

## Supplementary material

Table S1: Parameters monitored in each Region (VEN: Veneto; EMR: Emilia-Romagna; FVG: Friuli-Venezia Giulia; LOM: Lombardy; PIE: Piedmont)

Parameter	Unit	VEN	EMR	FVG	LOM	PIE
Website for groundwater sampling information		<a href="https://www.arpa.veneto.it/temi-ambientali/acqua/file-e-allegati/documenti/acque-interne/acque-sotterranee">https://www.arpa.veneto.it/temi-ambientali/acqua/file-e-allegati/documenti/acque-interne/acque-sotterranee</a>	<a href="https://www.arpae.it/it/temi-ambientali/acqua/dati-acque/acque-sotterranee/reti-e-di-monitoraggio-acque-sotterranee/il-monitoraggio-chimico-delle-acque-sotterranee">https://www.arpae.it/it/temi-ambientali/acqua/dati-acque/acque-sotterranee/reti-e-di-monitoraggio-acque-sotterranee/il-monitoraggio-chimico-delle-acque-sotterranee</a>	<a href="http://cmsarpa.regione.fvg.it/cms/tema/acqua/acque-sotterranee/">http://cmsarpa.regione.fvg.it/cms/tema/acqua/acque-sotterranee/</a>	<a href="https://www.arpalombardia.it/Pages/Acque-Sotterranee/Quelita.aspx#">https://www.arpalombardia.it/Pages/Acque-Sotterranee/Quelita.aspx#</a>	<a href="https://www.regione.piemonte.it/web/temi/ambiente-territorio/ambiente/acqua/dati-monitoraggio-delle-acque-sotterranee#">https://www.regione.piemonte.it/web/temi/ambiente-territorio/ambiente/acqua/dati-monitoraggio-delle-acque-sotterranee#</a>
EC at 20°C	µS/cm	X	X	X	X	X
EC at 25°C	µS/cm				X	
Hardness	mg/L	X	X	X	X	X
Dissolved oxygen	mg/L		X	X	X	
Oxidability	mg/L O <sub>2</sub>		X			
Oxygen at saturation	%		X		X	
pH	Units of pH	X	X	X	X	X
pH at sampling	Units of pH	X				
Eh	mV	X	X	X		
Temperature	°C	X	X	X	X	
Temperature at source	°C				X	
COD	mg/L O <sub>2</sub>				X	
TOC	mg/L		X			
δ18O	‰ VSMOW		X			
δ2H	‰ VSMOW		X			
Ca	mg/L	X	X	X	X	X
Mg	mg/L	X	X	X	X	X
Na	mg/L	X	X	X	X	X
K	mg/L	X	X	X	X	X
HCO <sub>3</sub> <sup>-</sup>	mg/L	X	X	X	X	X
Cl	mg/L	X	X	X	X	X
SO <sub>4</sub> <sup>2-</sup>	mg/L	X	X	X	X	X
Al	µg/L	X				
Sb	µg/L	X	X	X	X	X
As	µg/L	X	X	X	X	X
Organic N	mg/L				X	
Total N	mg/L N				X	
Be	µg/L				X	
Ba	µg/L	X	X	X		
B	µg/L	X	X	X	X	X
Cd	µg/L	X	X	X	X	X
Free CN	µg/L		X	X	X	
Total CN	µg/L	X				
Cr (VI)	µg/L	X	X	X	X	X
Total Cr	µg/L	X	X	X	X	X
Fe	µg/L	X	X	X	X	X
F	µg/L*		X	X	X	X
P	mg/L			X		
Total P	mg/L	X			X	
NH <sub>4</sub> <sup>+</sup>	mg/L**	X	X	X	X	X
Mn	µg/L	X	X	X	X	X
Hg	µg/L	X	X	X	X	X
Ni	µg/L	X	X	X	X	X

NO <sub>3</sub> <sup>-</sup>	mg/L	X	X	X	X	X
NO <sub>2</sub> <sup>-</sup>	µg/L ***	X	X	X	X	X
PO <sub>4</sub> <sup>3-</sup>	mg/L		X		X	X
Pb	µg/L	X	X	X	X	X
Cu	µg/L	X	X	X	X	X
Se	µg/L		X	X	X	X
V	µg/L	X	X	X	X	X
Zn	µg/L	X	X	X	X	X

\*mg/L in PIE; \*\*µg/L in EMR and LOM; \*\*\*mg/L in PIE and FVG

Table S2: Number of total analysed water samples and % of usable values that constitute the final database after the validation and cleaning processes

Analyte	Total measured values	Total values <D.L.	Considered D.L.	% Usable values
Na (mg/L)	3994	23	<1,0	99,4%
Cl (mg/L)	3972	82	<1,0	97,9%
Ba (µg/L)	1266	34	<5,0; <10,0	97,3%
SO <sub>4</sub> <sup>2-</sup> (mg/L)	3962	288	<1,0	92,7%
K (mg/L)	4001	314	<1,0	92,2%
NO <sub>3</sub> <sup>-</sup> (mg/L)	3978	944	<0,5; <1,0; <2,0	76,3%
B (µg/L)	2890	1026	<0,05; <0,10; <5,00; <10,00; <20,00; <50,00; <100,00	64,5%
Mn (µg/L)	3897	1797	<0,5; <0,1 <5,0; <10,0	53,9%
Zn (µg/L)	3825	1825	<5; <10; <20; <25; <30; <50	52,3%
Total P (mg/L)	1662	845	<0,004; <0,010; <0,020; <0,030; <0,050	49,2%
Fe (µg/L)	3895	2158	<5; <10; <20; <50	44,6%
P (mg/L)	3181	1898	<0,004; <0,010; <0,020; <0,030; <0,050	40,3%
NH <sub>4</sub> <sup>+</sup> (mg/L)	3982	2394	<0,02; <0,04; <0,05; <0,10	39,9%
F (µg/L)	3414	2120	<50; <100; <150; <200; <250; <300; <500	37,9%
Ni (µg/L)	3894	2419	<0,5; <1,0; <2,0; <5,0	37,9%
As (µg/L)	2872	1786	<0,5; <1,0; <2,0; <3,0	37,8%
Total Cr (µg/L)	3884	2853	<0,5; <1,0; <2,0; <3,0; <5,0	26,5%
Cr (IV) (µg/L)	3197	2496	<0,5; <2,0; <3,0; <5,0	21,9%
Cu (µg/L)	2693	2121	<1; <2; <5; <10	21,2%
V (µg/L)	1895	1494	<1; <5; <10; <20	21,2%
NO <sub>2</sub> <sup>-</sup> (µg/L)	3867	3184	<5; <10; <20; <30; <50	17,7%
Total CN (µg/L)	224	185	<0,5; <5,0	17,4%
Se (µg/L)	1663	1400	<0,5; <1,0; <2,0; <3,0; <5,0	15,8%
Hg (µg/L)	2126	1864	<0,02; <0,03; <0,04; <0,10; <0,20; <0,50; <1,00	12,3%
Cd (µg/L)	3897	3421	<0,025; <0,040; <0,050; <0,100; <0,500	12,2%
Pb (µg/L)	3897	3440	<0,4; <0,8; <1,0; <2,0; <2,5	11,7%
Free CN (µg/L)	1459	1302	<2; <10; <20	10,8%
Sb (µg/L)	1887	1694	<0,10; <0,25; <0,50; <1,00; <2,00	10,2%

Table S3: Descriptive statistics of all parameters in the dataset according to the aquifer type.

	Phreatic						Semiconfined						Confined					
Parameter	Measured values	<D.L.	Min	Max	Mean	Median	Measured values	<D.L.	Min	Max	Mean	Median	Measured values	<D.L.	Min	Max	Mean	Median
Hardness (mg/L)	2223	-	13,0	4950,0	322,3	302,0	268	-	2,0	564,0	222,4	208,0	1141	-	42,0	1503,0	286,9	254,0
T (°C)	1596	-	6,0	26,3	15,2	15,0	275	-	10,4	22,5	15,1	14,9	777	-	8,0	31,0	15,2	15,0
pH (Units of pH)	2193	-	5,5	8,7	7,3	7,3	268	-	6,5	8,4	7,6	7,7	1136	-	6,0	9,1	7,5	7,6
EC (µS/cm)	2212	-	63,0	35603,0	704,2	570,0	273	-	172,5	2053,0	482,6	459,0	1135	-	91,0	6284,0	682,3	563,0
HCO <sub>3</sub> <sup>-</sup> (mg/L)	2106	-	23,0	1564,0	320,5	319,0	266	-	116,0	591,0	295,6	298,5	1093	-	44,0	2385,0	363,6	314,0
Ca (mg/L)	2226	-	7,8	450,1	90,3	86,6	268	-	1,0	150,9	62,3	58,5	1141	-	10,1	276,0	72,5	61,1
Cl (mg/L)	2196	12	1,0	14362,0	64,2	16,0	258	10	1,0	463,0	13,6	5,0	1112	24	1,0	1870,0	54,7	14,0
Fe (µg/L)	628	1514	5,0	20100,0	945,1	149,5	177	88	6,0	2800,0	332,3	123,0	601	531	7,0	21200,0	1488,6	590,0
NH <sub>4</sub> <sup>+</sup> (mg/L)	512	1700	0,0	50,0	1,4	0,2	160	107	0,0	10,7	1,3	0,7	557	584	0,0	43,2	3,2	1,3
Mg (mg/L)	2225	-	1,0	816,0	24,3	19,0	267	-	4,7	52,0	16,3	15,0	1141	-	3,1	229,0	26,3	22,3
NO <sub>3</sub> <sup>-</sup> (mg/L)	1904	307	1,0	190,0	26,2	22,1	117	151	1,0	51,0	19,0	17,0	615	522	1,0	166,0	17,6	13,0
K (mg/L)	2080	146	0,3	423,1	5,9	1,9	264	4	0,6	10,0	1,5	1,1	992	152	0,2	95,1	2,7	1,7
Na (mg/L)	2222	2	0,9	8310,5	38,4	10,2	267	-	1,0	256,0	11,4	7,0	1142	-	1,0	1253,0	56,1	17,6
SO <sub>4</sub> <sup>2-</sup> (mg/L)	2170	39	1,0	1888,0	53,5	35,0	230	38	1,0	130,0	26,5	26,0	904	220	1,0	526,0	42,2	24,0
Sb (µg/L)	13	974	0,3	11,0	2,7	1,0	-	254	-	-	-	-	-	228	-	-	-	-
As (µg/L)	385	1143	1,0	342,0	9,1	3,0	149	115	1,0	250,0	20,0	5,0	333	468	1,0	434,0	15,7	4,0
Org N (µg/L)	59	626	0,2	20,2	2,4	0,7	11	245	0,2	4,7	0,8	0,4	11	79	0,2	2,6	0,8	0,5
Be (µg/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ba (µg/L)	586	4	8,5	1059,0	126,7	79,0	-	-	-	-	-	-	584	4	10,0	2536,0	287,7	180,5
B (µg/L)	889	656	0,1	1965,0	143,1	71,0	102	166	6,0	290,0	42,6	20,0	652	138	0,1	2120,0	333,1	174,0
Cd (µg/L)	84	2053	0,0	0,7	0,1	0,1	18	250	0,0	0,8	0,1	0,1	30	1105	0,0	1,0	0,1	0,1
Free CN (µg/L)	-	886	-	-	-	-	-	242	-	-	-	-	1	185	12,0	12,0	12,0	12,0
Total CN (µg/L)	-	154	-	-	-	-	-	-	-	-	-	-	-	7	-	-	-	-
Total Cr (µg/L)	438	1699	0,5	68,0	4,8	3,0	25	243	2,0	24,0	4,9	3,0	269	855	0,5	20,0	4,4	3,4
Cr IV (µg/L)	235	1676	0,5	52,0	5,2	3,0	36	232	2,0	14,8	3,6	2,9	132	536	0,5	11,5	3,7	3,0

F (µg/L)	441	1407	29,0	1064,0	168,4	137,0	41	215	27,0	360,0	91,7	76,0	519	525	45,0	3000,0	305,9	190,0
Total P (mg/L)	351	675	0,0	8,9	0,2	0,1	159	97	0,0	1,1	0,2	0,1	48	108	0,0	1,5	0,2	0,1
Mn (µg/L)	870	1275	1,0	2863,0	182,6	57,0	187	78	1,0	1522,0	94,1	66,0	741	390	1,0	2659,0	149,0	76,0
Hg (µg/L)	24	1279	0,0	1,5	0,1	0,1	2	266	0,0	0,1	0,0	0,0	5	302	0,0	0,1	0,1	0,0
Ni (µg/L)	766	1369	0,5	236,4	6,5	3,0	22	246	1,0	61,0	5,5	2,0	342	792	0,5	53,4	3,4	2,0
NO <sub>2</sub> <sup>-</sup> (µg/L)	233	1910	5,0	1085,0	72,5	35,0	38	230	5,0	168,0	23,9	12,0	44	1056	10,0	3191,0	181,4	40,0
PO <sub>4</sub> <sup>3-</sup> (mg/L)	497	1214	0,0	23,0	0,4	0,1	149	107	0,0	3,2	0,6	0,4	363	624	0,0	1,4	0,1	0,1
Pb (µg/L)	76	2063	0,4	8,4	2,0	1,1	8	260	1,0	2,0	1,4	1,2	21	1113	0,8	7,0	2,9	2,2
Cu (µg/L)	293	1097	1,0	124,0	12,9	8,0	7	5	1,0	2,0	1,3	1,0	67	967	1,0	365,0	13,5	5,5
Se (µg/L)	60	927	1,0	23,0	4,6	3,0	5	249	1,0	18,0	7,6	5,0	18	210	1,0	30,9	7,2	3,0
V (µg/L)	114	1035	1,0	284,0	5,0	1,1	27	229	1,0	2,5	1,4	1,4	49	185	1,0	3,5	1,3	1,0
Zn (µg/L)	984	1099	5,0	11900,0	224,6	58,0	167	101	5,0	1824,0	110,4	32,0	540	583	5,0	12689,0	324,8	67,0

Table S4: Comparison between chemical and physical data in the semi-confined and confined aquifers in cold and warm seasons (cold season includes fall and winter months, while warm season includes spring and summer months). \* parameters significantly different between seasons (Kruskal-Wallis value < 0.05)

Cold season								Warm season								Kruskal-Wallis
Variable	total obs	missing obs	valid obs	Min	Max	Mean	Std. Dev.	total obs	missing obs	valid obs	Min	Max	Mean	Std. Dev.		
Hardness (mg/l)	691	8	683	2.0	1470.0	277.4	162.0	737	11	726	42.0	1503.0	272.0	166.7	0.289	
T (°C)	691	184	507	8.0	23.6	15.1	1.6	737	192	545	9.8	31.0	15.3	1.9	0.029*	
pH	691	14	677	6.0	8.8	7.6	0.4	737	10	727	6.1	9.1	7.5	0.4	0.022*	
Eh (mV)	691	498	193	195.0	266.2	27.7	115.6	737	522	215	175.7	292.0	33.3	121.9	0.673	
EC (µS/cm)	691	7	684	92.0	5537	642.7	543.9	737	13	724	91.0	6284	644.5	565.7	0.979	
Ca (mg/l)	691	8	683	1.0	275.5	71.7	42.7	737	11	726	10.1	276	69.5	42.7	0.186	
Mg (mg/l)	691	9	682	3.4	213	24.5	19.7	737	11	726	3.1	229	24.3	20.3	0.700	
Na (mg/l)	691	8	683	1.2	1061	47.3	95.9	737	11	726	1.0	1253	48.1	101.5	0.995	
K (mg/l)	691	7	684	0.1	28.3	2.1	2.8	737	9	728	0.1	95	2.3	4.4	0.585	
HCO <sub>3</sub> <sup>-</sup> (mg/l)	691	35	656	44.0	2214	353.1	221.1	737	34	703	45.0	2385	347.6	215.1	0.740	
SO <sub>4</sub> <sup>2-</sup> (mg/l)	691	20	671	0.5	400	32.7	45.7	737	16	721	0.5	526	31.1	47.6	0.201	
Cl (mg/l)	691	13	678	0.5	1670	45.0	141.3	737	11	726	0.5	1870	46.5	155.9	0.246	
PO <sub>4</sub> (mg/l)	691	70	621	0.001	3.2	0.1	0.3	737	115	622	0.001	2	0.1	0.3	0.436	
NO <sub>3</sub> <sup>-</sup> (mg/l)	691	13	678	0.01	161	9.4	15.7	737	10	727	0.0	166	9.2	15.7	0.420	
NO <sub>2</sub> <sup>-</sup> (mg/l)	691	50	641	0.1	3191	7.8	127.2	737	10	727	0.1	1299	5.0	57.0	0.906	
NH <sub>4</sub> <sup>+</sup> (mg/l)	691	9	682	0.001	43.2	1.4	3.6	737	11	726	0.0	42	1.4	3.9	0.670	
F (µg/l)	691	54	637	1.0	2800	125.3	245.8	737	74	663	1.0	3000	125.8	254.0	0.995	
Fe (µg/l)	691	19	672	0.1	18527	671.3	1700.7	737	12	725	0.1	21200	692.9	1893.9	0.864	
Mn (µg/l)	691	19	672	0.001	2659	92.5	201.6	737	13	724	0.0	2420	90.9	203.0	0.893	
As (µg/l)	691	185	506	0.01	434	8.1	30.1	737	178	559	0.0	274	7.4	25.9	0.927	
Ba (µg/l)	691	403	288	0.1	2059	279.1	283.9	737	437	300	0.1	2536	292.1	328.1	0.781	
B (µg/l)	691	187	504	0.0	1980	214.5	332.7	737	183	554	0.0	2120	204.8	318.1	0.237	
Zn (µg/l)	691	17	674	0.1	9166	137.8	609.3	737	20	717	0.1	12689	140.9	653	0.884	

Table S5: Comparison between chemical and physical data in the phreatic aquifers in cold and warm seasons. \* parameters significantly different between seasons (Kruskal-Wallis value < 0.05)

Cold season								Warm season								Kruskal-Wallis
Variable	total obs	missing obs	valid obs	Min	Max	Mean	Std. Dev.	total obs	missing obs	valid obs	Min	Max	Mean	Std. Dev.		
Hardness (mg/l)	1023	8	1015	33.0	4950	329.7	284.0	1220	12	1208	13.0	3644.0	316.0	181.7	0.648	
T (°C)	1023	325	698	6.0	22.8	15.1	2.1	1220	322	898	6.5	26.3	15.3	2.2	0.315	
pH	1023	39	984	5.7	8.6	7.3	0.4	1220	11	1209	5.5	8.7	7.3	0.4	0.258	
Eh (mV)	1023	827	196	-95.0	504	146.0	84.9	1220	1005	215	121.0	498	158.1	99.4	0.040*	
EC (µS/cm)	1023	14	1009	63.0	30073	727.2	1702.6	1220	17	1203	63.0	35603	684.9	1229.9	0.087	
Ca (mg/l)	1023	8	1015	8.4	450	91.2	46.3	1220	9	1211	7.8	367	89.6	42.8	0.531	
Mg (mg/l)	1023	9	1014	1.3	816	25.4	48.0	1220	9	1211	1.0	807	23.4	31.4	0.903	
Na (mg/l)	1023	7	1016	0.5	7370	45.3	380.7	1220	12	1208	0.5	8311	32.5	283.9	0.656	
K (mg/l)	1023	8	1015	0.1	423	6.0	23.8	1220	9	1211	0.1	416	5.1	22.1	0.202	
HCO <sub>3</sub> <sup>-</sup> (mg/l)	1023	67	956	28.0	1564	319.2	164.1	1220	70	1150	23.0	1472	321.6	146.8	0.311	
SO <sub>4</sub> <sup>2-</sup> (mg/l)	1023	25	998	0.5	1743	53.5	93.1	1220	9	1211	0.5	1888	51.8	85.5	0.669	
Cl (mg/l)	1023	23	1000	0.5	12713	78.7	721.2	1220	12	1208	0.5	14362	51.7	495.2	0.773	
PO <sub>4</sub> <sup>3-</sup> (mg/l)	1023	251	772	0.001	23	0.129	0.947	1220	281	939	0.0	5.3	0.1	0.4	0.014*	
NO <sub>3</sub> <sup>-</sup> (mg/l)	1023	21	1002	0.01	190	22.7	21.5	1220	11	1209	0.0	158	22.3	20.6	0.867	
NO <sub>2</sub> <sup>-</sup> (mg/l)	1023	90	933	0.1	734	7.119	35.903	1220	10	1210	0.1	1085	8.6	49.0	0.271	
NH <sub>4</sub> <sup>+</sup> (mg/l)	1023	9	1014	0.001	50	0.4	2.5	1220	22	1198	0.0	41	0.3	1.9	0.695	
F (µg/l)	1023	196	827	1.0	935	43.6	94.4	1220	199	1021	1.0	1064	38.8	94.4	0.091	
Fe (µg/l)	1023	52	971	0.1	14630	253.6	1087.8	1220	49	1171	0.1	20100	296.7	1269.7	0.402	
Mn (µg/l)	1023	50	973	0.001	2863	72.7	228.9	1220	48	1172	0.0	2650	75.2	230.7	0.319	
As (µg/l)	1023	366	657	0.01	342	2.4	15.4	1220	349	871	0.0	235	2.2	10.5	0.462	
Ba (µg/l)	1023	720	303	0.1	870	122.5	140.7	1220	933	287	0.1	1059	129.4	149.5	0.411	
B (µg/l)	1023	354	669	0.01	1965	92.3	198.6	1220	344	876	0.0	1670	74.8	155.5	0.255	
Zn (µg/l)	1023	59	964	0.1	5890	96.2	370.6	1220	101	1119	0.1	11900.0	114.7	612.6	0.057	

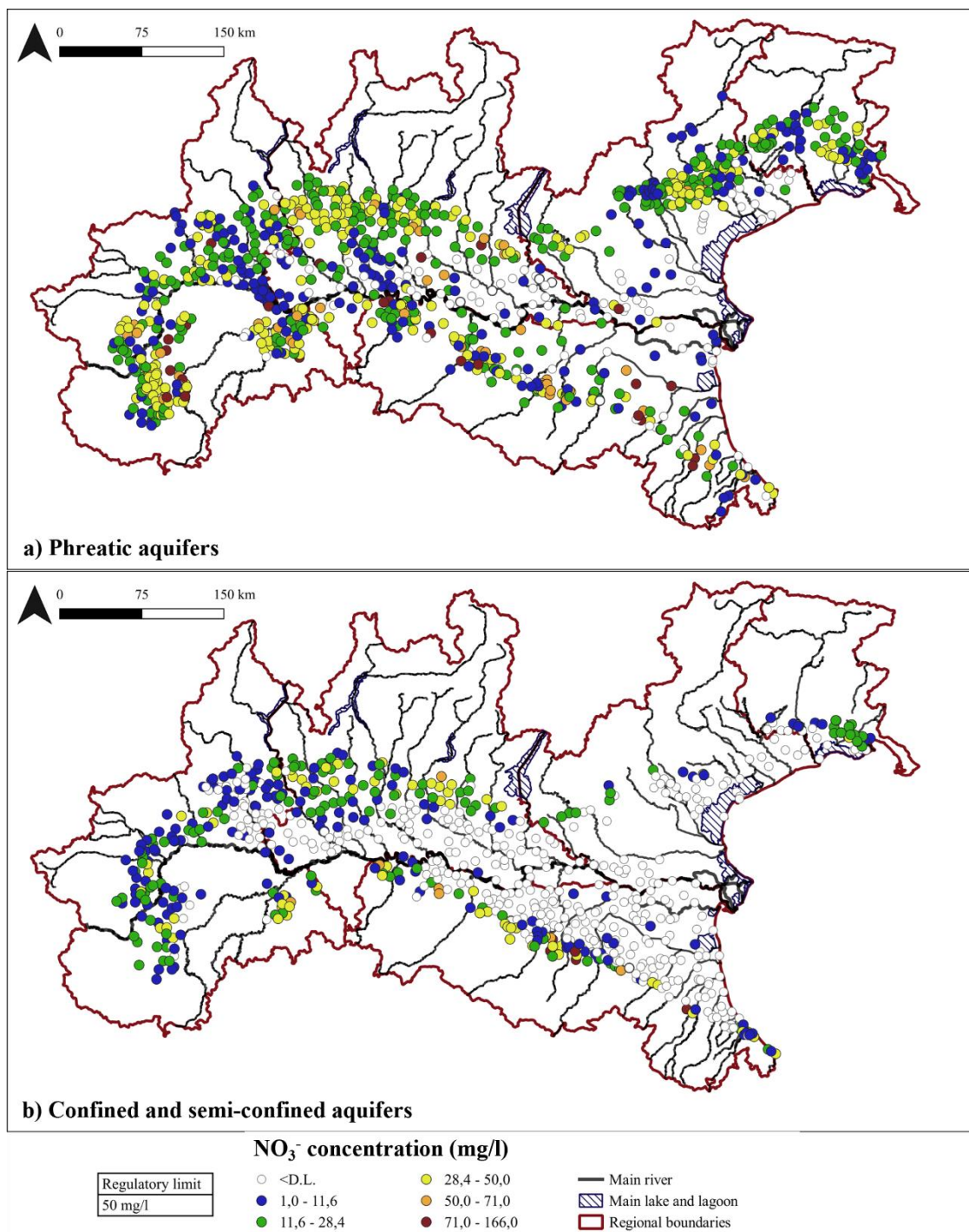


Figure S1: NO<sub>3</sub><sup>-</sup> distribution in the (a) phreatic, and (b) semi-confined and confined aquifers.

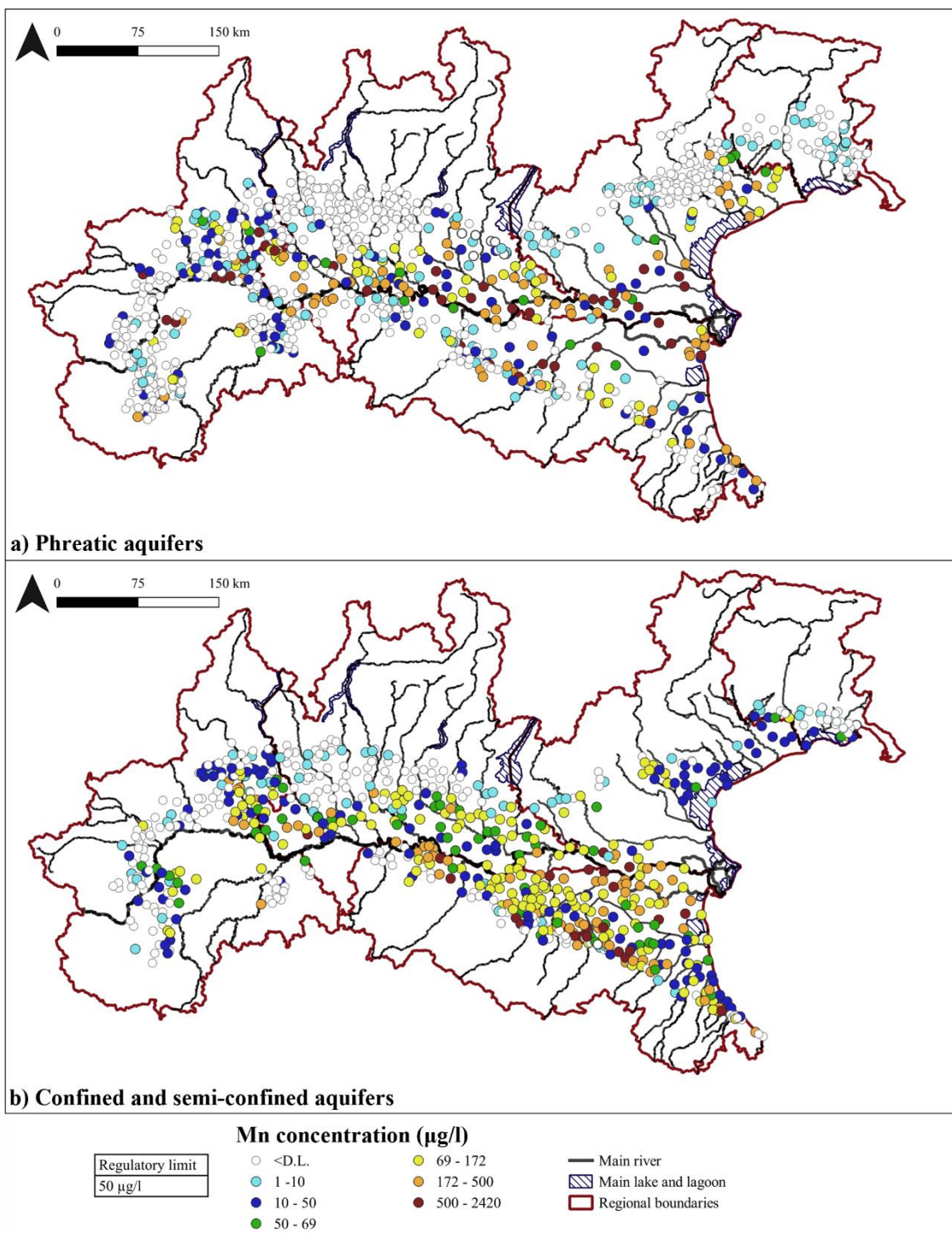


Figure S2: Mn distribution in the (a) phreatic, and (b) semi-confined and confined aquifers.