Progetto PRIN 2022 PNRR D.D.1409 del 14 settembre 2022 - "Are facultative cave species drivers of metal contaminants into subterranean environments? (METALCAVE)", (P2022CYF9L- CUP H53D23007660001) - PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) - MISSIONE 4 COMPONENTE 2 INVESTIMENTO 1.1 - "Fondo per il Programma Nazionale della Ricerca (PNR) e Progetti di Ricerca di Rilevante Interesse Nazionale (PRIN)".

Preliminary data on the presence of trace elements in cave water and soil

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Cave soil is a complex matrix composed by materials produced *in situ* and by inputs from surface environments. External inputs are mediated by different atmospheric agents, such as wind, gravity and water fluxes, but also by species able to exploit both surface and subterranean environments (troglophiles and trogloxenes). Independently by the way used to get into the caves, external inputs may be contaminated by pollutants of diverse typology and origin. Once pollutants get into the cave, they are unlikely recycled and can produce substantial harmful effects to the local biodiversity, compromising the entire ecosystem. Nonetheless, besides being bioaccumulated through the local trophic pyramid, pollutants from cave soil can penetrate groundwater, polluting our most important reserve of unfrozen freshwater and therefore representing an important hazard for human health. Developing a monitoring protocol is of high importance to preserve the ecosystem functionality and to avoid negative impacts on human population.

We specifically focused on the concentration of the following biologically available and potentially toxic metals: As, Ba,Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Mo, Ni, Zn, Rb, Se, Sr, Y, Zr, Ag, Ba, Tl, V. Hg, Pb, Bi and Rare Lands from La to Lu. Trace elements analysis was conducted using the inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer, ElanDRCe model). Samples were prepared according to the following phases: Drying; Weighing; Acid Digestion; Evaporation; Bring to volume; Storage. According to D. Lgs. 152/2006, from a first, summary evaluation, the content of trace elements in the cave waters demonstrated particularly high values (orange cells in Table I) only in 2 sites for Mn, Cr and Al.

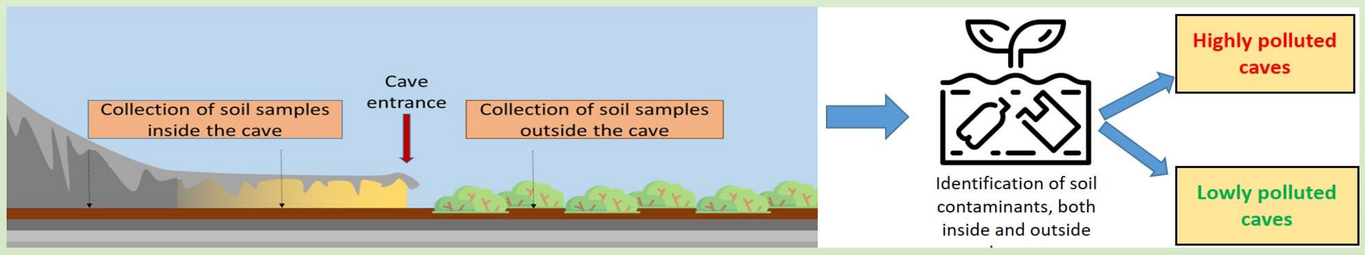


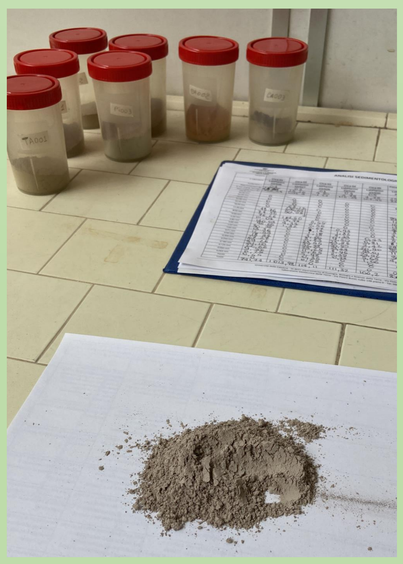
Table I: trace elements accumulation in cave waters. Orange cells reports high values according to D. Lgs. 152/2006

	Al27	As75	Ba138	Bi209	Cd112	Co59	Cr52	Cu63	Mn55	Mo98	Ni60	Pb208	Se82	Sr88	U238	Zn64
Cartiera	148,07	0,08	3,70	0,00	0,01	0,41	3,71	0,87	23,93	-0,09	2,79	0,40	0,24	62,56	0,25	0,88
Calcaferro	1044,95	8,01	21,53	0,00	0,07	1,73	3,70	6,99	128,79	0,99	25,41	0,36	2,49	289,55	0,73	17,74
Forra	17,76	0,13	251,66	0,00	0,01	0,27	10,79	0,33	4,10	-0,18	5,33	0,17	0,25	529,86	0,18	0,75
Piastre	11,19	0,12	94,96	0,00	0,00	0,15	2,30	0,43	0,80	-0,14	2,83	0,13	0,16	369,11	0,10	-0,07
Speloncaccia afotica	109,80	0,10	181,52	0,00	0,02	0,45	0,75	0,50	21,01	-0,22	5,24	0,30	0,16	417,60	0,07	1,40
Tasso	5,27	0,05	253,49	0,00	0,00	0,25	0,29	0,25	0,52	-0,21	5,40	-0,02	0,17	360,53	0,25	-0,26

According to D. Lgs. 152/2006, from a first summary evaluation, the content of trace elements in the cave soils demonstrated particularly high values (orange cells in Table II) only in 2 sites for As, V and Zn

Table II: trace elements accumulation in cave soils. Orange cells reports high values according to D. Lgs. 152/2006

	Rio Freddo Fuori Grotta	S. Eustachio Fuori	S. Eustachio Fotica	S. Eustachio Afotica	Solstizio d'Inverno Fuori	Solstizio d'Inverno Fotica	Solstizio d'Inverno Afotica	Speloncaccia Fotica Esterna	Speloncaccia Fotica Intermedia	Speloncaccia Afotica	Grotta del Tasso di Sofignano esterna	Grotta del Tasso di Sofignano Afotica 1^ stanza	Grotta del Tasso di Sofignano Afotica 2^ stanza	Grotta del Tasso di Sofignano Fotica	Tana di Maggiano Fuori	Tana di Maggiano Afotica	Grotta di Torri Fuori	Grotta di Torri Afotica	Uccole Fuori	Uccole Afotica
As75	47,82	33,01	47,45	41,31	33,03	38,41	39,18	14,39	20,32	17,27	19,47	35,45	24,09	26,40	41,31	38,59	17,51	35,64	15,90	19,48
Ba138	9,95	29,21	65,46	39,24	92,40	53,44	47,56	647,87	774,93	633,33	693,22	1016,25	811,43	537,37	198,23	7,31	569,50	396,45	82,80	166,40
Bi209	0,03	0,12	0,02	0,02	0,34	0,17	0,09	0,46	0,38	0,34	0,43	0,36	0,51	0,27	0,31	0,03	0,23	0,12	0,12	0,36
Cd112	0,53	0,43	1,02	0,28	1,13	1,37	3,20	1,26	1,16	1,09	2,91	3,90	1,35	1,41	2,00	0,17	0,64	0,42	0,43	0,69
Co59	11,41	23,00	11,89	12,60	14,52	22,54	16,30	33,14	30,76	25,07	30,53	105,79	34,40	35,52	13,83	23,67	19,63	12,68	12,61	12,81
Cr52	-5,09	12,29	-6,88	-1,02	27,44	9,54	2,69	100,81	96,73	72,67	119,05	72,47	147,46	73,96	32,44	-5,91	70,47	26,26	18,03	36,12
Cu63	3,73	9,67	20,48	10,97	23,28	15,65	19,38	85,92	78,02	70,16	88,18	61,40	106,29	58,59	40,35	9,88	50,38	26,96	20,55	42,93
Mn55	65,13	287,32	286,01	291,00	309,91	166,77	228,51	2561,99	2221,56	1915,43	1424,05	7514,53	1218,46	1867,71	5467,36	88,76	1035,31	443,81	296,23	304,77
Mo98	0,28	1,26	0,39	0,54	0,78	0,45	0,41	0,59	0,65	0,64	0,57	1,16	0,76	0,78	0,80	0,28	0,65	0,25	0,98	0,99
Ni60	39,23	27,74	42,15	35,30	46,63	48,71	47,36	93,61	74,33	58,24	99,02	92,27	105,75	73,69	45,36	32,75	60,29	48,55	17,14	34,29
Pb208	4,68	10,80	6,38	6,32	27,01	11,29	4,88	40,14	28,09	31,95	21,44	48,63	23,99	22,11	102,93	25,60	15,40	11,39	22,46	26,20
Sr88	130,19	159,47	119,37	95,88	92,30	103,92	55,67	98,54	103,15	75,68	158,30	146,04	91,79	342,74	45,64	11,30	217,94	278,14	82,90	140,67
U238	0,49	0,23	0,19	0,16	0,76	0,45	0,35	1,68	1,66	1,58	1,88	1,18	1,97	1,22	0,83	0,08	1,17	0,58	0,41	1,11
V51	57,54	74,06	56,04	51,22	99,92	76,91	64,09	147,88	160,93	131,34	161,78	136,81	201,21	122,76	101,02	43,23	115,03	84,10	62,19	87,63
Zn64	36,03	27,80	78,94	78,09	119,54	77,02	65,79	218,30	170,19	159,37	174,17	157,39	222,56	133,51	191,28	68,16	97,60	64,06	48,28	173,14



	Cartiera Fuori	Cartiera Afotica	Cartiera Fotica	Calcaferro fuori	Calcaferro afotica	Calcaferro fotica	Forra Lucia Afotica Cascata	Forra Lucia Afotica 2^ Entrata	Forra Lucia Fuori	Forra Lucia Fotica	Grotta Bella Afotica Deep	Grotta Bella Afotica	Grotta Bella Fotica	Grotta Bella Fuori	Grotta Leonardo Fotica	Grotta Leonardo Afotica	Grotta Leonardo Fuori	Grotta delle Nottole Fuori	Grotta delle Nottole Fotica	Pozzo Cambiano Fotica	Pozzo Cambiano Afotica	Piastre Fuori	Piastre Fotica	Piastre Afotica
As75	33,71	19,79	39,42	941,88	452,71	327,34	16,17	18,02	32,96	19,29	39,43	70,59	52,39	38,51	33,33	42,01	41,11	49,46	45,52	41,80	31,17	19,14	17,03	21,62
Ba138	38,15	102,75	51,67	2451,46	702,75	2445,79	687,88	737,12	948,38	822,23	329,00	286,08	252,31	185,34	93,39	111,59	115,11	30,43	142,14	169,52	352,99	362,55	339,97	246,23
Bi209	0,15	0,34	0,09	1,53	0,25	1,43	0,40	0,33	0,43	0,34	0,19	0,14	0,15	0,20	0,09	0,10	0,16	0,05	0,06	0,04	0,15	0,45	0,30	0,21
Cd112	0,59	0,70	0,42	0,82	0,22	0,29	2,52	0,78	1,30	1,39	0,86	0,80	0,50	0,76	1,23	1,34	0,95	0,85	0,58	0,94	0,86	0,46	0,43	0,64
Co59	25,16	25,01	9,76	33,30	8,42	10,66	42,58	21,11	36,31	27,02	29,24	10,47	10,07	8,49	19,32	22,50	12,68	16,17	17,10	12,67	11,79	33,32	29,79	24,85
Cr52	25,62	57,55	7,16	72,23	29,13	74,94	133,29	87,82	178,42	107,03	42,80	18,21	28,47	11,31	12,79	17,45	17,11	-8,16	5,44	-0,60	2,90	179,46	136,40	82,30
Cu63	62,28	91,54	28,60	74,61	119,76	46,55	98,90	63,47	101,06	84,13	60,62	15,25	27,81	36,48	30,43	32,68	29,50	10,06	21,05	31,89	44,47	59,23	42,83	44,68
Mn55	368,28	1026,87	565,91	3642,13	711,77	245,94	3104,77	822,51	2080,18	1862,92	796,58	311,79	423,59	391,54	345,70	391,06	560,88	247,67	447,70	492,51	762,98	1936,31	1262,79	1023,34
Mo98	0,31	0,62	0,43	31,37	14,97	14,30	1,36	0,54	0,96	5,01	1,65	8,26	0,96	0,86	0,43	0,43	0,36	0,33	0,40	0,92	0,76	0,31	0,41	0,34
Ni60	61,77	97,88	46,06	92,64	78,06	43,28	107,18	66,60	113,50	83,39	48,79	32,92	36,17	35,12	43,99	56,56	47,75	41,89	44,36	35,97	38,34	138,38	114,15	90,56
Pb208	11,72	16,94	18,55	122,21	29,15	58,23	25,16	16,96	22,99	47,80	14,68	7,00	11,35	22,19	5,40	5,76	21,23	10,02	4,82	5,24	5,85	26,49	87,80	13,95
Sr88	124,89	30,85	208,90	47,49	34,56	42,28	96,24	151,53	148,69	101,14	118,24	99,72	156,11	223,56	106,60	124,73	114,87	115,81	121,77	136,56	145,89	184,08	489,52	447,04
U238	0,52	1,08	0,32	1,57	3,75	2,55	1,76	1,62	2,55	1,46	0,80	0,30	0,54	0,75	0,51	0,64	0,57	0,17	0,30	0,38	0,55	1,69	1,30	1,06
V51	88,60	123,93	72,52	367,67	197,29	257,62	172,72	134,55	286,10	142,24	131,72	122,29	119,56	85,51	67,94	81,14	79,28	61,62	67,22	63,96	59,18	172,44	125,95	107,46
Zn64	93,68	141,28	97,80	260,60	116,09	232,24	179,87	166,97	188,01	224,43	135,41	62,98	101,32	1994,49	130,47	164,59	164,46	44,37	77,40	141,10	273,53	166,84	129,58	98,04