

Table S1: Characteristics of ground-based thermo-pluviometric and snow depth gauges.

Name	ID	Altitude (m a.s.l.)	Type	Managing authority	Observation period
ENDESA	RT-2695	700	Pluviometer	SIRMIP	from Dec-2006
Ponte Tavola	RT-2698	709	Pluviometer	SIRMIP	from Dec-2006
Ussita	RT-1651	749	Pluviometer	SIRMIP	from Nov-2003
	RT-1653		Thermometer		
Gualdo	RT-3150	1000	Pluviometer	SIRMIP	from Jul-2017
	RT-3152		Thermometer		
Casali	-	1090	Pluviometer	CNR-IRPI	from Jun-2022
			Thermometer		
Pizzo Tre Vescovi	RT-1787	1825	Thermometer	SIRMIP	from Aug-2002
	RT-1788		Snow depth		
Monte Bove Sud	RT-1851	1853	Pluviometer	SIRMIP	from Aug-2002
	RT-1853		Thermometer		from Aug-2002
	RT-1854		Snow depth		from Nov-2007
Casali	PR1	1071	Rain collector	CNR-IRPI	from Nov-2023
Ussita	PR2	770			
Val di Panico	PR3	1237			
Sorbo	PR4	983			

Table S2: Limit of Detection (LOD) and Limit of Quantitation (LOQ) values for cations.

Analyte	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
LOD (mg/L)	0.4	0.3	0.4	0.9
LOQ (mg/L)	1.3	1.2	1.3	2.9

Table S3: Limit of Detection (LOD) and Limit of Quantitation (LOQ) values for anions.

Analyte	Cl ⁻	SO ₄ ²⁻
LOD (mg/L)	0.8	1.0
LOQ (mg/L)	2.7	3.3

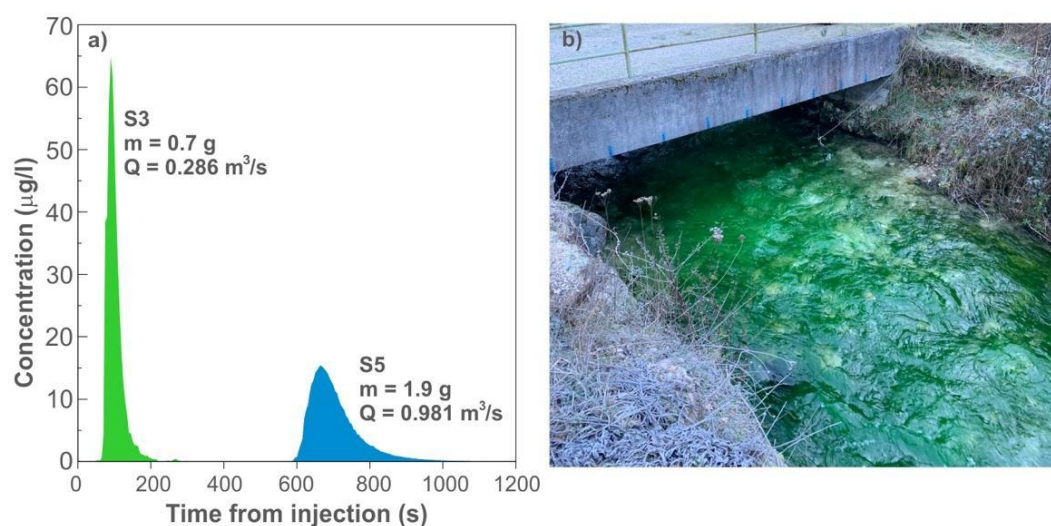


Figure S1: BTCs for S3 and S5 monitoring points on January 29, 2024, with details of: a) injected mass, and computed discharge; b) Na-Fluorescein passage in the monitoring point S5 during the test (b).

Table S4: Physical parameters (T: temperature, pH, EC: electrical conductivity) and major soluble ions of stream waters sampled in the Ussita catchment

ID	Date	T [°C]	pH	EC [μS/cm]	Ca ²⁺ [mg/L]	Mg ²⁺ [mg/L]	Na ⁺ [mg/L]	K ⁺ [mg/L]	HCO ₃ ⁻ [mg/L]	SO ₄ ²⁻ [mg/L]	Cl ⁻ [mg/L]
S1	23/11/2023	6.60	8.33	216.00	42.71	0.20	1.08	0.34	129.32	1.55	1.96
S1	19/01/2024		8.48		43.68	0.20	1.21	0.34	144.69	2.49	2.26
S1	19/03/2024	8.10	8.04		43.85	0.20	1.11	0.34	135.66	2.29	2.18
S1	09/05/2024	6.30	8.68	190.00	42.69	0.20	1.06	0.34	137.05	2.24	2.11
S1	10/07/2024	5.60	7.99	158.80	43.21	0.20	1.05	0.34	142.01	1.84	1.70
S2	23/11/2023	8.10	8.08	237.00	47.33	0.96	1.93	0.03	146.64	3.37	0.11
S2	19/03/2024	9.80	8.53	188.50	46.79	0.88	1.64	0.01	142.98	2.86	0.08
S3	19/01/2024	7.90	8.57	226.00	45.03	0.86	2.12	0.34	163.97	2.55	2.73
S3	19/03/2024	9.00	8.70	268.00	46.98	0.88	1.92	0.34	152.26	2.94	3.05
S3	09/05/2024	8.30	8.83	201.00	45.18	0.80	1.82	0.34	157.69	2.74	2.62
S3	10/07/2024	13.40	8.78	199.00	45.08	0.93	1.95	0.34	159.58	2.82	2.83
I1	09/05/2024	9.30	8.18	264.00	58.29	2.54	2.42	0.34	165.11	6.92	7.44
I2	01/02/2024	8.20	8.44	299.00	47.10	8.39	2.10	0.70	166.90	17.88	3.77
I2	19/03/2024	11.30	7.81	405.00	47.67	8.97	7.97	0.77	176.17	18.88	12.55
I2	09/05/2024	8.80	8.27	274.00	47.25	8.46	2.12	0.34	189.10	16.94	3.76
I2	10/07/2024	10.80	7.97	353.00	46.78	8.61	2.15	2.94	176.90	17.57	5.77
S5	23/11/2023	9.70	7.79	302.00	52.73	5.95	2.04	0.34	161.77	20.20	4.24
S5	19/01/2024	9.80	8.33	302.00	52.15	6.10	2.36	0.34	178.85	20.78	4.68
S5	19/03/2024	9.60	8.20	316.00	50.79	5.16	2.03	0.34	164.94	15.91	4.13
S5	09/05/2024	10.00	8.44	271.00	49.40	5.53	1.90	1.18	170.80	19.10	4.47
S5	10/07/2024	13.20	8.40	277.00	52.59	6.34	2.25	1.39	183.98	21.42	5.09

Table S5: Isotopic composition of δD and δ¹⁸O in stream and precipitation waters sampled within the Ussita catchment. For stream waters are also shown lc-excess values (na: not applicable).

ID	Date	Type	δD	δ ¹⁸ O	lc-excess
PR1	29/06/2023	Pluvio	-47.67	-8.21	na
PR1	21/07/2023	Pluvio	-30.48	-6.04	na
PR1	11/08/2023	Pluvio	-23.12	-5.73	na
PR1	22/09/2023	Pluvio	-30.7	-6.2	na
PR1	20/10/2023	Pluvio	-41.57	-7.44	na
PR1	02/11/2023	Pluvio	-35.68	-6.93	na

PR1	17/11/2023	Pluvio	-42.35	-8.12	na
PR1	07/12/2023	Pluvio	-79.4	-11.49	na
PR1	19/01/2024	Pluvio	-65.37	-10.06	na
PR1	19/03/2024	Pluvio	-55.85	-8.79	na
PR2	29/06/2023	Pluvio	-43.73	-7.6	na
PR2	21/07/2023	Pluvio	-28.89	-5.99	na
PR2	11/08/2023	Pluvio	-20.25	-5.08	na
PR2	22/09/2023	Pluvio	-26.07	-5.32	na
PR2	20/10/2023	Pluvio	-32.59	-6.42	na
PR2	02/11/2023	Pluvio	-31.51	-6.16	na
PR2	17/11/2023	Pluvio	-41.09	-7.49	na
PR2	07/12/2023	Pluvio	-63.37	-9.83	na
PR2	19/01/2024	Pluvio	-54.59	-8.84	na
PR2	19/03/2024	Pluvio	-47.17	-7.42	na
PR3	29/06/2023	Pluvio	-34.64	-6.04	na
PR3	21/07/2023	Pluvio	-23.23	-3.83	na
PR3	22/09/2023	Pluvio	-36.57	-7.43	na
PR3	20/10/2023	Pluvio	-49.51	-8.96	na
PR3	02/11/2023	Pluvio	-34.69	-6.41	na
PR3	17/11/2023	Pluvio	-49.03	-8.95	na
PR3	07/12/2023	Pluvio	-81.56	-12.14	na
PR3	19/01/2024	Pluvio	-75.1	-11.4	na
PR3	19/03/2024	Pluvio	-63.56	-10.17	na
PR4	29/06/2023	Pluvio	-47.06	-7.81	na
PR4	21/07/2023	Pluvio	-28.95	-6	na
PR4	11/08/2023	Pluvio	-18.81	-4.91	na
PR4	20/10/2023	Pluvio	-25.41	-5.53	na
PR4	02/11/2023	Pluvio	-15.34	-2.76	na
PR4	17/11/2023	Pluvio	-41.89	-7.77	na
PR4	07/12/2023	Pluvio	-65.39	-10.52	na
PR4	19/01/2024	Pluvio	-60.44	-9.67	na
PR4	19/03/2024	Pluvio	-56.51	-8.83	na
S2	29/06/2023	Stream	-70.06	-11.17	3.30

S2	21/07/2023	Stream	-67.57	-10.7	2.03
S2	11/08/2023	Stream	-69.1	-11.27	5.06
S2	22/09/2023	Stream	-68.28	-11.29	6.04
S2	20/10/2023	Stream	-65.77	-10.7	3.83
S2	02/11/2023	Stream	-69.58	-11.04	2.74
S2	17/11/2023	Stream	-68.25	-10.96	3.43
S2	07/12/2023	Stream	-68.52	-10.79	1.80
S2	19/01/2024	Stream	-67.85	-10.89	3.27
S2	19/03/2024	Stream	-67.66	-10.79	2.66
S3	19/01/2024	Stream	-68.26	-10.65	0.94
S3	19/03/2024	Stream	-67.35	-10.74	2.57
I2	01/02/2024	Stream	-70.24	-10.98	1.60
I2	19/03/2024	Stream	-68.07	-10.56	0.41
S5	29/06/2023	Stream	-70.35	-11.16	2.93
S5	21/07/2023	Stream	-68.09	-10.65	1.11
S5	11/08/2023	Stream	-68.58	-11.04	3.74
S5	22/09/2023	Stream	-67.65	-11.07	4.91
S5	20/10/2023	Stream	-66.08	-10.63	2.96
S5	02/11/2023	Stream	-69.4	-10.85	1.40
S5	17/11/2023	Stream	-67.01	-10.51	1.07
S5	07/12/2023	Stream	-69.34	-10.97	2.42
S5	19/01/2024	Stream	-67.33	-10.8	3.07

Table S6: Average (avg) and coefficient of variation (cv) for the physical parameters (T: temperature, pH, EC: electrical conductivity) and for major soluble ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , and Cl^-) of Ussita stream waters.

ID	S1	S2	S3	I1	I2	S5
Samples	5	2	4	1	4	5
T_avg [°C]	6.65	8.95	9.65	9.30	9.78	10.46
T_cv [%]	16	13	26	na	15	15
pH_avg	8.30	8.31	8.72	8.18	8.12	8.23
pH_cv [%]	4	4	1	na	4	3
EC_avg [$\mu\text{S}/\text{cm}$]	188.27	212.75	223.50	264.00	332.75	293.60
EC_cv [%]	15	16	14	na	18	6
Ca_avg [mg/L]	43.23	47.06	45.57	58.29	47.20	51.53

Ca_cv [%]	1	1	2	na	1	3
Mg_avg [mg/L]	0.20	0.92	0.87	2.54	8.61	5.82
Mg_cv [%]	0	6	6	na	3	8
Na_avg [mg/L]	1.10	1.79	1.95	2.42	3.59	2.12
Na_cv [%]	6	11	6	na	82	9
K_avg [mg/L]	0.34	0.02	0.34	0.34	1.19	0.72
K_cv [%]	0	71	0	na	100	73
HCO ₃ _avg [mg/L]	137.75	144.81	158.38	165.11	177.27	172.07
HCO ₃ _cv [%]	4	2	3	na	5	5
SO ₄ _avg [mg/L]	2.08	3.12	2.76	6.92	17.82	17.82
SO ₄ _cv [%]	18	12	6	na	5	11
Cl_avg [mg/L]	2.04	0.10	2.81	7.44	6.46	4.52
Cl_cv [%]	11	22	7	na	64	8

Table S7: Average (avg) and coefficient of variation (cv) for δD , $\delta^{18}O$, and lc-excess (lc) of Ussita stream and precipitation waters. na: not applicable

ID	PR1	PR2	PR3	PR4	S2	S3	I2	S5
Samples	10	10	9	9	10	2	2	9
δD _avg [mg/L]	-45.22	-38.93	-49.77	-39.98	-68.26	-67.81	-69.16	-68.20
δD _cv [%]	38	35	40	47	2	1	2	2
$\delta^{18}O$ _avg [mg/L]	-7.90	-7.02	-8.37	-7.09	-10.96	-10.70	-10.77	-10.85
$\delta^{18}O$ _cv [%]	23	22	32	35	2	1	3	2
lc_avg [mg/L]	na	na	na	na	3.42	1.76	1.01	2.62
lc_cv [%]	na	na	na	na	38	66	84	49