

## Article

# Geochemical markers as a tool for the characterization of a multi-layer sub-urban aquifer: the case study of Como (northern Italy)

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## Supplementary material

### Tables S1-S4

### Figure S1

**Table S1.** Location and type of water sampled in different sampling points.

Site	Easting (UTM 32N)	Northing (UTM 32N)	Elevation of ground level	Well screen m from ground level	Sampled aquifer
measure unit	m	m	m a.s.l.		-
CC2	511266	5071996	408.5	-	Surface water
CC1	511803	5072232	457	-	Surface water
CC3	507681	5072383	230	-	Surface water
S1	506346	5073366	199.2	12.50-15.50	Shallow aquifer
S2	506345	5073367	199.2	2-5	Shallow aquifer
S3	506172	5073235	199.3	2-10	Shallow aquifer
S4	506008	5073219	200.9	2-10	Shallow aquifer
S5	505920	5073217	200.6	2-10	Shallow aquifer
S6	506038	5073265	199.5	2-10	Shallow aquifer
S7	505942	5073258	200.3	2-5	Shallow aquifer
D1	506331	5072575	202.4	97-98	Deep aquifer
D2	506568	5073200	200.3	66.5-70	Deep aquifer
L1	506409	5073473	200	-	Surface water

**Table S2.** Physicochemical parameters and major ion data of all water samples, including ion balance.

Sample measure unit	Date -	Li µg/L	V µg/L	Mn µg/L	Co µg/L	Ni µg/L	As µg/L	Rb µg/L	Sr µg/L	U µg/L	Cd µg/L	Pb µg/L	Ag µg/L	δD <sub>VSMOW</sub> ‰	δ <sup>18</sup> O <sub>VSMOW</sub> ‰
CC2-May	03/05/2015	0.405	0.307	<LOD	<LOD	0.121	0.324	0.457	185.67	0.139	<LOD	<LOD	<LOD	-8.22	-55.4
CC2-October	04/10/2015	0.536	0.751	0.183	0.081	0.929	1.372	1.251	308.399	0.554	0.062	0.067	0.025	-7.97	-53.5
CC2- November	10/11/2015	0.76	0.916	0.203	0.092	1.105	1.618	1.585	361.532	0.728	0.066	0.115	0.025	-	-
CC1-May	03/05/2015	0.13	0.123	0.11	<LOD	<LOD	<LOD	0.145	142.464	0.026	<LOD	<LOD	<LOD	-8.18	-54.6
CC1-October	04/10/2015	<LOD	0.326	0.778	0.069	0.235	0.261	0.462	190.326	0.229	<LOD	0.064	0.025	-7.79	-50.1
CC1- November	10/11/2015	<LOD	0.324	0.694	0.06	0.263	0.316	0.565	208.308	0.224	0.054	0.068	0.025	-	-
CC3-May	03/05/2015	1.229	0.822	0.949	<LOD	0.635	2.61	0.977	308.736	1.212	<LOD	0.015	<LOD	-8.27	-55.3
CC3-October	04/10/2015	1.303	1.17	1.241	0.172	1.309	4.538	1.294	364.353	2.073	0.056	0.107	0.025	-7.81	-52.8
CC3- November	10/11/2015	1.6	1.09	0.791	0.198	1.445	4.796	1.382	397.596	2.602	0.059	0.109	0.024	-	-
S1-May	03/05/2015	1.923	0.124	333.64	0.91	6.123	23.638	10.382	409.532	0.448	<LOD	0.88	<LOD	-8.55	-58.6
S1-November	10/11/2015	2.416	0.562	419.929	0.559	6.723	28.076	9.179	294.028	0.344	0.109	<LOD	-0.095	-	-
S2-May	03/05/2015	0.468	0.013	114.973	0.004	6.783	1.668	4.664	372.144	<LOD	<LOD	<LOD	<LOD	-8.43	-58.1
S2-October	04/10/2015	0.511	0.187	79.42	0.137	3.4	1.529	5.898	381.054	0.122	<LOD	0.292	0.025	-8.94	-62.2
S2-November	10/11/2015	0.523	0.024	53.166	0.026	2.753	0.138	3.249	227.179	0.059	0.107	<LOD	<LOD	-	-
S3-5	02/05/2015	1.324	0.774	164.524	0.126	3.403	0.202	14.585	315.699	<LOD	<LOD	<LOD	<LOD	-9.01	-61.8
S3-October	05/10/2015	1.506	1.464	167.471	0.571	3.715	6.026	14.027	346.201	0.339	<LOD	0.57	0.025	-7.44	-52.8
S3-November	10/11/2015	1.624	0.45	172.274	0.132	3.293	<LOD	16.095	254.838	0.033	0.107	<LOD	<LOD	-	-
S4-May	02/05/2015	0.104	0.054	47.094	0.008	1.395	1.712	2.155	290.709	<LOD	<LOD	<LOD	<LOD	-8.68	-59.7
S4-October	05/10/2015	0.62	0.247	338.385	0.147	1.229	2.387	7.312	390.038	0.068	0.05	0.04	0.025	-7.79	-54.5
S4-November	11/11/2015	0.495	0.125	247.3	0.054	0.586	0.977	4.501	238.035	0.019	0.107	<LOD	<LOD	-	-
S5-May	02/05/2015	0.205	0.556	82.37	0.191	2.048	3.096	2.396	341.364	0.219	<LOD	<LOD	<LOD	-8.83	-60.4
S5-October	05/10/2015	0.276	2.649	0.071	0.118	1.592	21.517	1.159	423.167	1.414	0.053	0.004	0.025	-8.55	-57.5
S5-November	11/11/2015	0.347	1.242	62.417	0.707	2.275	26.377	0.999	250.165	0.793	0.118	<LOD	<LOD	-	-
S6-May	02/05/2015	1.522	1.106	151.291	0.273	0.803	7.134	6.322	388.759	0.269	<LOD	0.368	<LOD	-8.95	-61.8

S6-October	05/10/2015	1.163	2.072	45.65	0.383	0.162	4.129	2.482	232.974	0.613	0.114	<LOD	<LOD	-8.82	-63.1
S6-November	11/11/2015	0.8	1.548	25.854	0.102	0.746	7.288	2.02	223.279	0.443	0.061	0.139	0.025	-	-
S7-May	02/05/2015	0.156	0.306	210.779	0.031	1.205	1.271	2.552	379.041	<LOD	<LOD	<LOD	<LOD	-8.83	-60.9
S7-October	05/10/2015	0.76	0.384	251.445	0.346	1.483	2.021	6.27	390.367	0.095	<LOD	0.225	0.025	-9.09	-62.2
S7-November	11/11/2015	0.398	0.293	173.102	0.051	0.807	<LOD	3.599	254.244	0.026	0.107	<LOD	<LOD	-	-
D1-May	02/05/2015	2.106	0.002	9.872	0.016	0.326	175.847	1.066	411.028	0.046	<LOD	0.31	<LOD	-8.39	-55.2
D1-October	05/10/2015	2.152	0.078	12.871	0.062	0.374	233.177	1.551	447.582	0.108	0.057	0.043	0.025	-7.89	-53.9
D1-November	11/11/2015	1.944	<LOD	8.577	<LOD	<LOD	166.019	0.964	289.594	0.046	0.108	<LOD	<LOD	-	-
D2-May	02/05/2015	2.055	<LOD	8.689	0.008	0.007	105.11	1.399	452.427	0.058	<LOD	0.109	<LOD	-8.3	-54.5
D2-October	05/10/2015	2.019	0.136	10.945	0.048	0.815	101.447	1.401	445.411	0.095	<LOD	0.069	<LOD	-8.25	-54.5
D2-November	11/11/2015	2.296	<LOD	9.249	<LOD	<LOD	96.615	1.356	372.855	0.051	0.108	<LOD	<LOD	-	-
L1-May	20/05/2021	2.31	0.999	2.745	0.663	1.81	5.089	2.905	200.496	1.68	<LOD	0.11	<LOD	-	-
L1-October	10/10/2020	1.167	0.158	0.03	<LOD	1.489	3.652	1.721	164.21	0.746	<LOD	0.05	<LOD	-	-
Limit of detection (LOD)	-	0.005	0.005	0.015	0.004	0.007	0.042	0.008	0.092	0.005	0.008	0.024	0.013	-	-

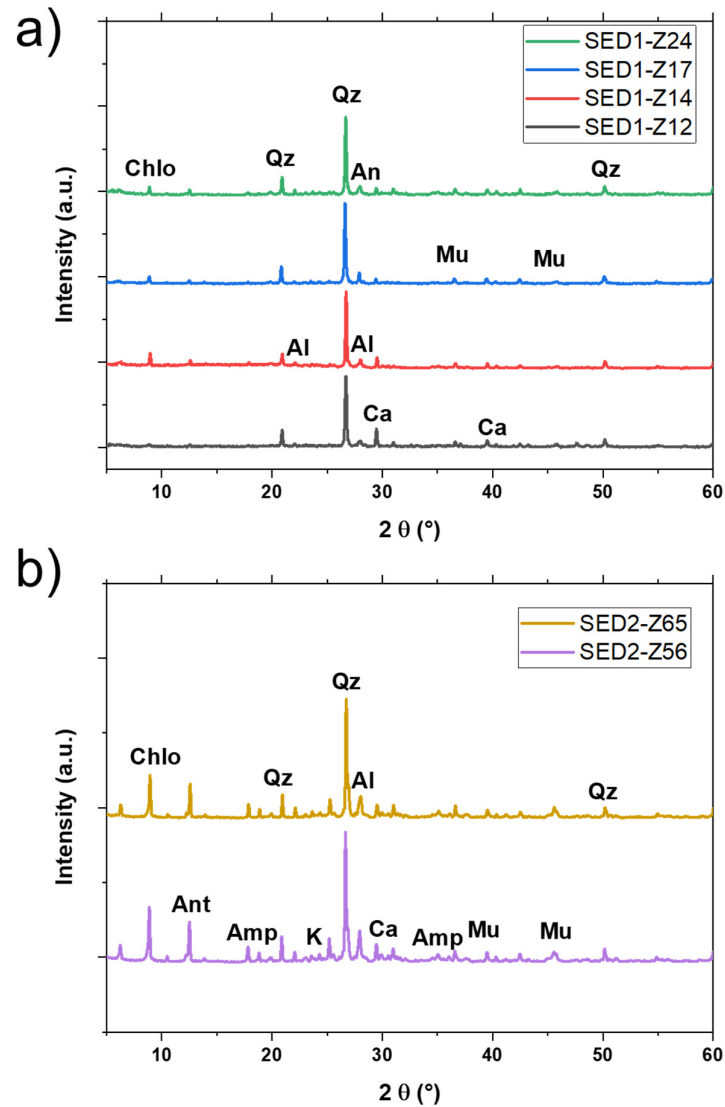
**Table S3.** Trace element concentration and isotopic values of all water samples.

Sample measure unit	Date -	Li µg/L	V µg/L	Mn µg/L	Co µg/L	Ni µg/L	As µg/L	Rb µg/L	Sr µg/L	U µg/L	δD <sub>VSMOW</sub> ‰	δ <sup>18</sup> O <sub>VSMOW</sub> ‰
CC2-May	03/05/2015	0.4046	0.3073	<LOD	<LOD	0.1214	0.3243	0.457	185.6698	0.1391	-8.22	-55.4
CC2-October	04/10/2015	0.5358	0.7506	0.1828	0.0812	0.9289	1.3719	1.2514	308.3987	0.5537	-7.97	-53.5
CC2-November	10/11/2015	0.7602	0.916	0.2033	0.0922	1.1052	1.6182	1.5854	361.5323	0.7284	-	-
CC1-May	03/05/2015	0.1296	0.1232	0.1101	<LOD	<LOD	<LOD	0.1447	142.4643	0.026	-8.18	-54.6
CC1-October	04/10/2015	<LOD	0.3257	0.778	0.0686	0.2349	0.2605	0.4618	190.3258	0.2286	-7.79	-50.1
CC1-November	10/11/2015	<LOD	0.3239	0.6944	0.0604	0.263	0.3157	0.5654	208.3084	0.2244	-	-
CC3-May	03/05/2015	1.2292	0.8217	0.9494	<LOD	0.6352	2.6104	0.9769	308.7358	1.2119	-8.27	-55.3
CC3-October	04/10/2015	1.303	1.1698	1.241	0.1723	1.3092	4.5381	1.2942	364.3525	2.0725	-7.81	-52.8
CC3-November	10/11/2015	1.6001	1.0898	0.7913	0.1981	1.4449	4.7955	1.3816	397.5956	2.6015	-	-
S1-May	03/05/2015	1.9234	0.124	333.6398	0.9099	6.1228	23.6379	10.3823	409.5324	0.448	-8.55	-58.6
S1-November	10/11/2015	2.4162	0.562	419.9294	0.559	6.7233	28.0764	9.1787	294.0276	0.3436	-	-
S2-May	03/05/2015	0.4684	0.0126	114.9732	0.0037	6.7827	1.6676	4.6635	372.1443	<LOD	-8.43	-58.1
S2-October	04/10/2015	0.511	0.1871	79.4202	0.1373	3.3998	1.5287	5.8981	381.0538	0.122	-8.94	-62.2
S2-November	10/11/2015	0.5225	0.0235	53.1657	0.0256	2.7529	0.1384	3.2488	227.1792	0.0585	-	-
S3-May	02/05/2015	1.324	0.7742	164.5236	0.1258	3.4028	0.2022	14.5845	315.6985	<LOD	-9.01	-61.8
S3-October	05/10/2015	1.5064	1.4644	167.471	0.5709	3.715	6.0262	14.0272	346.2007	0.3385	-7.44	-52.8
S3-November	10/11/2015	1.6241	0.4497	172.2741	0.1324	3.2931	<LOD	16.0947	254.838	0.0331	-	-
S4-May	02/05/2015	0.1044	0.0543	47.0937	0.0081	1.395	1.7116	2.1551	290.7088	<LOD	-8.68	-59.7
S4-October	05/10/2015	0.6198	0.2465	338.3847	0.1465	1.229	2.3865	7.3122	390.0381	0.0683	-7.79	-54.5
S4-November	11/11/2015	0.4947	0.1253	247.3001	0.0536	0.5855	0.9771	4.5009	238.0353	0.0187	-	-
S5-May	02/05/2015	0.2054	0.5564	82.3701	0.1907	2.0478	3.0963	2.396	341.3638	0.2186	-8.83	-60.4
S5-October	05/10/2015	0.2756	2.6488	0.0713	0.1175	1.5923	21.5171	1.1592	423.167	1.4139	-8.55	-57.5
S5-November	11/11/2015	0.3472	1.2424	62.4173	0.7071	2.2746	26.3766	0.9986	250.1649	0.7933	-	-
S6-May	02/05/2015	1.5224	1.1059	151.2906	0.273	0.8028	7.1343	6.3223	388.7593	0.2686	-8.95	-61.8
S6-October	05/10/2015	1.1627	2.072	45.65	0.383	0.1624	4.1291	2.4817	232.9742	0.6133	-8.82	-63.1
S6-November	11/11/2015	0.8001	1.5484	25.8543	0.1015	0.7455	7.2877	2.0203	223.2793	0.4432	-	-
S7-May	02/05/2015	0.1562	0.3056	210.7792	0.0306	1.2054	1.2714	2.5517	379.0409	<LOD	-8.83	-60.9
S7-October	05/10/2015	0.7599	0.3844	251.4454	0.3457	1.4827	2.0207	6.2696	390.3667	0.0946	-9.09	-62.2

S7-November	11/11/2015	0.3982	0.293	173.1019	0.0505	0.8069	<LOD	3.5987	254.2439	0.0261	-	-
D1-May	02/05/2015	2.106	0.002	9.8715	0.0157	0.3255	175.8472	1.0659	411.0277	0.0461	-8.39	-55.2
D1-October	05/10/2015	2.1524	0.0779	12.8714	0.0618	0.3735	233.1769	1.551	447.5819	0.1076	-7.89	-53.9
D1-November	11/11/2015	1.9444	<LOD	8.5766	<LOD	<LOD	166.0194	0.9639	289.5943	0.0463	-	-
D2-May	02/05/2015	2.0546	<LOD	8.6885	0.0075	0.0072	105.1099	1.3994	452.4271	0.0577	-8.3	-54.5
D2-October	05/10/2015	2.0193	0.1355	10.9454	0.0481	0.8146	101.4467	1.4014	445.4105	0.0948	-8.25	-54.5
D2-November	11/11/2015	2.2959	<LOD	9.2494	<LOD	<LOD	96.6146	1.3556	372.8549	0.0507	-	-
L1-May	20/05/2021	2.31	0.9989	2.7453	0.6628	1.8101	5.0889	2.9051	200.4959	1.6799	-	-
L1-October	10/10/2020	1.1665	0.158	0.0297	<LOD	1.4891	3.6516	1.7205	164.2097	0.7463	-	-
Limit of detection (LOD)	-	0.0048	0.005	0.015	0.0035	0.0071	0.0422	0.0076	0.0919	0.0048	-	-

**Table S4.** Concentration of different metals in the sediment samples (average values of 3 replicates, relative standard deviation <5%).

Sample Measure unit	Stratigraphic unit	Li	V	Mn	Co	Ni	As	Rb	Sr	U
	-	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
SED1-Z12	1	11.7	35.1	259.92	15.25	26.98	13.68	41.87	193.82	2.39
SED1-Z14	1	19.67	61.49	318.84	9.51	52.66	22.25	47.82	174.18	3.03
SED1-Z17	2	18.28	57	318.84	8.96	48.25	8.31	21.3	94.34	2.16
SED1-Z24	3	25.94	72.25	482.46	11.58	60.53	8.8	41.77	132.95	2.7
SED2-Z56	4	21.8	89.46	382.44	11.55	56.02	28.36	13.75	64.7	2.36
SED2-Z65	5	33.78	104.36	575.4	15.1	73.62	24.02	52.33	185.09	2.68
Limit of detection (LOD)	-	0.05	0.03	0.02	0.04	0.01	0.03	0.02	0.03	0.01



**Figure S1.** XRD spectra of sediment samples collected at different depths in core SED1 (a) and SED2 (b). Major peak patterns of the main minerals present in the samples are indicated by the abbreviations (Qz: quartz; Mu: muscovite; Al: albite; An: anorthite; K: K-feldspars; Amp: amphibole; Ca: calcite; Chlo: chlorite; Ant: antigorite).