfliger N, Jeannin P-Y, Zwahlen F (1999) Water vulnerability assessment in karst environments: a new method of defining protection areas using a multi-attribute approach and GIS tools (EPIK method). Environmental Geology 39(2):165–176. https://doi.org/10.1007/s002540050446

Longinelli, A., & Selmo, E. (2003). Isotopic composition of precipitation in Italy: A first overall map. Journal of Hydrology, 270(1–2), 75–88. https://doi.org/10.1016/S0022-1694(02)00281-0

Nolte, H., MacVicar, T. D., Tellkamp, F., & Krüger, M. (2018). Instant Clue: A Software Suite for Interactive Data Visualization and Analysis. Scientific Reports, 8(1), 12648. https://doi.org/10.1038/s41598-018-31154-6

Parkhurst, D., & Appelo, C. (2013). Description of input and examples for PHREEQC version 3: A computer program for speciation, batchreaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey Techniques and Methods, 6(A43).

Perrin, C.; Michel, C.; Andréassian, V. Improvement of a parsimonious model for streamflow simulation. J. Hydrol. 2003, 279, 275–289.

Sültenfuß, J., Roether, W., & Rhein, M. (2009). The Bremen mass spectrometric facility for the measurement of helium isotopes, neon, and tritium in water. Isotopes in Environmental and Health Studies, 45(2), 83–95. https://doi.org/10.1080/10256010902871929

Valéry, A.; Andréassian, V.; Perrin, C. 'As simple as possible but not simpler': What is useful in a temperature-based snow-accounting routine? Part 1–Comparison of six snow accounting routines on 380catchments. J. Hydrol. 2014, 517, 1166–1175

Vías JM, Andreo B, Perles MJ, Carrasco F, Vadillo I, Jiménez P (2006) Proposed method for groundwater vulnerability mapping in carbonate (karstic) aquifers: the COP method: Application in two pilot sites in Southern Spain. Hydrogeol J 14(6):912–925. https://doi.org/10.1007/s10040-006-0023-6

Vigna, B., & Banzato, C. (2015). The hydrogeology of high-mountain carbonate areas: An example of some Alpine systems in southern Piedmont (Italy). Environmental Earth Sciences, 74(1), 267–280. https://doi.org/10.1007/s12665-015-4308-8

White, W. B. (2002). Karst hydrology: Recent developments and open questions. Engineering Geology, 65(2–3), 85–105. https://doi.org/10.1016/S0013-7952(01)00116-8

https://www.undp.org/sustainable-development-goals https://onlinemasters.ohio.edu/blog/access-to-clean-water/ https://eur-lex.europa.eu/eli/dir/2020/2184/oj

