

Article

Natural Background Levels of Potentially Toxic Elements in Groundwater from a Former Asbestos Mine in Serpentinite (Balangero, North Italy)

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Supplementary Materials

Figure S1. Stiff diagrams. Colours of the polygons refer to the hydrogeological formation: red = SL; green = SERP; yellow = FGD; blue = BPA

Figure S2. Boxplots and Normal Q-Q plots of the MSs representative values: (a) total Cr; (b) Cr VI; (c) Ni; (d) Mn; (e) Fe; (f) Zn.

Figure S3. Frequency histograms of the MSs representative values (in µg/L)

Figure S4. Frequency histograms of the total available measurements, including ND. Concentrations are in µg/L.

Table S1. Physico-chemical parameters measured in the field, analytical results for major ions and charge balance error (%). GW = groundwater; SW = springwater; SL = Sesia Lanzo; SERP = Serpentinites; FGD = Fluvio-glacial Deposits; BPA = Balangero Plain Aquifer

Table S2. Minor and trace elements. Values in bold exceed the regulatory guidelines. GW = groundwater; SW = springwater; SL = Sesia Lanzo; SERP = Serpentinites; FGD = Fluvio-glacial Deposits; BPA = Balangero Plain Aquifer

Table S3. Total number of measurements of PTEs concentrations available for the evaluation of the NBLs. Values in bold exceed the regulatory limits for groundwater quality.

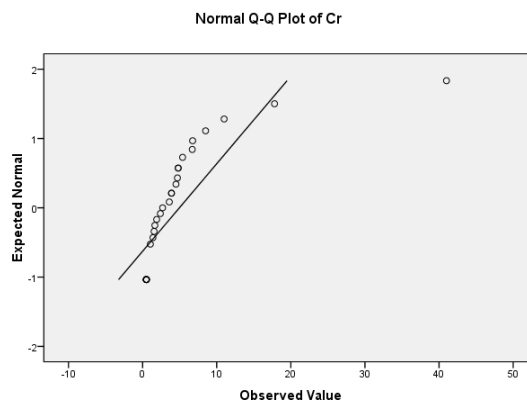
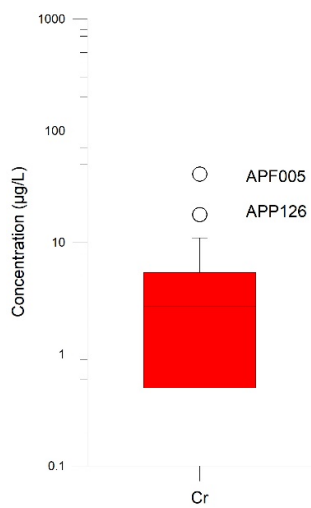
Table S4. Results of the trend analysis conducted for the MSs APP126 (a) and APE031 (b)

Table S5. Results of the Shapiro-Wilk tests to evaluate the normal or lognormal distribution of the representative PTEs values for each MS

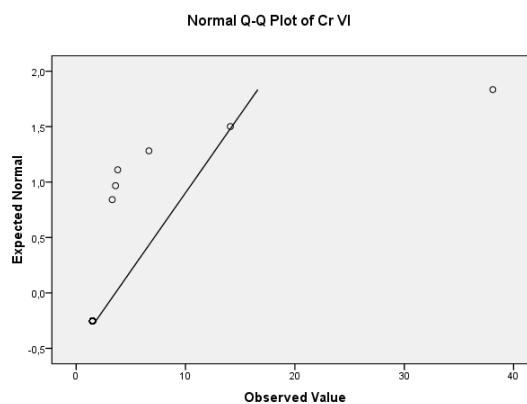
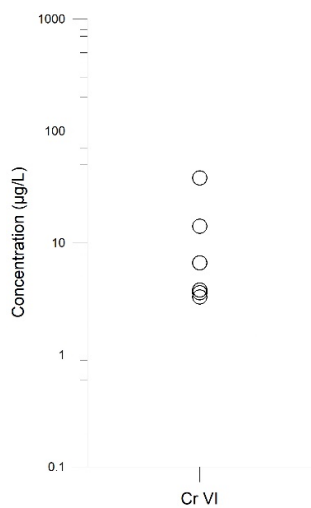
Table 6. Results of the statistical tests to evaluate the presence of normal or lognormal distribution of the total number of PTEs measurements.



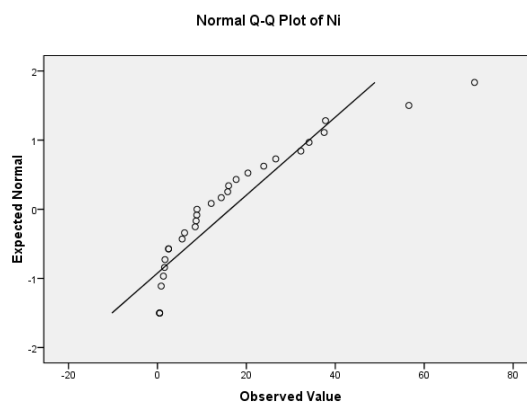
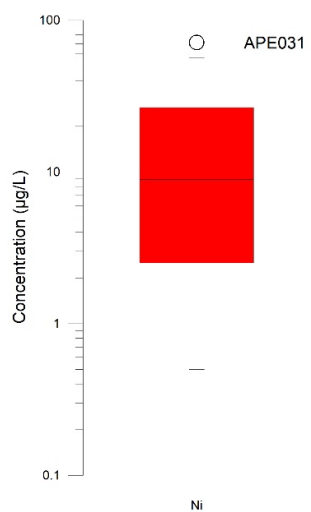
Figure S1. Stiff diagrams. Colours of the polygons refer to the hydrogeological formation: red = SL; green = SERP; yellow = FGD; blue = BPA.



(a)



(b)



(c)

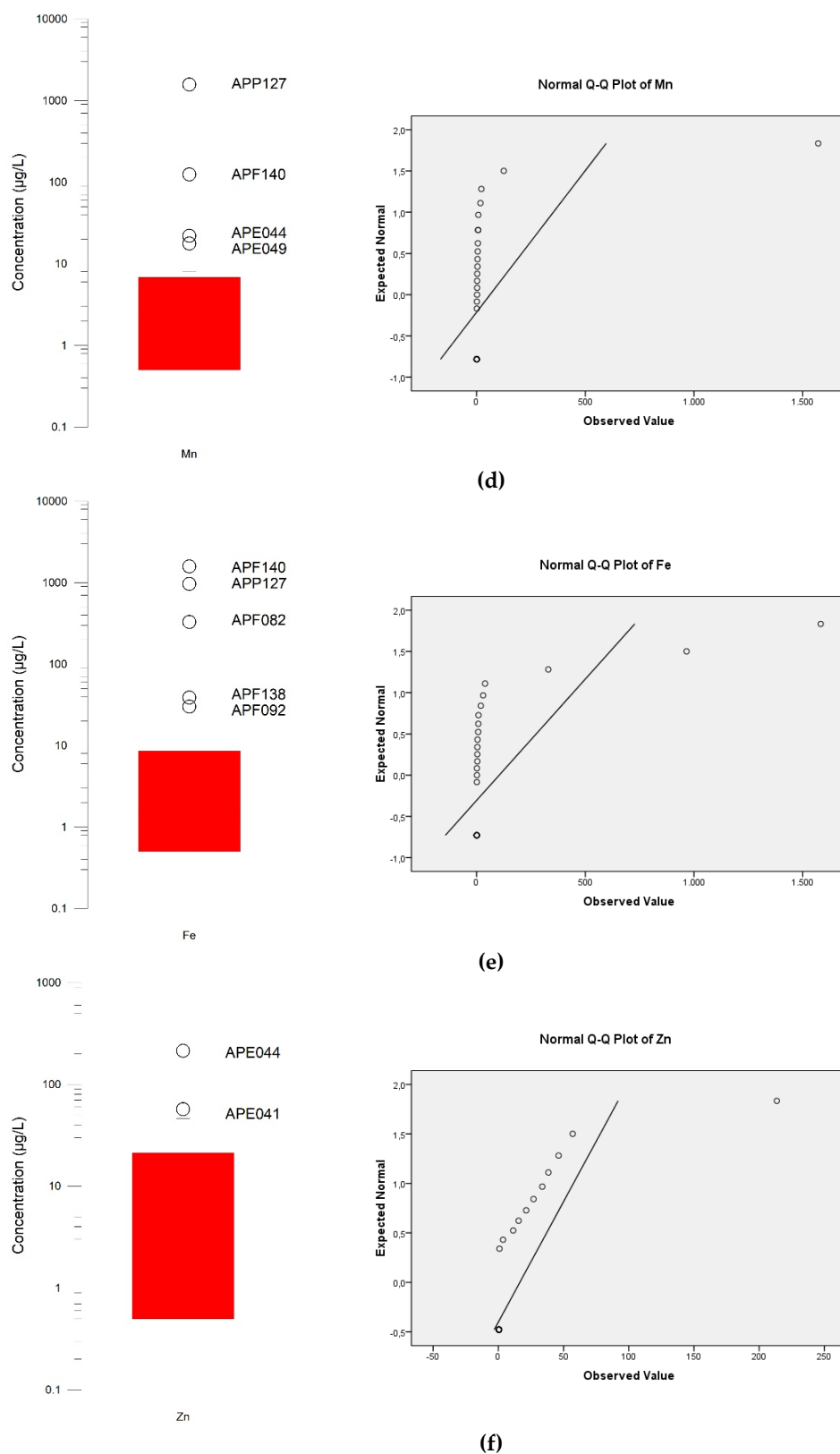


Figure S2. Boxplots and Normal Q-Q plots of the MSs representative values: (a) total Cr; (b) Cr VI; (c) Ni; (d) Mn; (e) Fe; (f) Zn.

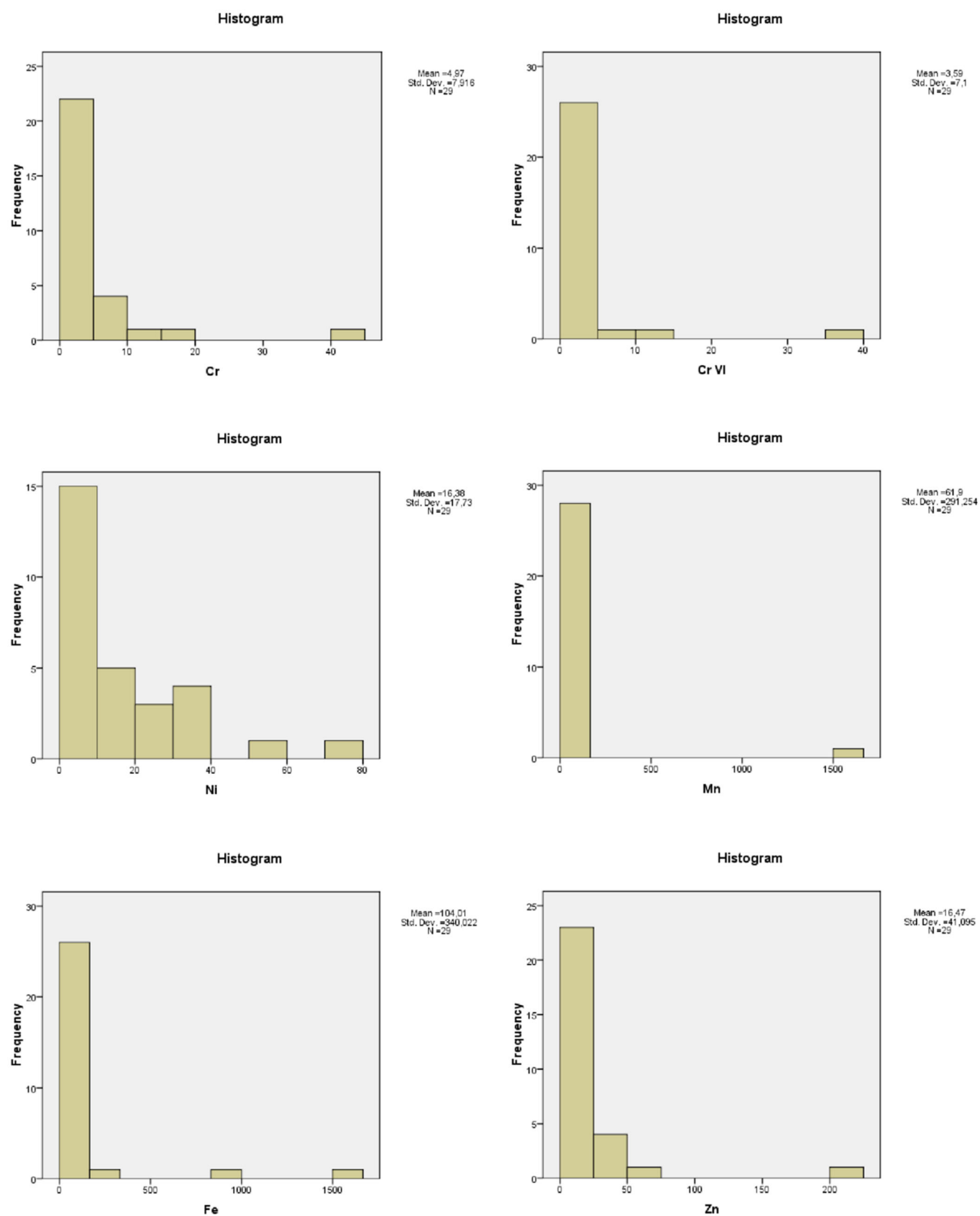


Figure S3. Frequency histograms of the MSs representative values (in µg/L)

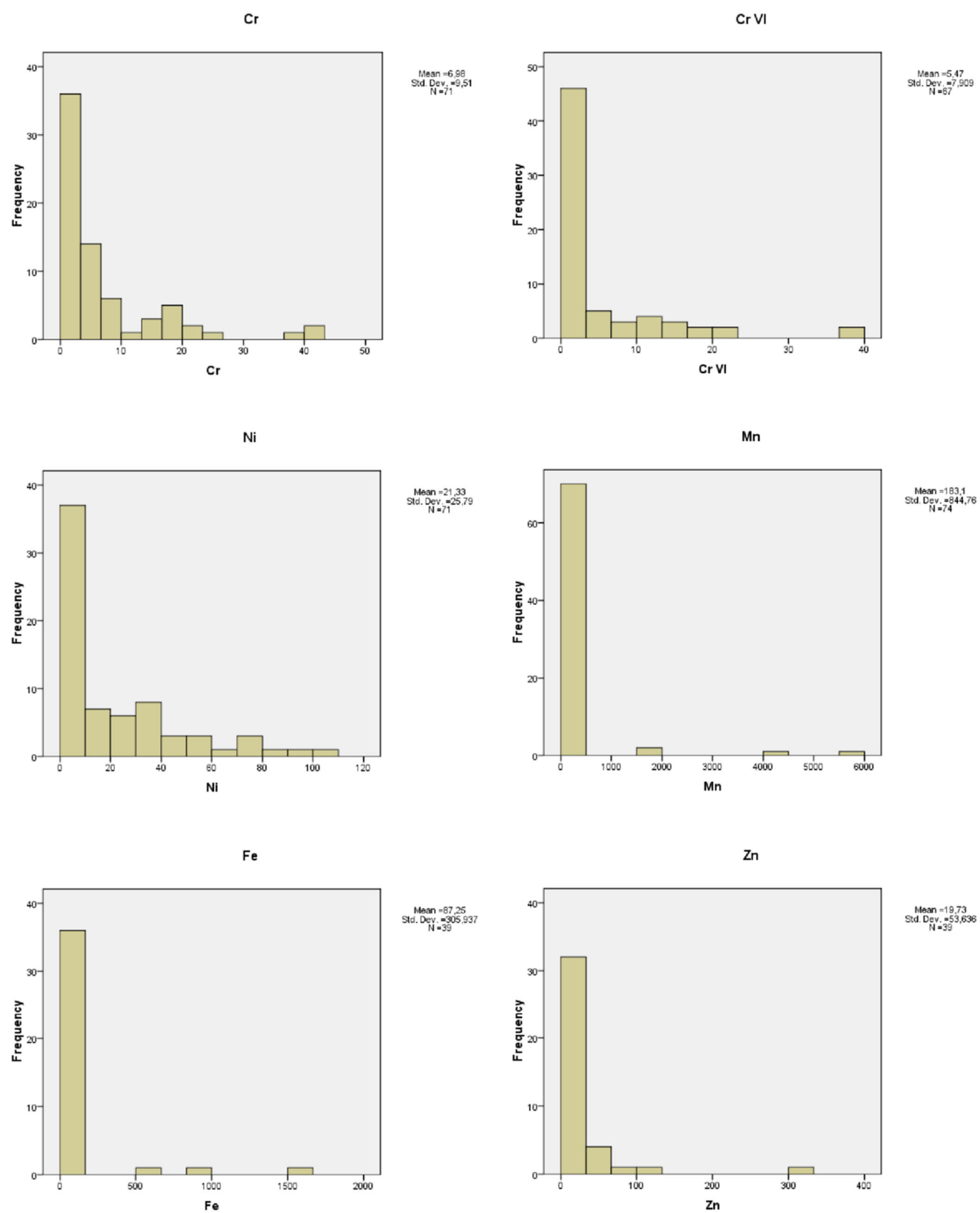


Figure S4. Frequency histograms of the total available measurements, including ND. Concentrations are in $\mu\text{g/L}$.

Table S1. Physico-chemical parameters measured in the field, analytical results for major ions and charge balance error (%). GW = groundwater; SW = springwater; SL = Sesia Lanzo; SERP = Serpentinities; FGD = Fluvioglacial Deposits; BPA = Balangero Plain Aquifer.

Sampling Station	Type	Unit	T °C	E.C. µS/cm	pH	Eh mV	Ca ²⁺ mg/L	Mg ²⁺ mg/L	Na ⁺ mg/L	K ⁺ mg/L	HCO ₃ ⁻ mg/L	Cl ⁻ mg/L	NO ₃ ⁻ mg/L	SO ₄ ²⁻ mg/L	Σ cations meq/L	Σ anions meq/L	Error %
APE031	GW	BPA	14.2	169.7	6.41	329	13.2	9.07	2.67	1.95	68.4	5.37	15.90	8.87	1.57	1.71	-4.4
APS096	GW	FGD	16.8	540.1	6.70	359	23	55.4	1.77	0.59	228.1	1.2	4.96	124	5.80	6.44	-5.2
APP126	GW	FGD	16.2	137.5	7.80	331	6.74	11.8	1.96	0.5	80.4	2.44	2.83	3.8	1.41	1.51	-3.6
APF082	GW	SL	11.0	90.9	6.17	421	10.6	3.92	0.7	<0.5	46.1	0.49	4.83	4.44	0.89	0.94	-2.5
APP128	GW	SL	28.7	491.3	6.65	366	16.4	43.5	7.21	<0.5	241.6	17.6	12.89	20.6	4.72	5.09	-3.8
APP127	GW	FGD	14.9	470.2	6.70	269	16.00	43.5	3.05	0.66	157.4	4.24	1.90	132.0	4.53	5.48	-9.5
APE059	GW	SERP	13.5	191.9	6.36	363	13.9	13.3	2.06	<0.5	96.5	1.97	0.40	19.2	1.89	2.04	-3.9
ASS078	SW	SERP	14.3	255.1	8.07	388	9.82	25.4	0.88	<0.5	137.9	3.54	6.69	19.9	2.63	2.88	-4.5
ASS058	SW	SERP	14.5	186.3	8.30	351	8.12	17.2	<0.5	<0.5	91.4	0.74	3.59	20.5	1.86	2.00	-3.8
ASS080	SW	SERP	17.8	241.8	8.04	352	9.57	22.4	1.37	<0.5	130.5	1.2	2.30	26.1	2.39	2.75	-7.0
APE047	GW	BPA	15.6	175.2	6.30	444	11.70	11.9	4.2	2.7	83.4	7.2	18.5	12.1	1.82	2.12	-7.7
APE108	GW	BPA	14.8	136.4	6.30	414	7.20	11.4	3.97	0.69	73.1	7.2	12.4	7.4	1.49	1.76	-8.3
APE044	GW	BPA	16.6	134.2	6.51	406	10.20	7.23	2.01	2.67	74.8	2.5	5.1	6.4	1.26	1.51	-9.1
APE045	GW	BPA	17.0	123.1	6.56	402	11.00	10	3	1.21	79.2	4.3	7.4	11.7	1.53	1.78	-7.5
APE040	GW	BPA	16.1	360.4	6.52	397	14.60	35.1	7.42	0.51	167.1	14.1	44.3	21.3	3.95	4.30	-4.2
APE041	GW	BPA	14.5	476.9	7.32	403	19.80	16.1	23.2	48.3	189.1	26.8	29.5	31.9	4.56	5.00	-4.6
APE046	GW	BPA	16.6	300.5	7.00	390	25.90	13.7	8.32	15.1	169.6	8.7	17.7	14.2	3.17	3.61	-6.5
APP091	GW	FGD	16.0	117.6	6.75	415	8.62	10.9	2.89	<0.5	73.7	5.5	7.7	6.1	1.47	1.61	-4.8
APE110	SW	FGD	14.9	543.4	6.95	374	15.80	64.1	1.46	<0.5	278.2	1.0	3.8	128.0	6.14	7.31	-8.7
APF092	SW	SL	19.9	61.0	7.38	392	5.29	1.87	3.93	<0.5	26.1	5.9	1.3	4.3	0.60	0.71	-8.0
ASP013	SW	SERP	13.8	438.1	7.70	399	17.80	44.7	4.35	1	266.0	3.2	4.3	47.0	4.78	5.50	-7.0
APP083	GW	FGD	13.3	106.5	7.70	392	6.98	8.74	2.52	0.52	76.7	2.0	2.1	1.5	1.19	1.38	-7.3
ASS079	SW	SL	15.3	266.2	7.10	419	16.20	23.6	2.85	<0.5	152.5	2.9	2.7	30.8	2.89	3.27	-6.2
APF111	GW	SERP	13.3	652.1	8.36	367	9.83	81.9	0.85	0.61	317.2	1.9	2.2	161.0	7.28	8.64	-8.5
APF139	GW	SERP	11.6	541.2	8.70	399	13.80	63.3	1.91	0.51	109.1	3.5	4.1	212.0	5.99	6.37	-3.0
APF005	GW	SERP	13.6	332.7	7.72	413	16.80	30.4	1.78	<0.5	113.5	4.1	5.8	85.9	3.43	3.86	-5.9
APF138	GW	SERP	8.9	583.3	7.65	393	27.60	52.6	2.83	<0.5	93.5	11.9	5.7	227.0	5.84	6.69	-6.7
APF140	GW	SERP	11.8	74.3	6.90	191	5.81	3.57	1.61	<0.5	51.6	2.2	0.04	0.4	0.67	0.92	-15.9
ASM137	SW	FGD	24.7	125.3	7.20	394	1.97	16.9	0.59	<0.5	74.4	0.61	6.7	1.64	1.53	1.38	5.1
ASC077	SW	SL	16.1	112.0	6.51	435	2.89	2.21	8.9	1.06	7.6	13.1	15.5	1.97	0.74	0.78	-2.9

Table S2. Minor and trace elements. Values in bold exceed the regulatory guidelines. GW = groundwater; SW = springwater; SL = Sesia Lanzo; SERP = Serpentinities; FGD = Fluvioglacial Deposits; BPA = Balangero Plain Aquifer.

Sampling Station	Unit	NH ₄ ⁺ mg/L	Si mg/L	Al µg/L	Cr µg/L	Cr VI µg/L	Co µg/L	Ni µg/L	Mn µg/L	Fe µg/L	Zn µg/L
APE031	BPA	<0.026	2.99	2.8	<1.0	<3.0	<1.0	65.2	60.2	8.0	<1.0
APS096	FGD	<0.026	5.52	<1.0	4.8	<3.0	<1.0	23.9	92.1	<1.0	<1.0
APP126	FGD	<0.026	11.7	<1.0	19.8	17.4	<1.0	<1.0	4.4	<1.0	<1.0
APF082	SL	0.05	2.71	10.2	4.2	<3.0	<1.0	6.7	1.8	20.8	<1.0
APP128	SL	<0.026	4.28	1.8	6.7	5.7	<1.0	25.3	15.6	<1.0	<1.0
APP127	FGD	<0.026	10.3	<1.0	<1.0	<3.0	6.6	10.9	5554	966	<1.0
APE059	SERP	0.03	4.44	<1.0	4.5	<3.0	<1.0	26.6	17.7	3.4	<1.0
ASS078	SERP	<0.026	12.9	<1.0	6.5	<3.0	<1.0	9.6	4.0	4.3	<1.0
ASS058	SERP	<0.026	9.72	2.5	1.2	<3.0	<1.0	1.5	<1.0	8.6	<1.0
ASS080	SERP	0.03	8.55	1.5	3.1	<3.0	<1.0	7.9	1.5	5.2	<1.0
APE047	BPA	<0.026	6.59	<1.0	1.3	<3.0	<1.0	59.5	<1.0	<1.0	<1.0
APE108	BPA	<0.026	6.06	<1.0	4.3	<3.0	<1.0	31.6	<1.0	<1.0	46.2
APE044	BPA	<0.026	1.95	<1.0	<1.0	<3.0	<1.0	41.0	31.3	13.1	307
APE045	BPA	<0.026	<1.0	<1.0	<1.0	<3.0	<1.0	37.5	2.7	<1.0	33.7
APE040	BPA	<0.026	6.87	<1.0	3.8	<3.0	<1.0	25.1	<1.0	1.7	<1.0
APE041	BPA	<0.026	1.85	<1.0	3.9	<3.0	<1.0	6.1	<1.0	<1.0	57.0
APE046	BPA	<0.026	5.04	<1.0	5.4	<3.0	<1.0	2.5	<1.0	<1.0	27.0
APP091	FGD	<0.026	4.73	<1.0	1.7	<3.0	<1.0	5.9	<1.0	<1.0	41.3
APE110	FGD	<0.026	<1.0	<1.0	3.6	<3.0	<1.0	17.7	<1.0	<1.0	11.4
APF092	SL	0.04	<1.0	17.8	<1.0	<3.0	<1.0	<1.0	10.1	58.4	<1.0
ASP013	SERP	<0.026	1.67	<1.0	6.3	3.8	<1.0	33.6	<1.0	<1.0	<1.0
APP083	FGD	<0.026	10.3	3.9	5.4	<3.0	<1.0	<1.0	<1.0	<1.0	<1.0
ASS079	SL	0.04	1.37	<1.0	4.8	<3.0	<1.0	16.0	4.0	<1.0	<1.0
APF111	SERP	<0.026	<1.0	<1.0	3.9	<3.0	<1.0	12.1	<1.0	<1.0	<1.0
APF139	SERP	<0.026	<1.0	<1.0	<1.0	<3.0	<1.0	8.9	2.1	19.5	<1.0
APF005	SERP	<0.026	8.88	<1.0	40.6	38.1	<1.0	<1.0	<1.0	2.5	<1.0
APF138	SERP	<0.026	8.03	<1.0	1.9	<3.0	<1.0	1.6	6.8	38.9	<1.0
APF140	SERP	<0.026	<1.0	18.3	<1.0	<3.0	<1.0	<1.0	125	1583	<1.0
ASM137	FGD	<0.026	7.11	<1.0	<1.0	<3.0	<1.0	15.8	<1.0	<1.0	<1.0
ASC077	SL	<0.026	10.7	<1.0	<1.0	<3.0	<1.0	<1.0	5.3	<1.0	3.6

Table S3. Total number of measurements of PTEs concentrations available for the evaluation of the NBLs. Values in bold exceed the regulatory limits for groundwater quality.

Sampling station	Date	Unit	Cr µg/L	Cr VI µg/L	Co µg/L	Ni µg/L	Mn µg/L	Fe µg/L	Zn µg/L
APE031	15/03/2012	BPA	1.0	<3.0	<1.0	94.9	<1.0	6.4	76.3
APE031	24/07/2015	BPA	1.09	<3.0	<1.0	71.3	1.0		
APE031	02/09/2016	BPA					3.3		
APE031	14/12/2016	BPA	1.3	<3.0	<1.0	58.4	1.3		
APE031	20/04/2017	BPA	1.4	<3.0	<1.0	71.3	<1.0		
APE031	27/07/2017	BPA	<1.0	<3.0	<1.0	75.3	11.8		
APE031	12/12/2017	BPA	<1.0	<3.0	<1.0	47.3	<1.0		
APE031	12/01/2018	BPA	1.1	<3.0	<1.0	46	13.6		
APE031	02/10/2018	BPA	38.6	<3.0	<1.0	109	8.3		
APE031	04/12/2018	BPA	<1.0	<3.0	<1.0	84	<1.0		
APE031	25/06/2019	BPA	<1.0	<3.0	<1.0	65.2	60.2	8	<1.0
APS096	23/03/2012	FGD	<1.0	<3.0	<1.0	29.0	1.8	2.7	<1.0
APS096	13/12/2016	FGD	6.6	5.5	<1.0	20.4	5.8		
APS096	25/06/2019	FGD	4.8	<3.0	<1.0	23.9	92.1	<1.0	<1.0
APP126	24/07/2015	FGD	20.6	20.5	<1.0	1.8	<1.0		
APP126	07/09/2015	FGD	14.2	14.1	<1.0	1.6	<1.0		
APP126	03/02/2016	FGD	17.8	14.4	<1.0	1.1	1.8		
APP126	18/07/2016	FGD	17.4	12.7	<1.0	3.2	<1.0		
APP126	14/12/2016	FGD	18.8	18.8	<1.0	1.4	1.2		
APP126	20/04/2017	FGD	16.5	14.1	<1.0	1.2	<1.0		
APP126	27/07/2017	FGD	26.1	22.0	<1.0	1.7	<1.0		
APP126	12/01/2018	FGD	12.2	12.1	<1.0	1.7	<1.0		
APP126	02/10/2018	FGD	22.4	12.8	<1.0	10.5	4.1		
APP126	04/12/2018	FGD	15.3	12.8	<1.0	2.7	<1.0		
APP126	25/06/2019	FGD	19.8	17.4	<1.0	<1.0	4.4	<1.0	<1.0
APF082	17/04/2012	SL	17.8	5.1	<1.0	34	6.9	639	30.5
APF082	25/06/2019	SL	4.2	<3.0	<1.0	6.7	1.8	20.8	<1.0
APP128	07/09/2015	SL	2.7	<3.0	<1.0	3.4	<1.0		
APP128	25/06/2019	SL	6.7	5.7	<1.0	25.3	15.6	<1.0	<1.0
APP127	24/07/2015	FGD	1.4	<3.0	<1.0	6.8	33.3		
APP127	03/02/2016	FGD	<1.0	<3.0	<1.0	2.5	<1.0		
APP127	18/07/2016	FGD	<1.0	<3.0	5.3	13.1	4331		
APP127	26/07/2016	FGD					1577		
APP127	02/09/2016	FGD					1566		
APP127	26/06/2019	FGD	<1.0	<3.0	6.6	10.9	5554	966	<1.0
APE059	26/06/2019	SERP	4.5	<3.0	<1.0	26.6	17.7	3.4	<1.0
ASS078	10/01/2013	SERP	6.9		<1.0	7.8	<1.0		
ASS078	26/06/2019	SERP	6.5	<3.0	<1.0	9.6	4	4.3	<1.0
ASS058	10/01/2013	SERP	1.6		<1.0	3.5	<1.0		
ASS058	26/06/2019	SERP	1.2	<3.0	<1.0	1.5	<1.0	8.6	<1.0
ASS080	03/04/2012	SERP	2.3	<3.0	<1.0	9.1	<1.0	1.8	<1.0
ASS080	26/06/2019	SERP	3.1	<3.0	<1.0	7.9	1.5	5.2	<1.0
APE047	11/01/2013	BPA	1.8		<1.0	53.6	<1.0		
APE047	29/06/2019	BPA	1.3	<3.0	<1.0	59.5	<1.0	<1.0	<1.0
APE108	11/01/2013	BPA	<1.0		<1.0	32.9	4.4		
APE108	29/06/2019	BPA	4.3	<3.0	<1.0	31.6	<1.0	<1.0	46.2
APE044	12/04/2012	BPA	<1.0	<3.0	<1.0	34.6	12.6	2.6	120
APE044	29/06/2019	BPA	<1.0	<3.0	<1.0	41	31.3	13.1	307
APE045	01/07/2019	BPA	<1.0	<3.0	<1.0	37.5	2.7	<1.0	33.7
APE041	01/07/2019	BPA	3.9	<3.0	<1.0	6.1	<1.0	<1.0	57
APE046	01/07/2019	BPA	5.4	<3.0	<1.0	2.5	<1.0	<1.0	27
APP091	30/03/2012	FGD	1.6	<3.0	<1.0	4.0	1.5	1.7	1.4

APP091	21/09/2015	FGD	2.3	<3.0	<1.0	6.7	<1.0		
APP091	04/12/2018	FGD	1.6	<3.0	<1.0	5.2	<1.0		
APP091	01/07/2019	FGD	1.7	<3.0	<1.0	5.9	<1.0	<1.0	41.3
APE110	02/07/2019	FGD	3.6	<3.0	<1.0	17.7	<1.0	<1.0	11.4
APF092	15/03/2012	SL	<1.0	<3.0	<1.0	2.2	3.5	1.6	1.2
APF092	02/07/2019	SL	<1.0	<3.0	<1.0	<1.0	10.1	58.4	<1.0
ASP013	12/03/2012	SERP	9.4	<3.0	<1.0	34.3	<1.0	<1.0	<1.0
ASP013	09/09/2015	SERP	8.5	9	<1.0	34.1	<1.0		
ASP013	02/07/2019	SERP	6.3	3.8	<1.0	33.6	<1.0	<1.0	<1.0
APP083	21/03/2012	FGD	7.0	6.8	<1.0	1.2	2.6	6.2	<1.0
APP083	07/09/2015	FGD	7.4	7.4	<1.0	<1.0	<1.0		
APP083	14/12/2016	FGD	6.5	6.5	<1.0	20.4	<1.0		
APP083	02/07/2019	FGD	5.4	<3.0	<1.0	<1.0	<1.0	<1.0	<1.0
ASS079	02/07/2019	SERP	4.8	<3.0	<1.0	16	4	<1.0	<1.0
APF111	03/07/2019	SERP	3.9	<3.0	<1.0	12.1	<1.0	<1.0	<1.0
APF139	03/07/2019	SERP	<1.0	<3.0	<1.0	8.9	2.1	19.5	<1.0
APF005	29/03/2012	SERP	41.4	38.1	<1.0	<1.0	<1.0	<1.0	<1.0
APF005	03/07/2019	SERP	40.6	38.1	<1.0	<1.0	<1.0	2.5	<1.0
APF138	04/07/2019	SERP	1.9	<3.0	<1.0	1.6	6.8	38.9	<1.0
APF140	04/07/2019	SERP	<1.0	<3.0	<1.0	<1.0	125	1583	<1.0
ASM137	04/07/2019	FGD	<1.0	<3.0	<1.0	15.8	<1.0	<1.0	<1.0
ASC077	22/10/2019	SL	<1.0	<3.0	<1.0	<1.0	5.3	<1.0	3.6
N			71	67	71	71	74	39	39
< LOD			18	46	69	8	36	18	26
%ND			25	69	97	11	49	46	67

Table S4. Results of the trend analysis conducted for the MSs APP126 **(a)** and APE031 **(b)**.

MS APP126	Trend results	Outcome
Cr	p-value = 0.4624, S = -4.0	rejected
Cr VI	p-value = 0.4624, S = -4.0	rejected
Mn	p-value = 0.5791, S = 3.0	rejected
Ni	p-value = 0.4624, S = -0.4	rejected

(a)

MS APE031	Trend results (2015–2019)	Outcome	Trend results (2012–2019)	Outcome
Cr	p-value = 0.8065, S = -2.0	rejected	p-value = 0.2655, S = 10.0	rejected
Mn	p-value = 0.2207, S = 6.0	rejected	p-value = 0.0248, S = 19.0	accepted
Ni	p-value = 0.6133, S = -3.0	rejected	p-value = 0.0127, S = -21.0	accepted

(b)

Table S5. Results of the Shapiro-Wilk tests to evaluate the normal or lognormal distribution of the representative PTEs values for each MS.

	All MSs (Table 1)			Excluding MSs APP127 and APF140		
	Shapiro-Wilk	Shapiro-Wilk (log)	Shapiro-Wilk (log) without ND	Shapiro-Wilk	Shapiro-Wilk (log)	Shapiro-Wilk (log) without ND
Cr	rejected	rejected	W = 0.961 p-value = 0.543	rejected	W = 0.939 p-value = 0.115	W = 0.961 p-value = 0.543
Cr VI	rejected	rejected	W = 0.851 p-value = 0.162	rejected	rejected	W = 0.852 p-value = 0.162
Ni	rejected	W = 0.931 p-value = 0.057	W = 0.949 p-value = 0.221	rejected	W = 0.936, p-value = 0.099	W = 0.944 p-value = 0.186
Mn	rejected	rejected	rejected	rejected	rejected	W = 0.972 p-value = 0.893
Fe	rejected	rejected	rejected	rejected	rejected	W = 0.914 p-value = 0.182
Zn	rejected	rejected	W = 0.940 p-value = 0.517	rejected	rejected	W = 0.940 p-value = 0.517

Table S6. Results of the statistical tests to evaluate the presence of normal or lognormal distribution of the total number of PTEs measurements.

All the available measurements (Table S3)			Excluding data from APP127 and APF140			
	D'Agostino	D'Agostino (log)	Shapiro-Wilk (log) without ND	D'Agostino	D'Agostino (log)	Shapiro-Wilk (log) without ND
Cr	rejected	z = 0.596 p-value = 0.551	z = 0.555 p-value = 0.579*	rejected	z = 0.205 p-value = 0.837	z = 0.462 p-value = 0.644*
Cr VI	rejected	rejected	W = 0.963 p-value = 0.573	rejected	rejected	W = 0.963 p-value = 0.573
Ni	rejected	z = -0.950 p-value = 0.314	z = -0.628 p-value = 0.530*	rejected	z = -1.00 p-value = 0.315	z = -0.778 p-value = 0.437*
Mn	rejected	rejected	rejected	rejected	rejected	W = 0.947 p-value = 0.122
Fe	rejected	rejected	rejected	rejected	rejected	rejected
Zn	rejected	rejected	W = 0.922 p-value = 0.264	rejected	rejected	W = 0.921 p-value = 0.264

* D'Agostino test.