

Supplemental Material

Tracing groundwater circulation in a valuable mineral water basin with geochemical and isotopic tools: the case of *FERRARELLE*, Riardo basin, Southern Italy

Elisa Sacchi¹, Emilio Cuoco², Harald Oster³, Vittorio Paolucci⁴, Dario Tedesco², Stefano Viaroli^{5*}

¹ Department of Earth and Environmental Sciences, University of Pavia, Via Ferrata 9, Pavia, Italy

² Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, University of Campania "L. Vanvitelli", Via Vivaldi 43, 81100 Caserta, Italy

³ Spurenstofflabor, Wachenheim, Germany

⁴ Ferrarelle S.p.A., Contrada Ferrarelle, Riardo, Italy

⁵ Sciences Department, University of Roma Tre, Largo S. L. Murialdo 1, 00145 Rome, Italy

*corresponding author stefano.viaroli@uniroma3.it

Table S1 Isotopic composition and rainwater amount collected at the precipitation monitoring stations P1 and P2

Station	Elevation	Monitoring period	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d-excess	Rain		Total rain	Amount weighted	
	<i>m a.s.l.</i>		‰	‰	‰	<i>mm</i>	<i>L</i>	<i>L</i>	$\delta^{18}\text{O}\text{‰}$	$\delta^2\text{H}\text{‰}$
P1	525	20/03/14 - 15/04/14	-7.39	-44.2	14.97	64	2	51.6	-7.14	-42.4
		15/04/14 - 27/05/14	-6.14	-35.5	13.61	143	4.5			
		27/05/14 - 25/07/14	-5.13	-29.9	11.15	201	6.3			
		25/07/14 - 19/09/14	-5.04	-26.5	13.85	195	6.1			
		19/09/14 - 12/12/14	-7.48	-41.9	17.97	124	3.9			
		12/12/14 - 12/02/15	-9.25	-56.0	17.98	318	10			
		12/02/15 - 21/04/15	-9.14	-56.7	16.40	226	7.1			
		21/04/15 - 12/10/15	-6.21	-39.1	10.60	175	5.5			
		12/10/15 - 18/02/16	-6.41	-37.8	13.45	108	3.4			
		18/02/16 - 07/04/16	-7.38	-43.1	15.95	89	2.8			
P2	150	20/03/14 - 15/04/14	-6.9	-42.3	12.93	80	2.5	57.4	-6.40	-38.6
		15/04/14 - 27/05/14	-5.13	-29.9	11.15	99	3.1			
		27/05/14 - 25/07/14	-5.04	-26.5	13.85	159	5			
		25/07/14 - 19/09/14	-4.52	-23.7	12.48	159	5			
		19/09/14 - 12/12/14	-7.37	-43.0	15.97	70	2.2			
		12/12/14 - 12/02/15	-8.59	-53.0	15.72	318	10			
		12/02/15 - 21/04/15	-8.72	-55.6	14.19	210	6.6			
		21/04/15 - 12/10/15	-4.97	-29.9	9.83	318	10			
		12/10/15 - 18/02/16	-5.94	-36.9	10.61	150	4.7			
		18/02/16 - 07/04/16	-6.81	-41.1	13.36	80	2.5			
		07/04/16 - 13/06/16	-5.15	-30.3	10.94	105	3.3			
		13/06/16 - 20/09/16	-6.07	-40.4	8.13	79	2.5			

Table S2 Isotopic composition of the monitored springs

Sample name	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d-excess	mean $\delta^{18}\text{O}$	std $\delta^{18}\text{O}$	mean $\delta^2\text{H}$	std $\delta^2\text{H}$
	‰	‰	‰	‰	‰	‰	‰
Gallo Inf.	-8.02	-49.3	14.85				
Gallo Matese	-8.05	-49.2	15.21	-8.31	0.20	-48.6	0.74
	-8.43	-48.3	19.17				
	-8.34	-47.8	18.89				
	-8.31	-47.8	18.69				
	-8.25	-48.7	17.33				
	-8.44	-48.4	19.15				
	-8.52	-49.0	19.21				
	-8.60	-49.3	19.49				
	-8.37	-49.6	17.40				
	-8.35	-48.6	18.22				
	-8.20	-49.2	16.37				
	-7.81	-46.8	15.69				
	-8.35	-48.9	17.90				
	-8.33	-48.5	18.13				
Grassano	-7.74	-47.4	14.59	-7.92	0.13	-46.4	0.42
	-8.09	-46.4	18.29				
	-7.97	-46.7	17.09				
	-7.97	-46.6	17.11				
	-7.71	-45.9	15.81				
	-7.95	-45.9	17.71				
	-8.06	-46.3	18.20				
	-7.96	-46.3	17.38				
	-7.80	-46.4	15.98				
	-7.72	-46.1	15.66				
	-7.83	-46.3	16.36				
	-8.07	-46.3	18.18				
	-8.04	-46.9	17.43				
	-7.91	-45.8	17.48				
Venafro	-7.15	-43.8	13.41	-7.33	0.17	-42.6	0.45
	-7.53	-42.9	17.39				
	-7.28	-42.7	15.55				
	-7.26	-42.4	15.69				
	-7.19	-41.9	15.65				
	-7.43	-42.4	17.01				
	-7.43	-42.6	16.83				
	-7.50	-42.5	17.50				
	-7.04	-41.6	14.70				
	-7.12	-42.6	14.35				
	-7.29	-42.8	15.57				
	-7.49	-42.4	17.48				
	-7.55	-43.4	17.02				
	-7.37	-43.0	15.96				
Triflisco	-6.68	-37.2	16.27	-6.63	0.09	-37.36	0.72
	-6.57	-38.0	14.59				
	-6.56	-37.1	15.35				
	-6.64	-38.3	14.86				
	-6.65	-37.6	15.65				
	-6.67	-37.7	15.74				
	-6.54	-37.0	15.36				

	-6.69	-38.1	15.39				
	-6.71	-37.1	16.59				
	-6.74	-37.9	15.98				
	-6.58	-37.2	15.45				
	-6.71	-37.1	16.58				
	-6.40	-37.6	13.59				
	-6.73	-35.3	18.50				
Rocchetta	-6.17	-33.7	15.67	-6.22	0.19	-34.1	0.62
	-6.19	-33.9	15.66				
	-6.32	-34.8	15.77				
	-6.38	-34.5	16.53				
	-6.29	-34.3	15.99				
	-5.79	-33.1	13.25				
	-6.41	-34.9	16.43				
Pozzi Croce	-6.20	-33.7	15.91	-6.30	0.19	-34.5	0.77
	-6.08	-33.6	15.02				
	-6.38	-35.2	15.90				
Lago verde	-6.44	-34.7	16.82	-6.60	0.16	-37.1	0.59
	-6.75	-37.5	16.53				
	-6.33	-36.7	13.99				
	-6.74	-38.0	15.93				
	-6.50	-36.2	15.83				
	-6.55	-37.3	15.11				
	-6.58	-36.7	15.99				
Fontana di Monte	-6.52	-37.4	14.76	-6.19	0.25	-33.2	1.25
	-6.83	-37.4	17.24				
	-6.47	-34.9	16.90				
	-6.41	-34.0	17.20				
	-6.73	-36.2	17.69				
	-6.02	-32.7	15.47				
	-5.87	-32.4	14.56				
	-5.86	-32.1	14.72				
	-6.22	-33.5	16.24				
	-6.10	-33.0	15.82				
	-6.22	-33.0	16.75				
	-6.09	-33.0	15.68				
	-6.21	-33.7	15.98				
Melito	-5.99	-32.0	15.94	-6.71	0.27	-35.8	0.37
	-6.24	-31.6	18.33				
	-6.43	-35.4	16.05				
	-6.72	-35.8	17.96				
	-6.97	-36.2	19.59				

Table S3 Isotopic composition of the monitored wells. ^a Samples collected at 100 L/min pumping rate; ^b Samples collected at 500 L/min pumping rate.

Sample name	Date	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d-excess	mean $\delta^{18}\text{O}$	std $\delta^{18}\text{O}$	mean $\delta^2\text{H}$	std $\delta^2\text{H}$
		‰	‰	‰	‰	‰	‰	‰
C1F	26/04/2010	-5.98	-36.6	11.25	-6.08	0.13	-36.6	0.04
	06/09/2010	-6.17	-36.6	12.71				
Eletta	26/04/2010	-6.29	-38.3	12.04	-6.35	0.08	-37.7	0.76
	06/09/2010	-6.41	-37.2	14.08				
F3	26/04/2010	-6.37	-38.4	12.56	-6.41	0.06	-37.6	1.06
	06/09/2010	-6.46	-36.9	14.78				
FM1	20/09/2011	-6.05	-33.7	14.73	-6.02	0.15	-32.9	0.83
	14/05/2012	-6.15	-33.0	16.23				
	05/11/2013	-5.86	-32.0	14.85				
FM2	20/09/2011	-6.02	-33.3	14.82	-6.10	0.07	-33.0	0.44
	14/05/2012	-6.14	-33.3	15.80				
	22/10/2013	-6.14	-32.5	16.58				
P12	27/04/2010	-6.30	-39.7	10.65	-6.25	0.08	-38.1	2.28
	07/09/2010	-6.19	-36.5	13.00				
P19	27/04/2010	-6.56	-40.1	12.42	-6.56	0.00	-38.8	1.81
	07/09/2010	-6.56	-37.5	14.93				
P2	27/04/2010	-6.35	-40.3	10.51	-6.44	0.14	-38.7	2.19
	07/09/2010	-6.54	-37.2	15.16				
P24	27/04/2010	-6.82	-41.9	12.67	-6.89	0.12	-38.1	1.26
	07/09/2010	-6.94	-39.7	15.87				
	27/09/2011	-6.94	-38.9	16.56				
	09/05/2012	-7.01	-37.6	18.43				
	13/05/2013	-6.92	-37.9	17.48				
	20/09/2013	-6.80	-37.6	16.80				
	20/05/2014	-6.97	-38.2	17.56				
	17/09/2014	-6.96	-37.1	18.55				
	21/05/2015	-7.01	-37.7	18.37				
	02/10/2015	-6.68	-37.2	16.23				
	10/05/2016	-6.96	-37.7	17.99				
	23/09/2016	-6.68	-37.1	16.34				
	23/05/2017	-6.88	-37.5	17.53				
	30/05/2019	-7.02	-37.7	18.50				
	10/09/2019	-6.73	-37.4	16.48				
P2C	26/04/2010	-6.01	-36.9	11.15	-6.12	0.16	-36.6	0.50
	06/09/2010	-6.24	-36.2	13.65				
S5	27/04/2010	-6.74	-41.2	12.74	-6.76	0.09	-37.4	1.13
	29/09/2010	-6.72	-37.9	15.88				
	13/05/2013	-6.69	-37.6	15.95				
	02/10/2013	-6.65	-36.7	16.47				
	23/09/2011	-6.74	-38.0	15.85				

	10/05/2012	-6.79	-37.5	16.87				
	20/05/2014	-6.67	-36.4	16.94				
	17/09/2014	-6.89	-37.1	18.03				
	20/05/2015	-6.88	-37.3	17.71				
	02/10/2015	-6.75	-36.3	17.67				
	11/05/2016	-6.83	-37.2	17.46				
	23/09/2016	-6.78	-37.1	17.12				
	23/05/2017	-6.93	-37.0	18.42				
	06/09/2017	-6.56	-37.0	15.45				
	27/05/2019	-6.73	-36.6	17.29				
	11/09/2019	-6.77	-36.9	17.26				
TW1	27/04/2010	-5.97	-36.6	11.19	-6.04	0.10	-36.1	0.65
	29/09/2010	-6.11	-35.6	13.19				
TW24	26/04/2010	-6.89	-42.7	12.45	-6.92	0.11	-38.1	1.37
	07/09/2010	-6.92	-39.6	15.80				
	27/09/2011	-6.95	-38.9	16.69				
	10/05/2012	-7.00	-38.0	18.05				
	13/05/2013	-7.05	-37.5	18.94				
	20/09/2013	-6.87	-37.3	17.68				
	20/05/2014	-6.99	-38.1	17.79				
	19/09/2014	-6.75	-37.7	16.32				
	20/05/2015	-7.01	-37.5	18.63				
	02/10/2015	-6.98	-37.3	18.52				
	11/05/2016	-6.88	-37.5	17.54				
	20/09/2016	-6.88	-38.0	17.00				
	23/05/2017	-7.13	-37.5	19.57				
	06/09/2017	-6.71	-37.8	15.82				
	11/09/2019	-6.92	-37.1	18.25				
	29/05/2019	-6.85	-37.4	17.41				
TW26	27/04/2010	-6.10	-36.6	12.16	-6.14	0.05	-36.6	0.06
	06/09/2010	-6.17	-36.5	12.81				
TW30	26/04/2010	-6.44	-37.8	13.68	-6.52	0.17	-36.3	1.02
	06/09/2010	-6.46	-39.0	12.71				
	23/09/2011	-6.62	-37.4	15.63				
	09/05/2012	-6.78	-36.6	17.69				
	15/05/2013	-6.37	-36.3	14.63				
	20/09/2013	-6.50	-35.8	16.25				
	20/05/2014	-6.68	-36.4	17.01				
	17/09/2014	-6.71	-36.1	17.61				
	20/05/2015	-6.71	-36.2	17.52				
	30/09/2015	-6.70	-35.8	17.79				
	13/05/2016	-6.41	-35.4	15.88				
	22/09/2016	-6.23	-35.1	14.78				
	23/05/2017	-6.41	-35.3	16.00				
	06/09/2017	-6.30	-35.7	14.67				

	27/05/2019	-6.50	-36.0	16.01				
	11/09/2019	-6.43	-35.7	15.78				
TW31	23/09/2011	-6.92	-38.6	16.80	-6.87	0.13	-37.6	0.42
	10/05/2012	-6.84	-37.3	17.48				
	13/05/2013	-6.90	-38.1	17.12				
	02/10/2013	-6.75	-37.5	16.51				
	22/05/2014	-6.95	-37.9	17.68				
	22/09/2014	-6.79	-37.1	17.16				
	26/05/2015	-6.96	-37.9	17.79				
	13/10/2015	-6.94	-37.4	18.16				
	16/05/2016	-6.77	-37.1	17.08				
	27/09/2016	-6.82	-37.8	16.80				
	18/05/2017	-6.84	-37.4	17.31				
	07/09/2017	-6.62	-37.4	15.56				
	28/05/2019	-7.18	-37.8	19.59				
	12/09/2019	-6.93	-37.2	18.22				
TW4	26/04/2010	-6.20	-37.3	12.35	-6.20	0.00	-36.3	1.34
	06/09/2010	-6.20	-35.4	14.24				
TW6	27/04/2010	-6.48	-38.2	13.60	-6.44	0.16	-35.8	0.96
	06/09/2010	-6.59	-38.0	14.68				
	05/04/2011	-6.20	-35.3	14.30				
	11/04/2011	-6.24	-36.1	13.80				
	23/09/2011	-6.47	-36.4	15.31				
	09/05/2012	-6.51	-35.9	16.22				
	22/05/2014	-6.30	-35.1	15.38				
	19/09/2014	-6.57	-35.4	17.14				
	20/05/2015	-6.53	-35.7	16.53				
	23/09/2015	-6.89	-36.9	18.26				
	13/05/2016	-6.37	-35.0	16.00				
	24/09/2016	-6.50	-35.8	16.16				
	23/05/2017	-6.56	-35.0	17.47				
	06/09/2017	-6.42	-35.7	15.65				
	28/05/2019	-6.42	-35.5	15.87				
	11/09/2019	-6.28	-35.0	15.22				
TW6^a	15/05/2013	-6.35	-35.7	15.10				
	16/09/2013	-6.27	-34.7	15.46				
TW6^b	17/05/2013	-6.52	-35.6	16.58				
	22/09/2013	-6.32	-34.9	15.73				

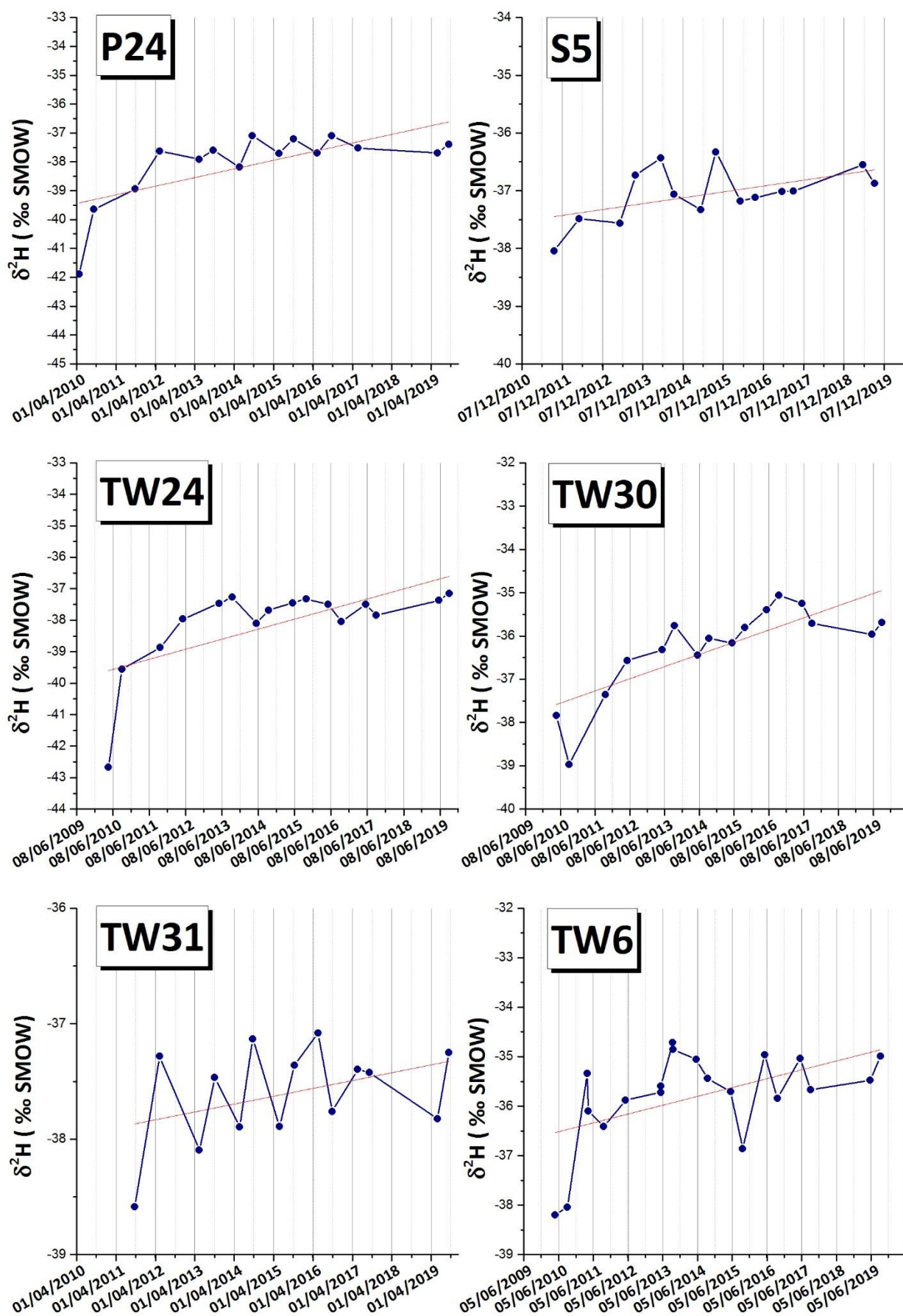


Fig S1 $\delta^2\text{H}$ temporal trends in groundwater from the monitored wells of the Ferrarelle basin

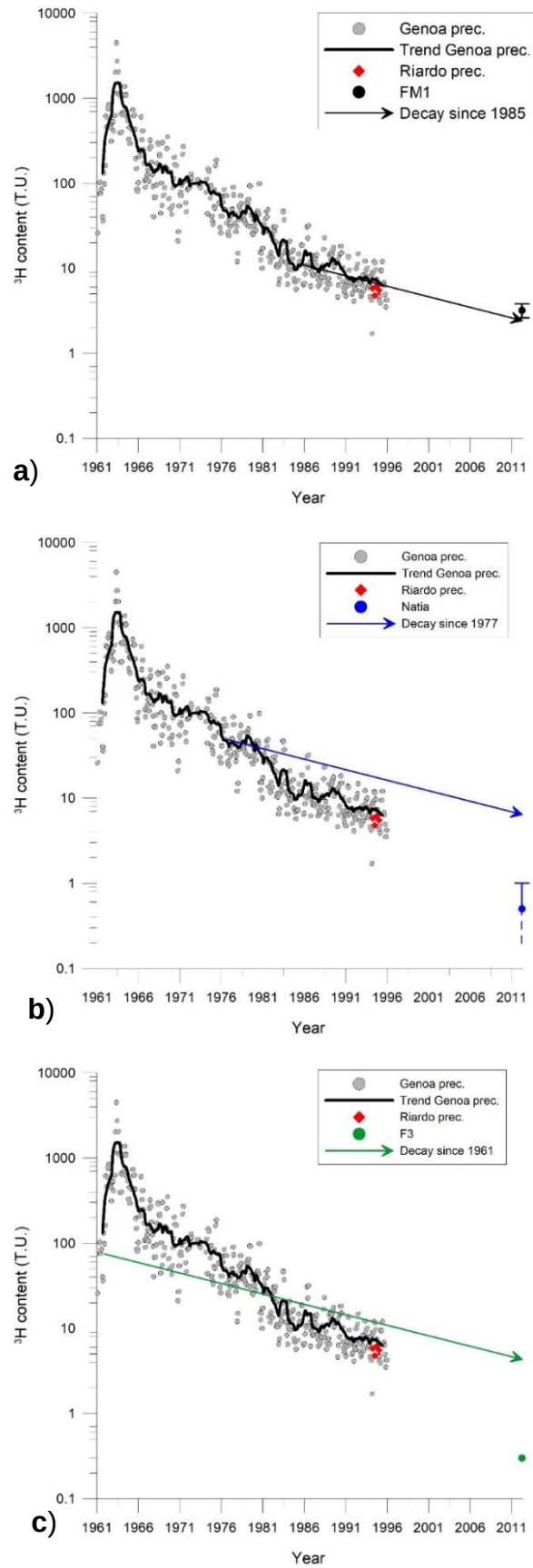


Fig. S2 Plots displaying the Tritium concentration in precipitation from the Genoa monitoring station (IAEA/WMO 2020, grey dots) and the relative trend (black curve), together with the concentration measured in precipitation from the Riardo station in 1992-1993 (red dots) (Longinelli, 1994). Tritium concentrations in groundwater from (a) FM1, (b) Natia and (c) F3, measured in 2012, compared to the concentration expected after decay, assuming that groundwater infiltrated in the year indicated by CFCs dating (arrow).

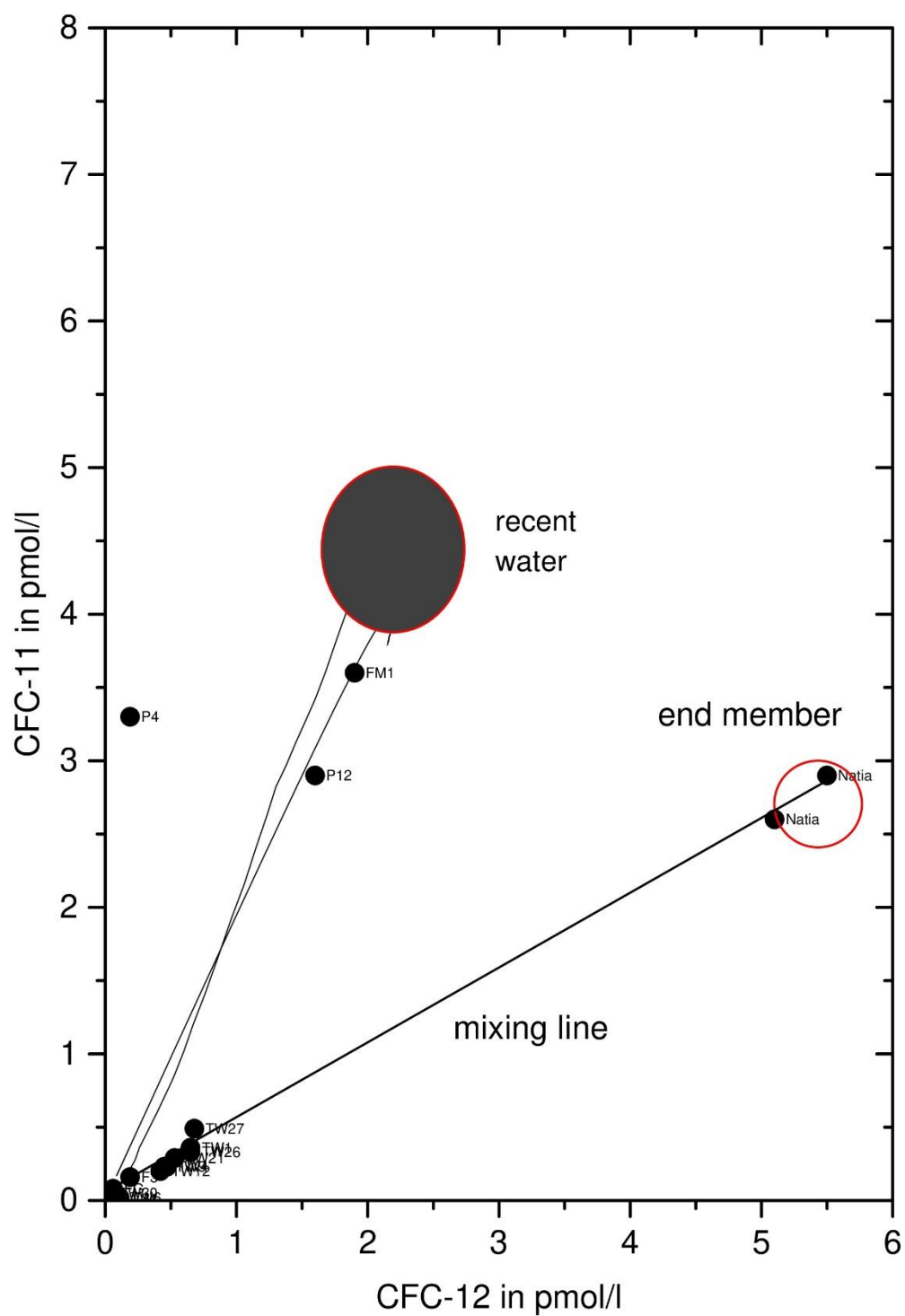


Fig. S3 Binary plot of CFC-11 versus CFC-12 concentrations in groundwater. Most of the samples fall on a mixing line having as end-members Natia (younger groundwater) and old CFC-free groundwater.

Table S4 Percent contribution of old CFC-free groundwater and of younger water (Natia-type) calculated for the samples falling on the mixing line between the two end-members (Fig. S3) using the CFC-12 and CFC-11 concentrations. The 1 sigma deviation between the two independent tracers is small for most of the samples, indicating a good agreement.

Sample name	Date	Old comp. % <i>age > 70 years</i>	Young comp. % <i>age 36 years</i>	1 sigma %
TW26	14/10/2015	88	12	1
TW27	14/10/2015	85	15	3
TW12	23/09/2014	92	8	1
TW9	23/09/2014	92	8	1
TW4	23/09/2014	91	9	1
TW21	22/09/2014	90	10	1
FG	22/09/2014	98	2	1
TW30	04/06/2013	99	1	1
TW1	04/06/2013	87	13	1
Natia	05/06/2013	0	104	1
Natia	22/05/2012	5	95	2
F3	23/05/2012	95	5	2
TW6	23/05/2012	99	1	1
TW24	23/05/2012	100	0	1