

An integrated approach for investigating the salinity evolution in a Mediterranean coastal karst aquifer

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Supplementary Materials

Figures

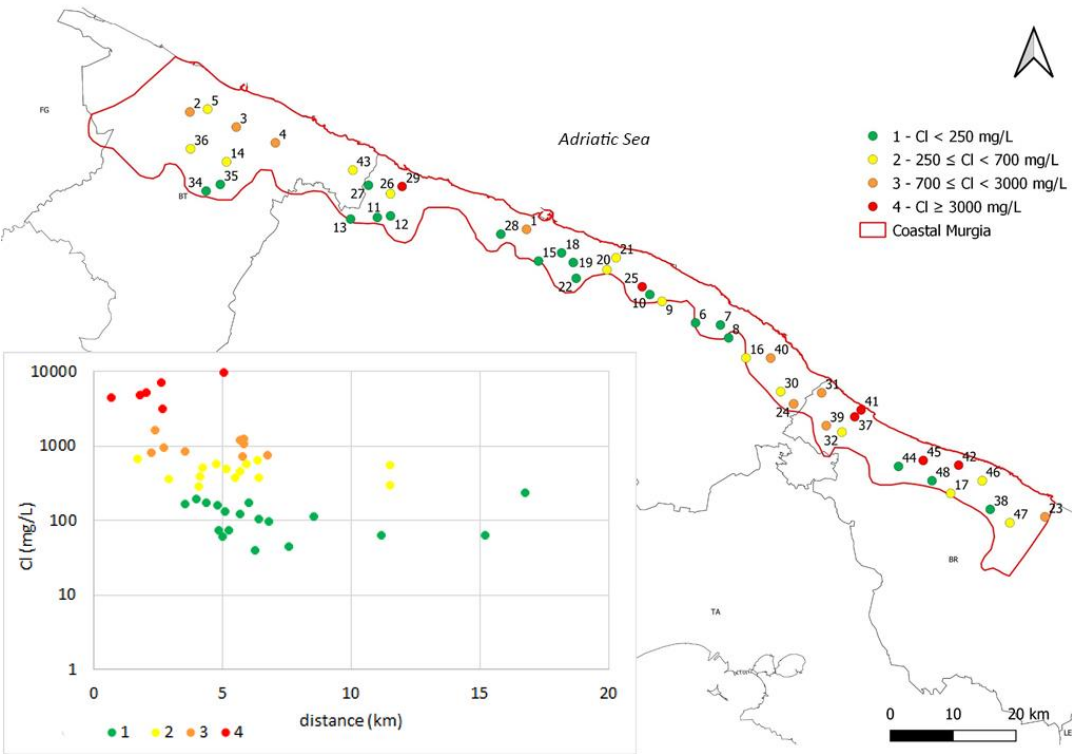


Figure S1. Map of chloride concentrations and chart of chloride concentrations vs distance from coastline.

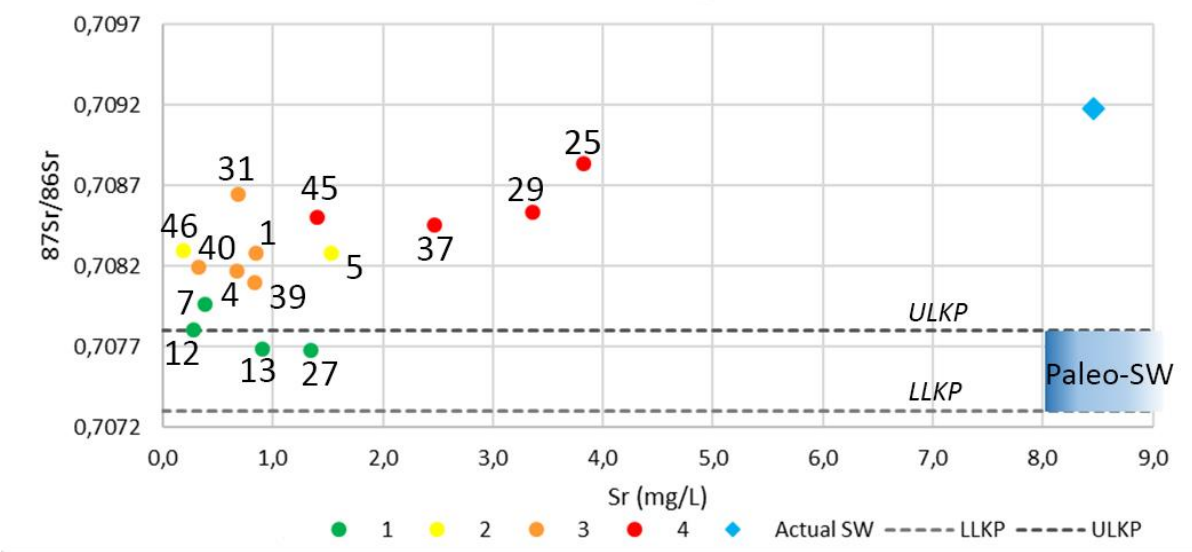


Figure S2. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio vs Sr concentration observed in the MWs of the Coastal Murgia. The meaning of dots colours is the same of the figure S1. The light blue diamond represents the value of the actual seawater. ULKP = upper limit of the Cretaceous platform, LLKP = lower limit of the Cretaceous platform. Blue rectangle represents the range of paleo-seawater

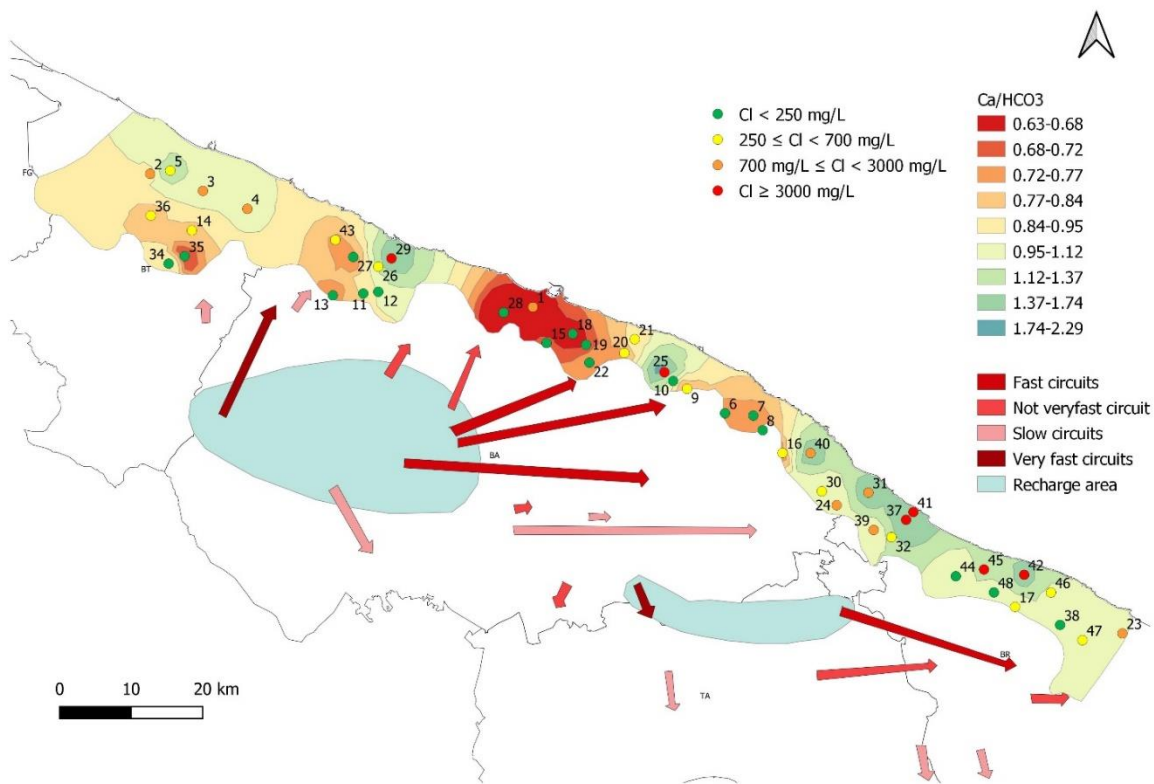


Figure S3. Map of chloride concentration at the monitoring wells and the spatial interpolation of Ca/HCO₃ ratio (Inverse Distance Squared Weighted method). Arrows and recharge areas overlap the circuits and recharge area described by Tulipano et al. [41]

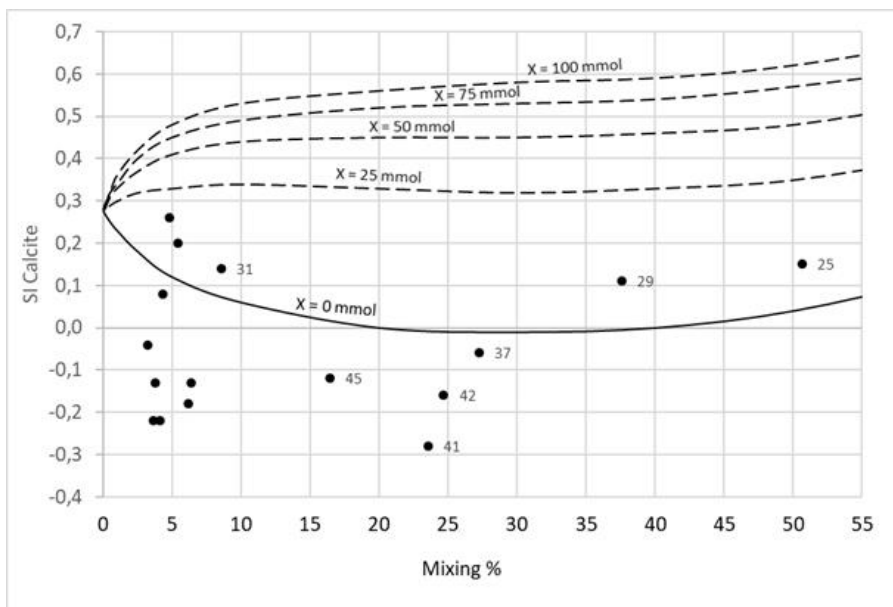


Figure S4. Simulated calcite Saturation Indexes (SI). Comparison between pure mixing (continuous line) and coupled model mixing+ion exchange (dashed lines) at different exchanger concentrations. Black dots indicate the calcite SI for the sampled waters (mixing > 3%)

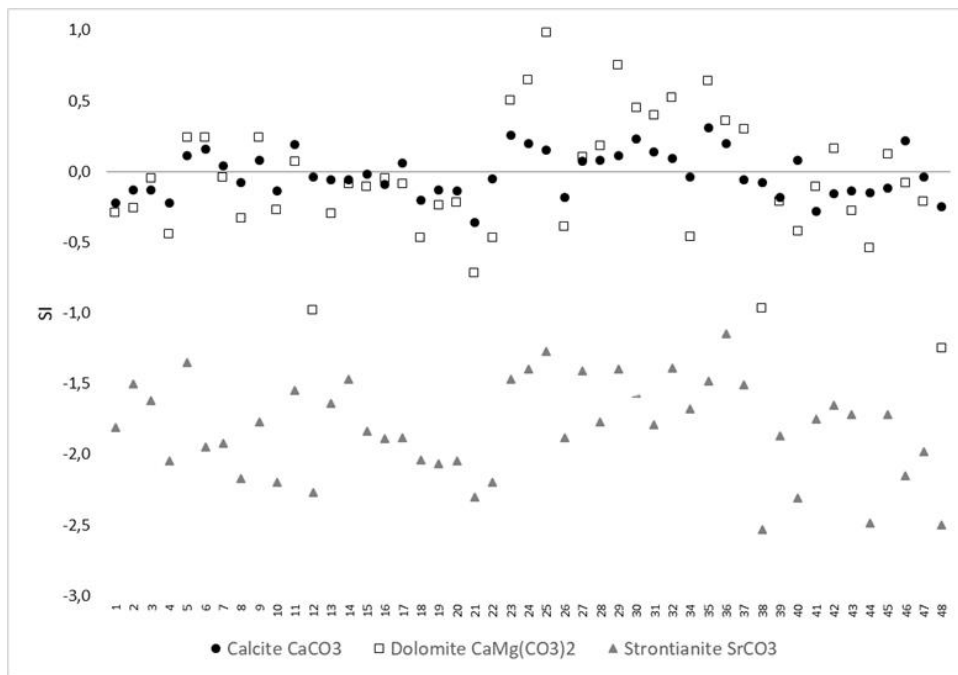


Figure S5. Carbonate mineral Saturation Indexes for the 47 groundwater samples

Tables

Table S1. Constructive features of monitoring wells. In italic and underscore are indicated MWs not equipped with in-place pumps

ID	Depth (m)	Casing	Casing depth (m)	Screen depth (from-to) (m)
<u>1</u>	51.56	PVC	51.56	13.7-51.56
<u>2</u>	102	steel	92	85.35 -92
<u>3</u>	150	steel	125	112.7-125
<u>4</u>	112	steel	112	85.7-112
<u>5</u>	403	PVC	403	16.5-403
<u>6</u>	200	steel	403	169.7-175.7; 181.2-200
<u>7</u>	n.a.	n.a.	n.a.	n.a.
<u>8</u>	355	n.a.	n.a.	n.a.
<u>9</u>	303	steel	300	177.87-202.12
<u>10</u>	281	steel	281	180-200
<u>11</u>	543	n.a.	n.a.	n.a.
<u>12</u>	500.5	steel	350	237.5-243.0; 336.1-341.7
<u>13</u>	487	steel	410	359.3-365.4; 371.6-380; 402.1-408.2
<u>14</u>	250	steel	205.5	185-203
<u>15</u>	200.3	steel	205.5	76.8-83; 107.8-114; 126.4-132.6; 138-145
<u>16</u>	380	steel	380	330-380
<u>17</u>	265	steel	265	179-265
<u>18</u>	63	PVC	63	17-63
<u>19</u>	126.7	n.a.	n.a.	n.a.
<u>20</u>	143.5	n.a.	n.a.	n.a.
<u>21</u>	n.a.	n.a.	n.a.	n.a.
<u>22</u>	n.a.	n.a.	n.a.	n.a.
<u>23</u>	50	steel	44.6	24.7-44.6

<u>24</u>	500.5	PVC	500.5	125-500.5
<u>25</u>	500	PVC	500.5	110-500
<u>26</u>	205	steel	196.3	179.12-194.78
<u>27</u>	300	steel	200	51-177
<u>28</u>	230	steel	200	71.34-200
<u>29</u>	177	steel	177	51-177
<u>30</u>	280	n.a.	n.a.	n.a.
<u>31</u>	n.a.	n.a.	n.a.	n.a.
<u>32</u>	n.a.	n.a.	n.a.	n.a.
<u>34</u>	400	n.a.	300	250-300
<u>35</u>	400	n.a.	n.a.	n.a.
<u>36</u>	176	n.a.	n.a.	n.a.
<u>37</u>	n.a.	n.a.	n.a.	n.a.
<u>38</u>	n.a.	n.a.	n.a.	n.a.
<u>39</u>	n.a.	n.a.	n.a.	n.a.
<u>40</u>	n.a.	n.a.	n.a.	n.a.
<u>41</u>	15	steel	n.a.	2.00-15.0
<u>42</u>	50	steel	n.a.	3.0-50.0
<u>43</u>	n.a.	PVC	n.a.	45-65
<u>44</u>	n.a.	n.a.	n.a.	n.a.
<u>45</u>	65	n.a.	n.a.	n.a.
<u>46</u>	n.a.	n.a.	n.a.	n.a.
<u>47</u>	n.a.	n.a.	n.a.	n.a.
<u>48</u>	n.a.	n.a.	n.a.	n.a.

Table S2. Analytical methods applied for anions, cations, trace elements and dissolved organic carbon analysis and relative detection limits

Parameters	Analytical method	Detection Limits
Cl ⁻ (mg/L)	Ion-Exchange Chromatography	0.03
Br ⁻ (mg/L)	Ion-Exchange Chromatography	0.02
NO ₃ ⁻ (mg/L)	Ion-Exchange Chromatography	0.04
SO ₄ ²⁻ (mg/L)	Ion-Exchange Chromatography	0.02
NH ₄ ⁺ (mg/L)	UV/Vis Spectrophotometry	0.02
Na (mg/L)	Inductively Coupled Plasma Mass Spectrometry	0.1
Mg (mg/L)	Inductively Coupled Plasma Mass Spectrometry	0.1
K (mg/L)	Inductively Coupled Plasma Mass Spectrometry	0.1
Ca (mg/L)	Inductively Coupled Plasma Mass Spectrometry	0.1
Li (µg/L)	Inductively Coupled Plasma Mass Spectrometry	0.1
B (µg/L)	Inductively Coupled Plasma Mass Spectrometry	0.5
Rb (µg/L)	Inductively Coupled Plasma Mass Spectrometry	0.2
Sr (µg/L)	Inductively Coupled Plasma Mass Spectrometry	0.2
DOC (mg/L)	Combustion Catalytic Oxidation/Non Dispersive Infrared (NDIR)	0.004

Table S3. In the table are indicated the main statistics of measured parameters discussed in the paper

Min Max Mean Median St. Dev.

T (°C)	16.8	25.4	18.7	18.2	1.8
pH	6.6	7.3	7.0	6.9	0.2
EC (µS/cm)	711	19590	3400	1740	4452
DO (mg/L)	0.1	9.7	5.3	5.2	2.4
ORP (mV)	-97	161	88	99	47
NH ₄ ⁺ (mg/L)	<0.02	1.1	0.1	0.03	0.2
Cl ⁻ (mg/L)	39.1	9684.1	1114.9	388.5	1984.2
Br ⁻ (mg/L)	0.2	33.0	4.0	1.5	6.7
NO ₃ ⁻ (mg/L)	15.5	126.6	39.9	31.5	25.0
SO ₄ ²⁻ (mg/L)	13.0	1225.3	149.6	56.0	247.1
HCO ₃ ⁻ (mg/L)	296.8	1039.1	446.2	432.4	105.6
Na (mg/L)	24.1	4927.0	594.2	203.4	1046.4
K (mg/L)	1.7	198.7	26.8	9.9	44.8
Mg (mg/L)	10.4	661.3	98.2	59.4	124.9
Ca (mg/L)	80.4	317.1	134.3	119.7	50.6
Li (µg/L)	0.8	126.7	19.8	9.9	26.6
B (µg/L)	34.3	2309.0	291.3	154.4	429.5
Rb (µg/L)	1.1	57.4	8.3	4.2	11.4
Sr (µg/L)	137.0	3825.0	936.6	676.0	830.9
DOC (mg/L)	0.4	11.0	1.0	0.6	1.5

Table S4. In the table are indicated MWs, chloride concentration, the groundwater (GW) group based on chloride concentration, mixing percentage ($f_{\text{sea}}\%$), the Na/Cl, Cl/HCO₃ and Ca/HCO₃ ratios and the cluster groups. In italic and underscore are indicated MWs not equipped with in-place pumps. The limits of GW groups are: 1) Cl⁻ < 250 mg/L; 2) 250 ≤ Cl⁻ < 700 mg/L; 3) 700 mg/L ≤ Cl⁻ < 3000 mg/L; 4) Cl⁻ ≥ 3000 mg/L. Na/Cl < 0.90 indicates MWs affected by SWI. Cl/HCO₃ < 0.5 indicates MWs no affected by SWI; 0.5 < Cl/HCO₃ < 1.3 indicates MWs slightly affected by SWI; 1.3 < Cl/HCO₃ < 2.8 indicates MWs moderately affected by SWI; 2.8 < Cl/HCO₃ < 6.6 indicates MWs injuriously affected by SWI and Cl/HCO₃ > 6.6 indicates MWs highly affected by SWI. Ca/HCO₃ around 1 is typical of carbonate dissolution, around 0.5 is typical of dolomite dissolution and >1 can be attributed to mixing with seawater and possible reverse ion exchange processes.

ID	Cl ⁻ (mg/L)	GW Group	$f_{\text{sea}}\%$	Na/Cl	Cl/HCO ₃	Ca/HCO ₃	Cluster Group
<u>1</u>	813	3	4.1	0.93	2.8	0.6	Cluster D
<u>2</u>	751	3	3.8	0.90	2.6	0.9	Cluster D
<u>3</u>	1238	3	6.4	0.84	5.2	1.0	Cluster D
<u>4</u>	721	3	3.6	0.82	3.0	1.0	Cluster D

<u>5</u>	581	2	2.9	0.71	3.4	1.3	Cluster D
6	173	1	0.8	0.77	0.6	0.7	Cluster A
7	164	1	0.7	0.70	0.6	0.7	Cluster A
8	73	1	0.3	0.85	0.3	0.7	Cluster A
9	376	2	1.8	0.82	1.5	0.7	Cluster C
10	120	1	0.5	0.73	0.5	0.6	Cluster A
11	113	1	0.5	0.92	0.4	0.8	Cluster A
12	45	1	0.1	1.12	0.2	1.0	Cluster A
13	64	1	0.2	0.95	0.2	0.7	Cluster A
14	549	2	2.7	0.77	2.1	0.8	Cluster C
15	105	1	0.4	0.77	0.4	0.7	Cluster A
16	573	2	2.9	0.81	2.1	0.6	Cluster C
17	376	2	1.8	0.83	1.8	0.9	Cluster C
18	191	1	0.9	0.74	0.7	0.6	Cluster A
19	158	1	0.7	0.82	0.6	0.7	Cluster A
20	289	2	1.4	0.74	1.1	0.7	Cluster B
21	659	2	3.3	0.90	3.2	0.9	Cluster D
22	95	1	0.4	0.94	0.4	0.8	Cluster A
23	941	3	4.8	0.83	4.5	1.1	Cluster D
<u>24</u>	1059	3	5.4	0.89	4.6	0.8	Cluster D
<u>25</u>	9684	4	50.6	0.78	42.9	2.3	Cluster E
26	514	2	2.6	0.78	2.0	0.9	Cluster C
27	133	1	0.6	0.87	0.4	0.6	Cluster A
28	176	1	0.8	1.00	0.6	0.6	Cluster A
<u>29</u>	7196	4	37.6	0.83	26.1	2.0	Cluster E
30	457	2	2.3	0.75	1.9	0.8	Cluster C
31	1657	3	8.6	0.76	8.7	1.7	Cluster E
32	498	2	2.5	0.79	0.8	0.3	not included in the cluster analysis
34	233	1	1.1	0.58	0.9	1.0	Cluster B
35	64	1	0.2	1.03	0.2	0.6	Cluster A
36	298	2	1.4	0.86	1.2	0.7	Cluster C

37	5227	4	27.3	0.87	23.5	1.7	Cluster E
38	39	1	0.1	0.95	0.2	0.9	Cluster A
39	1199	3	6.2	0.87	4.4	0.8	Cluster D
40	857	3	4.4	0.74	3.4	1.7	Cluster D
41	4523	4	23.6	0.82	20.3	1.6	Cluster E
42	4735	4	24.7	0.81	20.1	1.6	Cluster E
43	389	2	1.9	0.81	1.4	0.7	Cluster C
44	61	1	0.2	0.85	0.3	0.8	Cluster A
45	3162	4	16.4	0.85	13.2	1.3	Cluster E
46	357	2	1.7	0.82	1.7	1.1	Cluster C
47	638	2	3.2	0.85	2.9	1.0	Cluster D
48	74	1	0.3	1.01	0.3	0.9	Cluster A