

Evaluation of PM2.5 sources in Skopje Urban Area using positive matrix factorization

Dejan Mirakovski^{1,2}, Afrodita Zendelska^{1,2*}, Blazo Boev^{1,2}, Marija Hadzi-Nikolova^{1,2}, Tena Shijakova-Ianova^{1,2}, Nikolinka Doneva¹, Ivan Boev¹, Gorgi Dimov¹, Elena Doneva², Ana Mihailovska²

¹Faculty of Natural and Technical Sciences, Goce Delcev University, Stip, North Macedonia

²AMBICON Laboratory, Goce Delcev University, Stip, North Macedonia

*Corresponding author: afrodita.zendelska@ugd.edu.mk

Appendix A: Sampling and analysis details

Table A.1. Sampling stations and details about PM2.5 sampling and analysis.

Country, City		North Macedonia, Skopje	
Municipality		Karposh	Novo Lisiche
Coordinates	X	4 650 585	4 647 405
	Y	7 532 044	7 538 493
Type of sampling station		UB	UT
Sampler		PNS 18T-DM-6.1 Comde Derenda	PNS 18T-DM-6.1 Comde Derenda
Flow rate (m ³ /h)		2.3	2.3
Filter matrix		PTFE	PTFE
No. samples		376	367
Species		Elements, BC, WSI	Elements, BC, WSI
Chemical analysis		EDXRF, Spectrophotometer, Optical transmissometer	EDXRF, Spectrophotometer, Optical transmissometer
Sampling calendar	Start	29.10.2020	29.10.2020
	End	04.12.2021	04.12.2021

(UB - Urban Background; UT- Urban-Traffic; WSI – Water soluble ions; BC - Black Carbon;
EDXRF – energy dispersive X-ray fluorescence spectrometer)

Appendix B. PMF data input

Table B.2. Descriptive statistic -Karposh urban background data set

	Units	N	Mean	SD	Minimum	Maximum	C.V.	95 th %	5 th %
PM2.5	$\mu\text{g}/\text{m}^3$	331	36.40	24.18	3.30	167.35	0.66	87.81	11.69
Na	ng/m^3	331	10.425	9.143	1.070	87.353	0.877	27.943	5.176
Mg		331	35.095	39.657	0.519	271.873	1.130	97.926	1.863
Al		331	107.718	140.459	1.536	928.900	1.304	338.586	7.892
Si		331	286.289	329.589	1.460	2212.996	1.151	844.820	19.509
S		331	158.655	75.975	19.358	467.932	0.479	319.400	68.170
K		331	305.563	296.774	32.398	1570.100	0.971	872.200	55.809
Ca		331	683.073	481.733	7.955	3247.775	0.705	1532.248	71.644
Ti		331	14.016	15.260	0.608	111.611	1.089	40.119	2.032
Cr		331	0.825	0.671	0.025	4.053	0.813	2.127	0.151
Mn		331	3.993	2.351	0.050	15.422	0.589	7.930	0.579
Fe		331	266.110	211.006	14.097	1540.138	0.793	620.022	48.082
Co		331	0.031	0.020	0.003	0.113	0.646	0.077	0.014
Ni		331	0.388	0.327	0.025	1.435	0.841	1.007	0.076
Cu		331	5.700	4.374	0.101	25.627	0.767	13.291	0.234
Zn		331	36.834	34.976	3.474	253.341	0.950	102.608	8.761
As		331	1.486	3.123	0.327	15.608	2.101	10.686	0.375
Sc		331	1.618	0.134	0.692	3.723	0.083	1.610	1.610
V		331	1.789	0.793	0.442	5.337	0.443	3.159	0.533
Rb		331	0.394	0.320	0.008	1.276	0.811	0.988	0.050
Sb		331	1.603	0.598	0.305	3.122	0.373	2.769	0.501
Ba		331	3.553	4.171	0.039	65.199	1.174	8.521	1.762
Ce		331	0.150	0.110	0.003	1.697	0.735	0.288	0.031
Sm		331	0.007	0.006	0.001	0.030	0.845	0.021	0.002
W		331	0.059	0.066	0.003	0.282	1.113	0.209	0.008
Pb		331	8.671	5.245	0.176	38.176	0.605	17.848	2.291
Th		331	0.036	0.044	0.000	0.146	1.233	0.126	0.003
Cl		331	80.930	88.546	0.207	628.315	1.094	239.502	4.040
Se		331	0.708	0.575	0.025	3.776	0.812	2.064	0.201
Cd		331	4.576	1.448	0.503	12.990	0.316	6.445	2.643
EC		331	6022.96	2931.34	389.68	14844.52	0.487	10829.35	1703.23
NH ₄		331	1056.23	829.85	45.45	4234.07	0.786	2901.27	145.43
SO ₄		331	5664.07	9937.10	9.09	44267.09	1.754	36904.06	418.12
NO ₃		331	2156.86	3050.58	9.09	17204.40	1.414	8821.60	25.45

Table B.2. Descriptive statistic -Novo Lisiche urban exposed data set

	Units	N	Mean	SD	Minimum	Maximum	C.V.	95 th %	5 th %
PM2.5	µg/m ³	255	45.68	28.85	10.51	165.61	0.63	104.47	16.03
Na	ng/m ³	255	14.690	32.978	0.214	435.500	2.245	35.873	5.747
Mg		255	44.240	41.085	0.503	387.685	0.929	107.387	2.573
Al		255	124.186	129.011	2.366	1150.468	1.039	318.957	15.422
Si		255	340.465	306.990	3.977	2837.400	0.902	769.318	52.311
S		255	185.804	120.843	31.165	696.555	0.650	435.384	66.978
K		255	385.263	399.742	43.726	2432.802	1.038	1210.378	64.470
Ca		255	1158.023	737.345	5.186	5689.805	0.637	2372.790	222.834
Ti		255	16.328	13.686	0.514	119.671	0.838	37.929	3.940
Cr		255	1.356	1.121	0.025	8.509	0.827	3.094	0.176
Mn		255	4.898	2.438	0.298	15.885	0.498	8.985	1.604
Fe		255	430.872	256.085	27.692	2026.031	0.594	837.294	123.955
Co		255	0.029	0.021	0.003	0.143	0.702	0.070	0.005
Ni		255	0.452	0.414	0.025	4.167	0.915	1.158	0.095
Cu		255	7.632	5.790	0.176	64.861	0.759	16.036	1.453
Zn		255	47.279	38.891	4.557	264.099	0.823	127.433	12.285
As		255	1.420	3.132	0.101	16.866	2.205	11.328	0.375
Sc		255	1.636	0.156	0.201	2.653	0.095	1.841	1.610
V		255	2.068	0.863	0.496	4.934	0.417	3.557	0.609
Rb		255	0.485	0.381	0.023	1.810	0.785	1.199	0.068
Sb		255	1.792	0.723	0.356	5.639	0.403	2.986	0.795
Ba		255	6.382	4.800	0.157	35.999	0.752	14.002	1.859
Ce		255	0.206	0.999	0.003	16.071	4.849	0.222	0.027
Sm		255	0.006	0.004	0.001	0.022	0.749	0.014	0.003
W		255	0.057	0.063	0.003	0.234	1.105	0.195	0.008
Pb		255	9.116	5.534	0.831	42.645	0.607	18.442	2.233
Th		255	0.033	0.043	0.000	0.145	1.274	0.127	0.002
Cl		255	112.643	117.561	0.076	907.729	1.044	332.427	6.188
Se		255	0.799	0.778	0.025	4.657	0.974	2.517	0.250
Cd		255	4.748	1.307	0.831	11.504	0.275	7.592	3.653
EC		255	15436.51	8444.12	2490.00	38625.00	0.547	33083.14	4904.00
NH ₄		255	868.70	794.15	27.27	4704.45	0.91	2298.82	118.17
SO ₄		255	4126.41	6335.67	9.09	53938.79	1.54	11026.00	558.12
NO ₃		255	2240.81	2969.53	9.09	18742.76	1.32	8000.85	25.45

Appendix C. PMF source profiles (% of species and concentration of species)

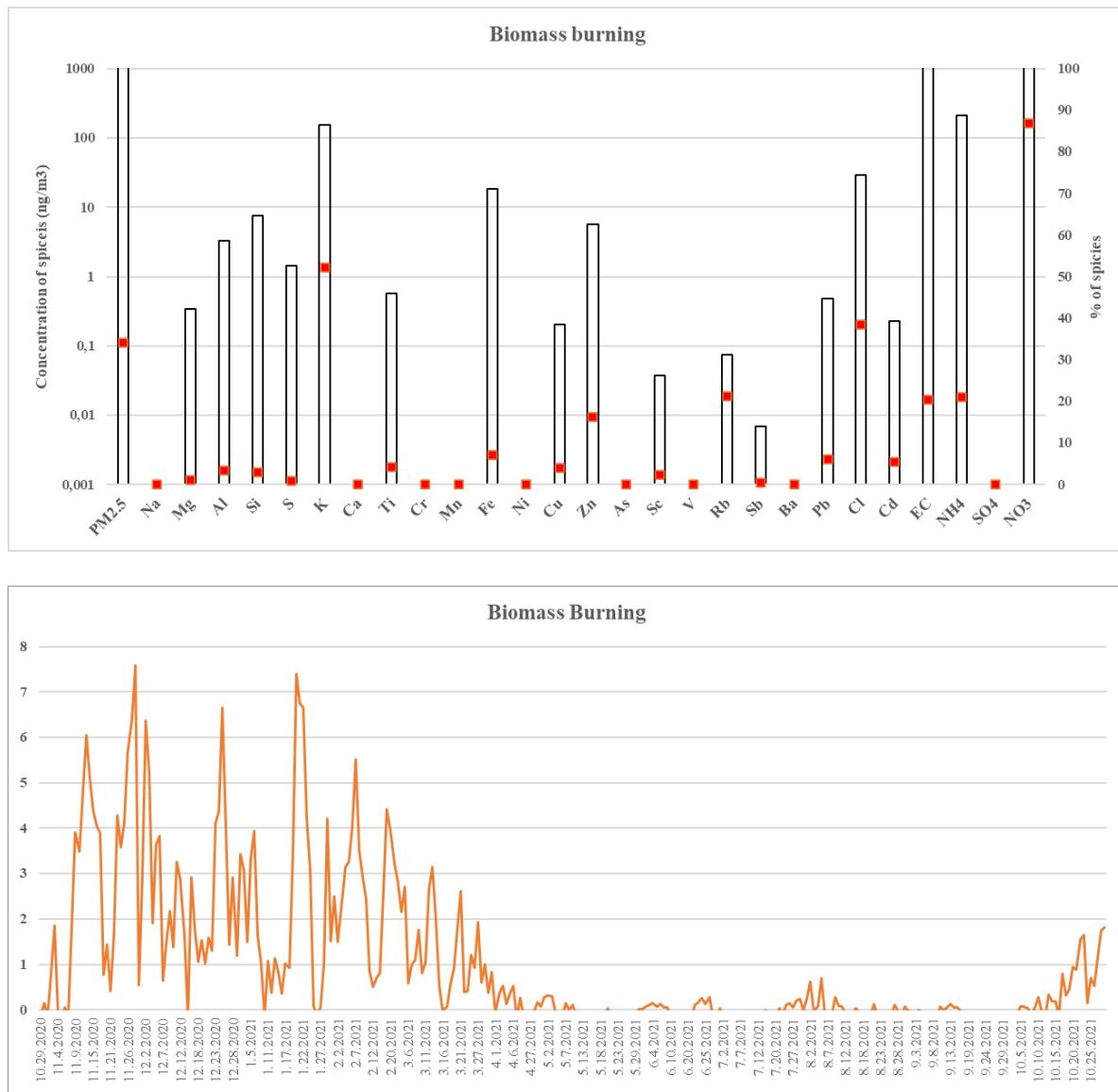


Figure C1. Biomass burning profiles and temporal distribution – Karposh urban background site

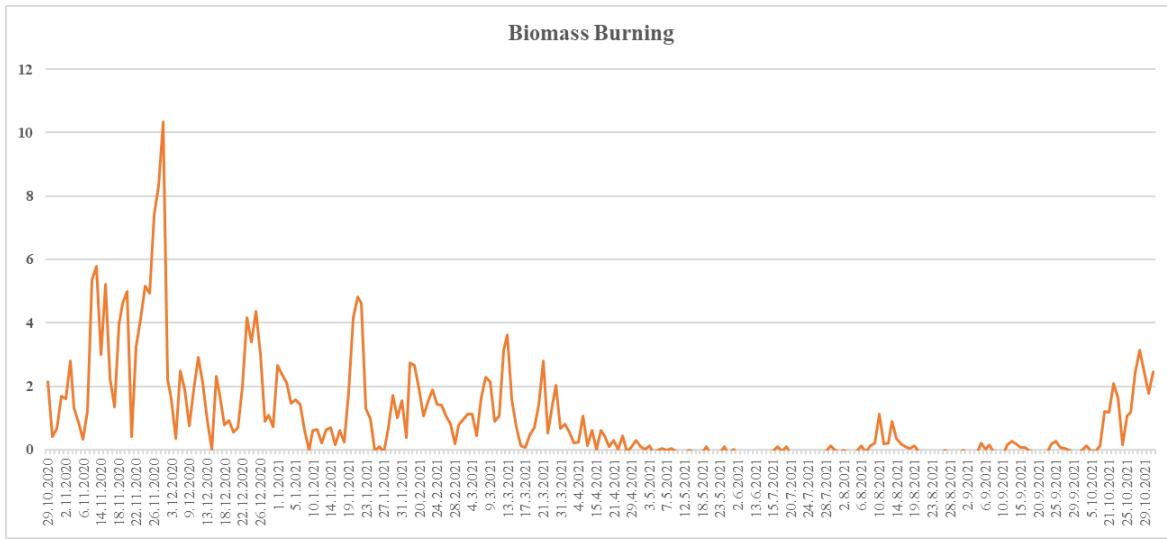
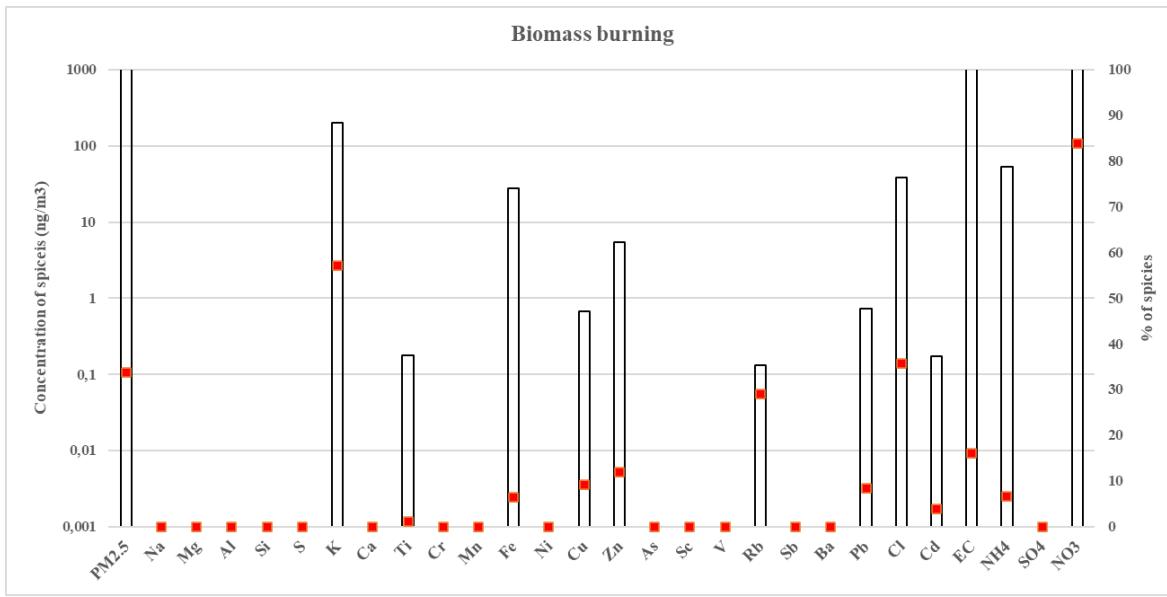


Figure C2. Biomass burning profiles and temporal distribution – Novo Lische urban exposed site

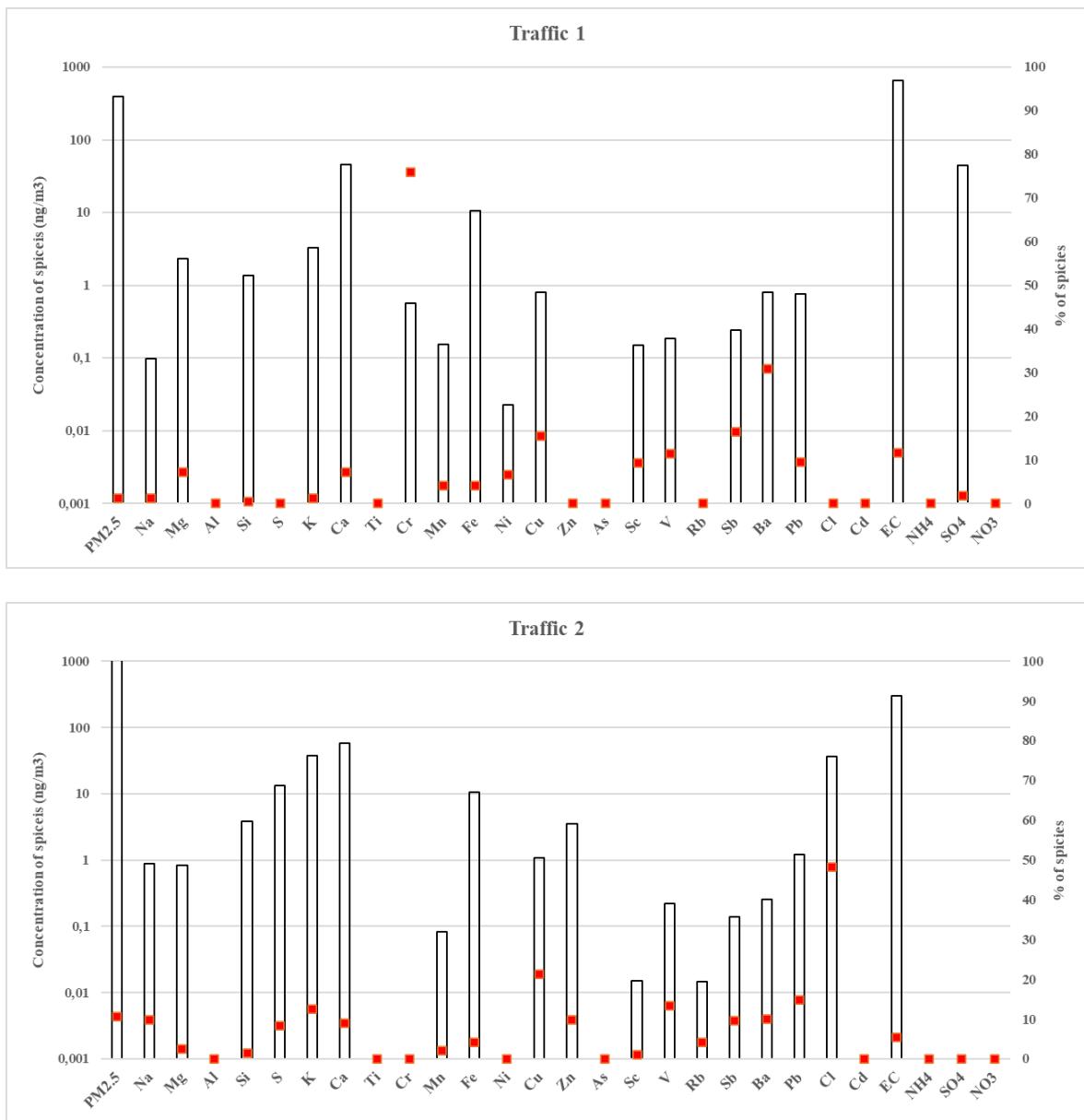


Figure C3. Traffic related profiles – Karposh urban background site

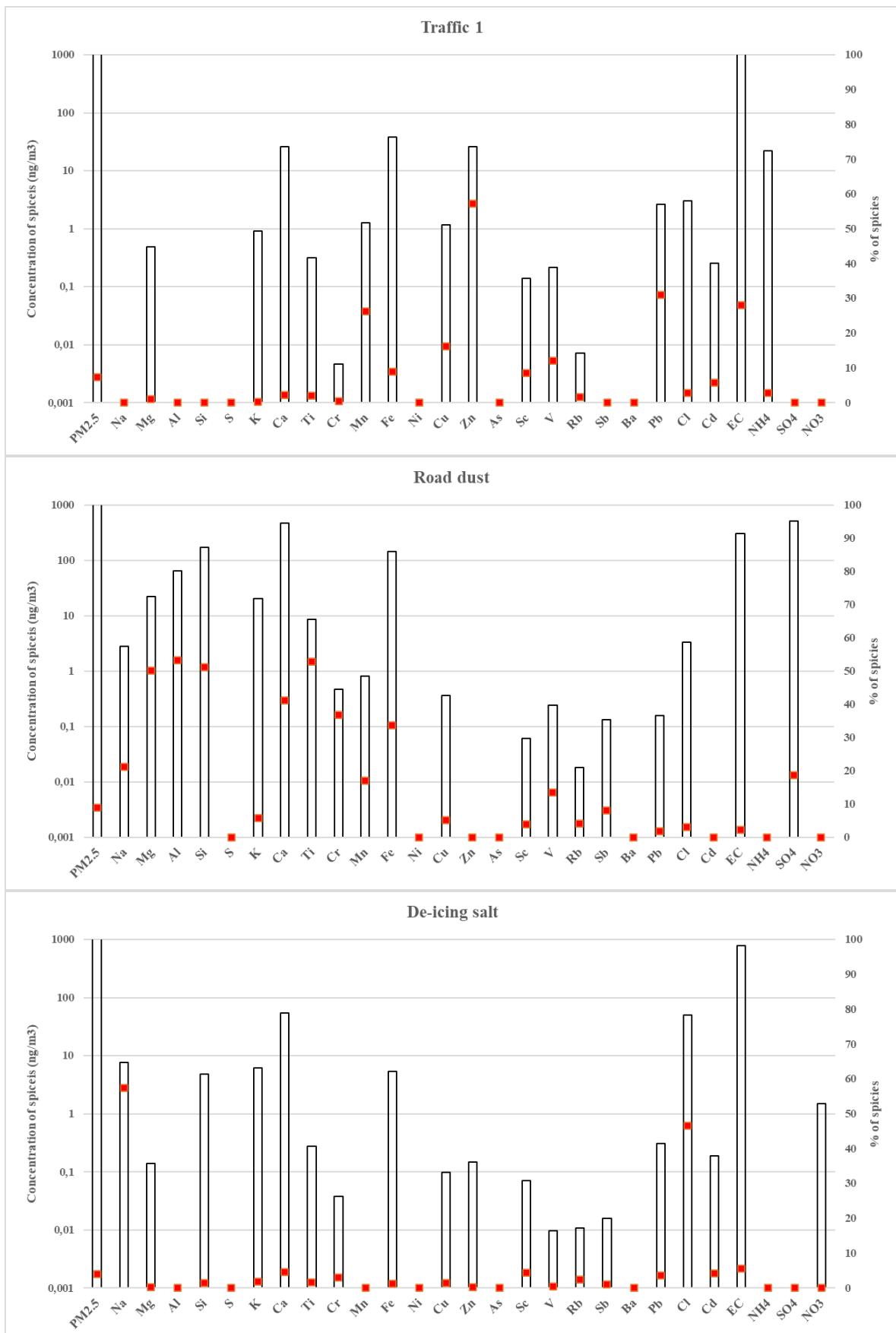


Figure C4. Traffic related profiles – Novo Lisiche urban exposed site

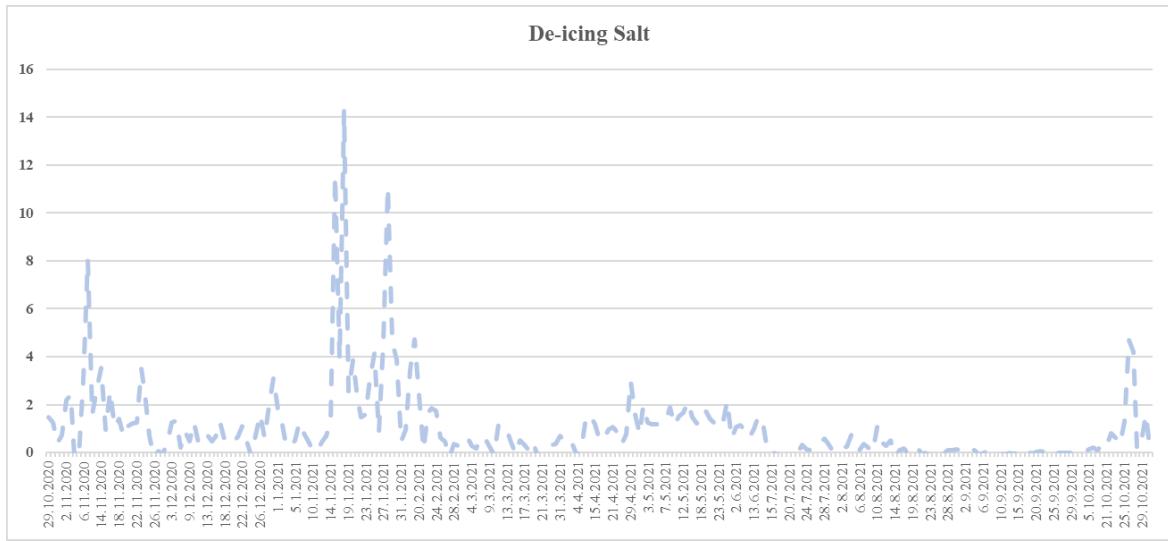
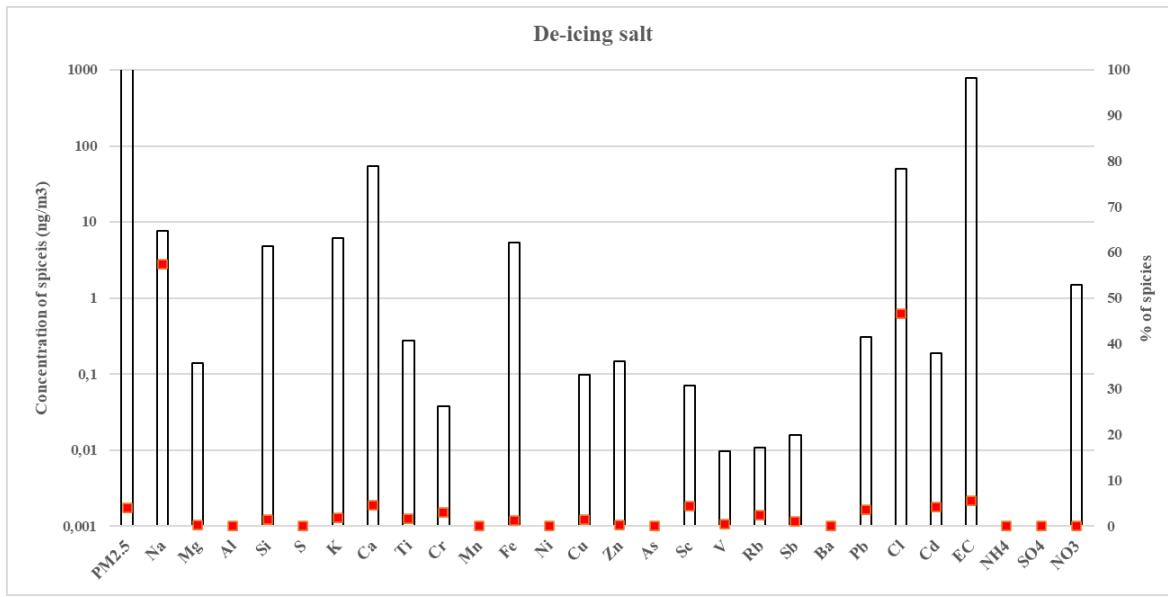
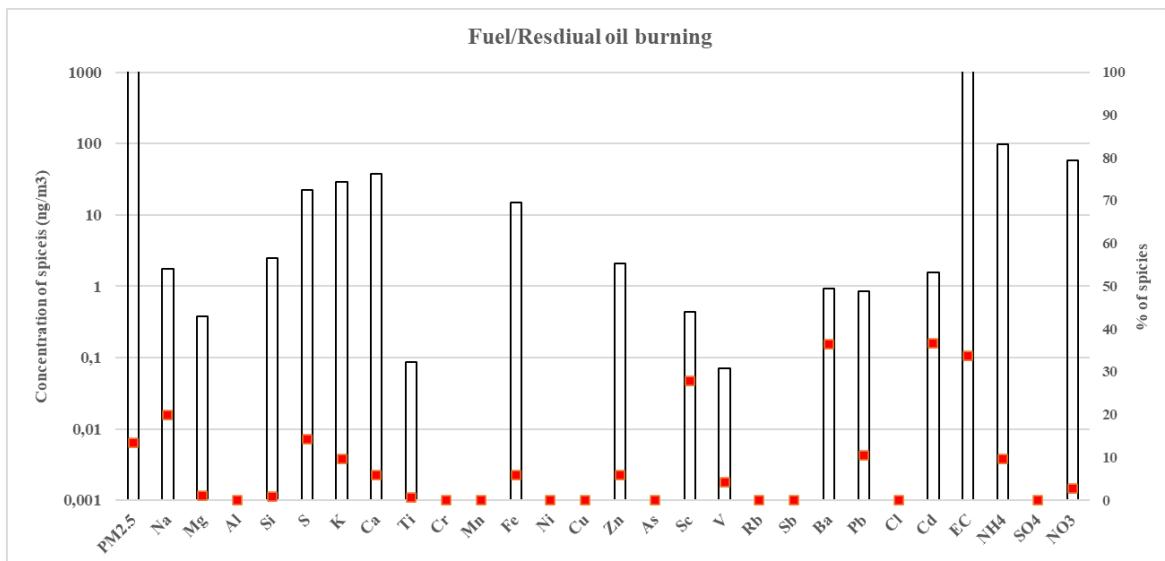
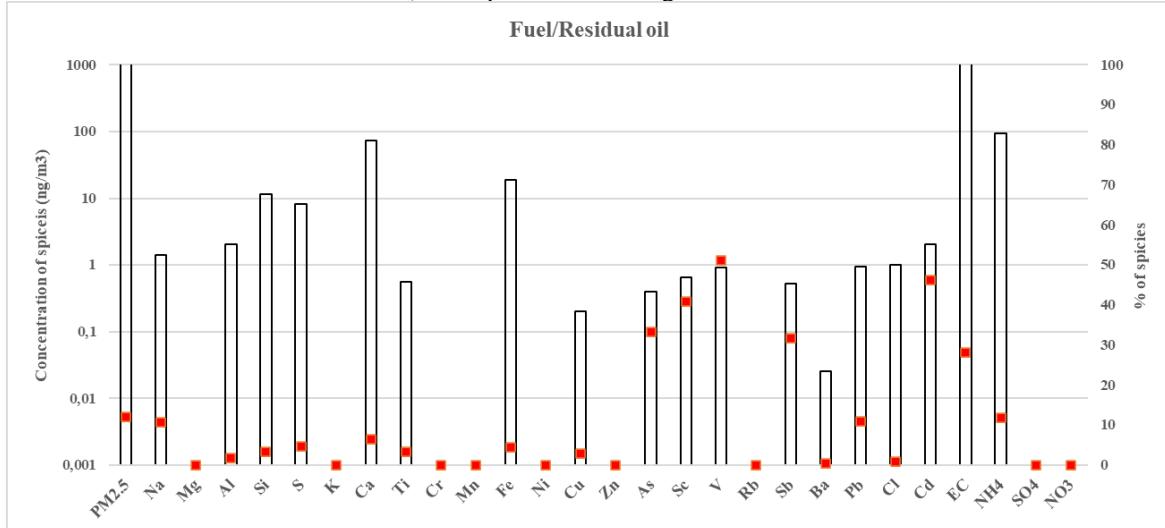


Figure C5. De-icing salt profile and temporal distribution – Novo Lische urban exposed site



a) Karposh urban background site



b) Novo Lische urban exposed site

Figure C6. Fuel/Residual oil burning profiles

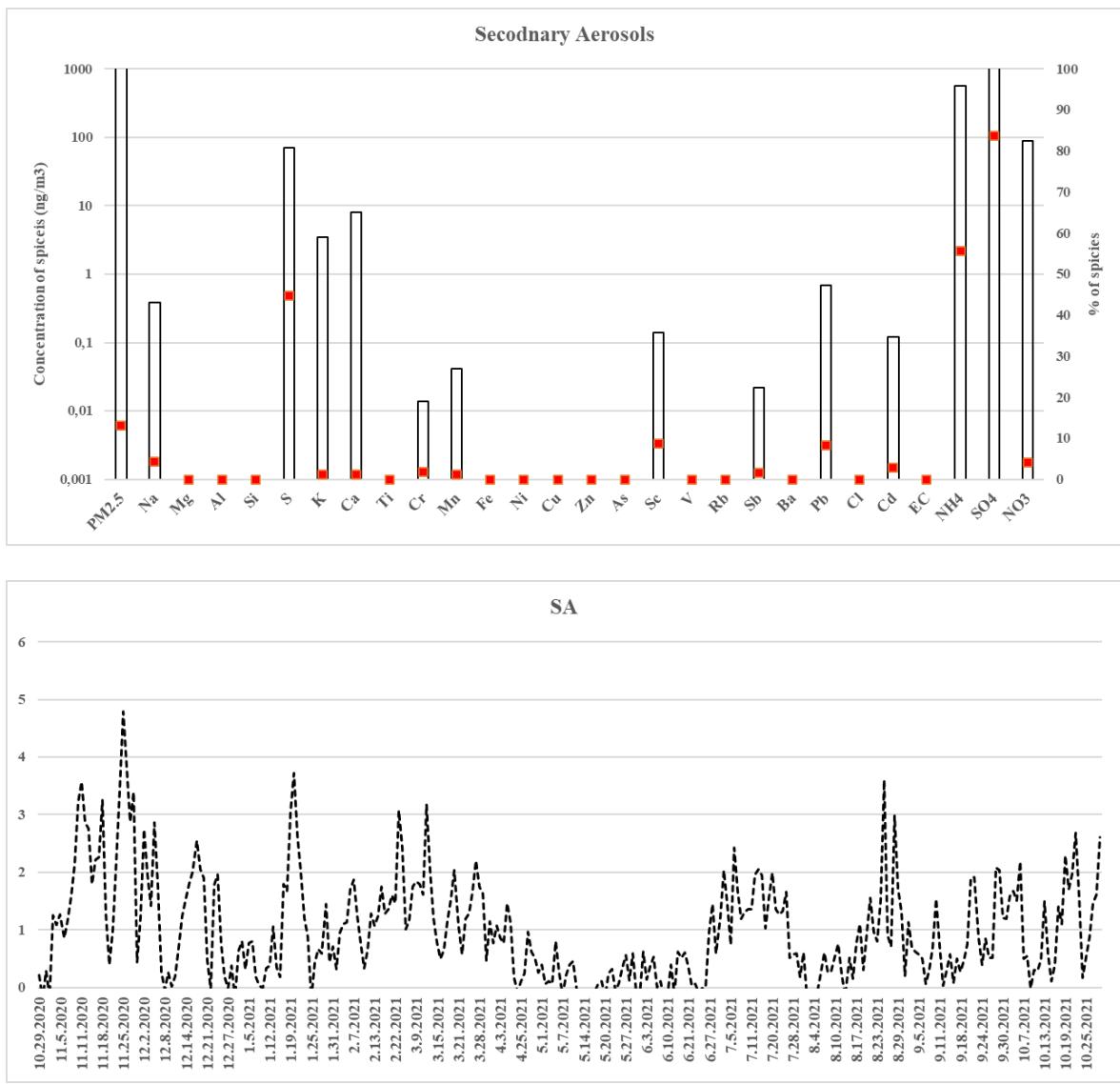


Figure C7. Secondary Aerosols profiles and temporal distribution – Karposh urban background site

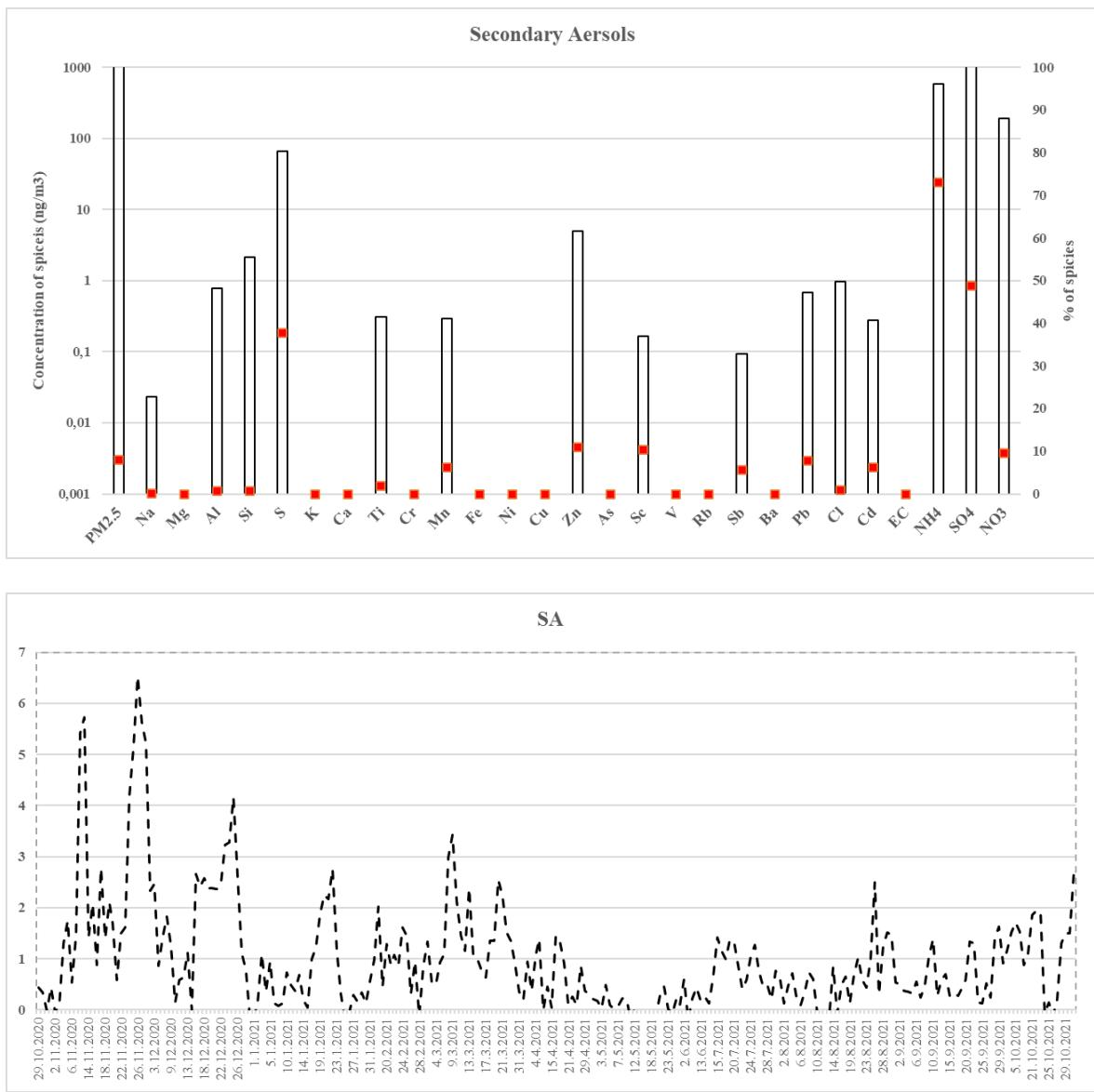


Figure C8. Secondary Aerosols profiles and temporal distribution – Novo Lische urban exposed site

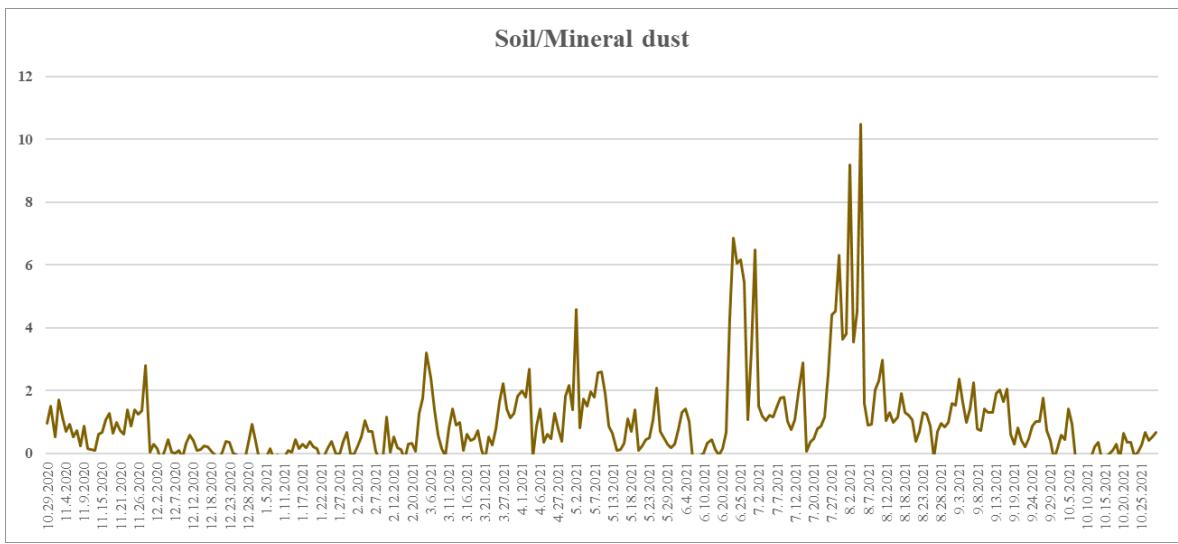
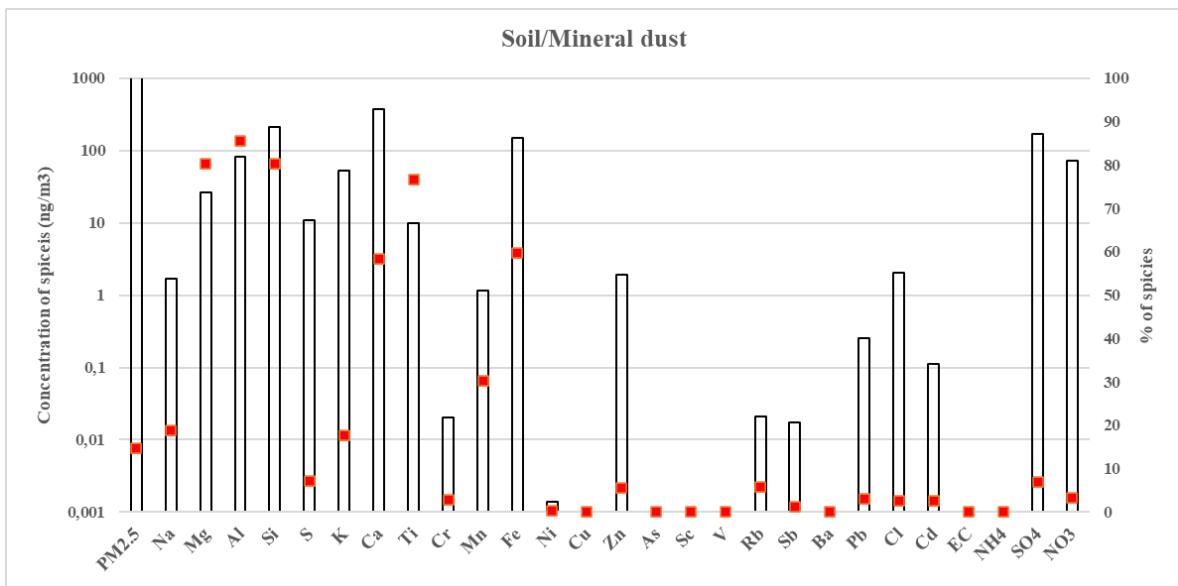


Figure C9. Open fire burning profiles and temporal distribution – Karposh urban background site

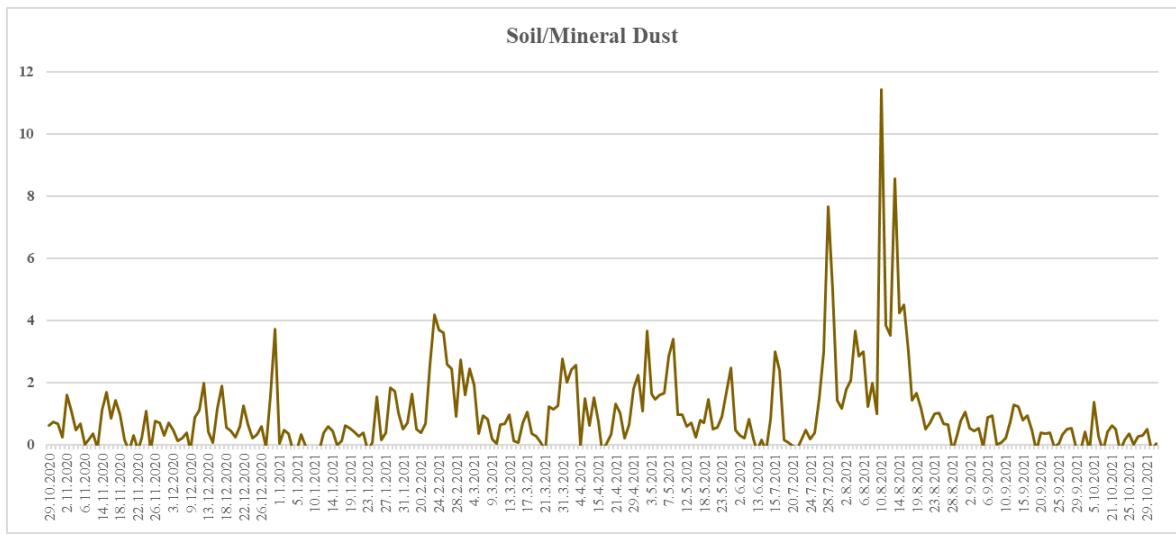
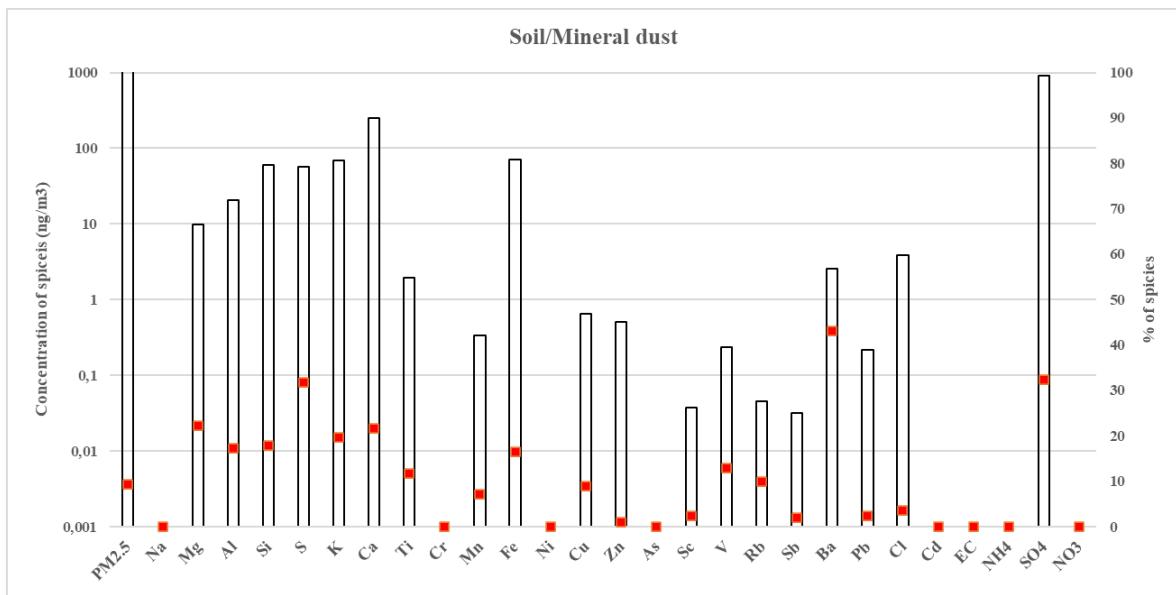


Figure C10. Open fire burning profiles and temporal distribution – Novo Lische urban exposed site

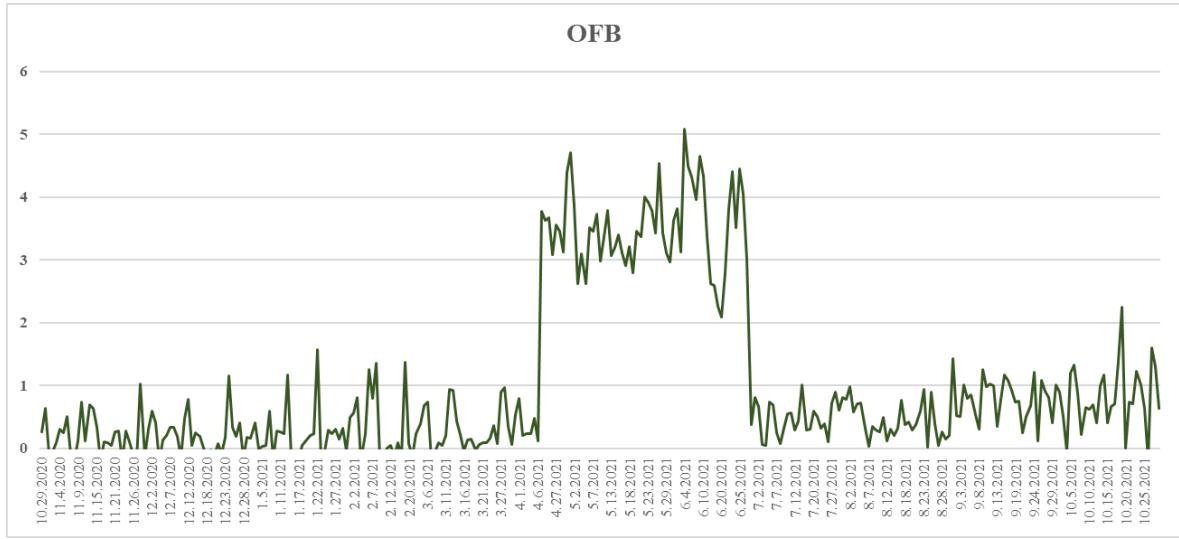
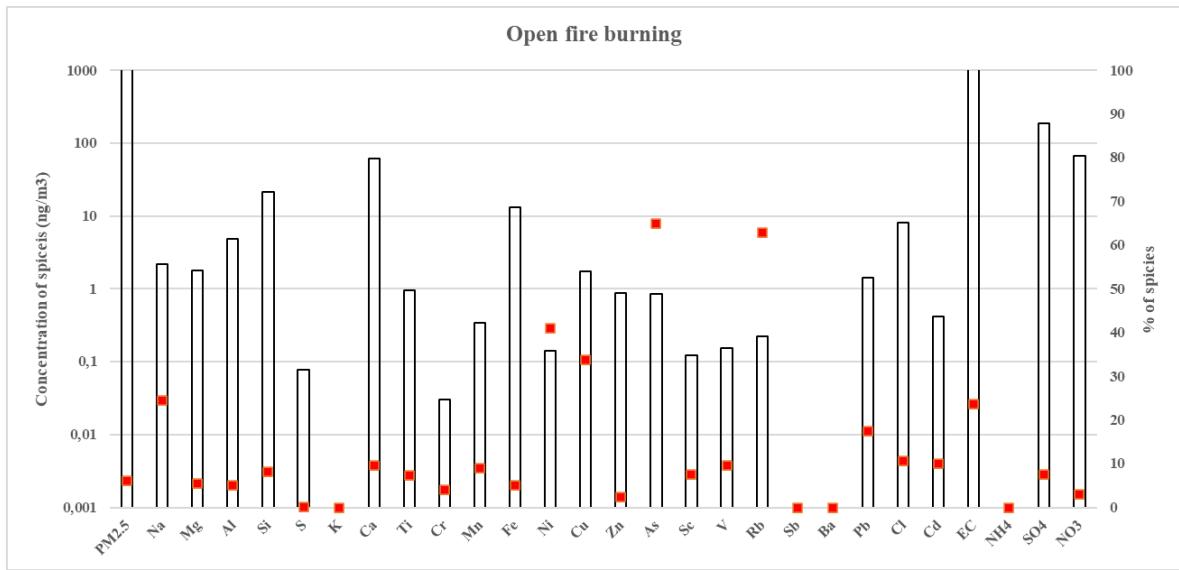


Figure C11. Open fire furning profiles and temporal distribution – Karposh urban background site

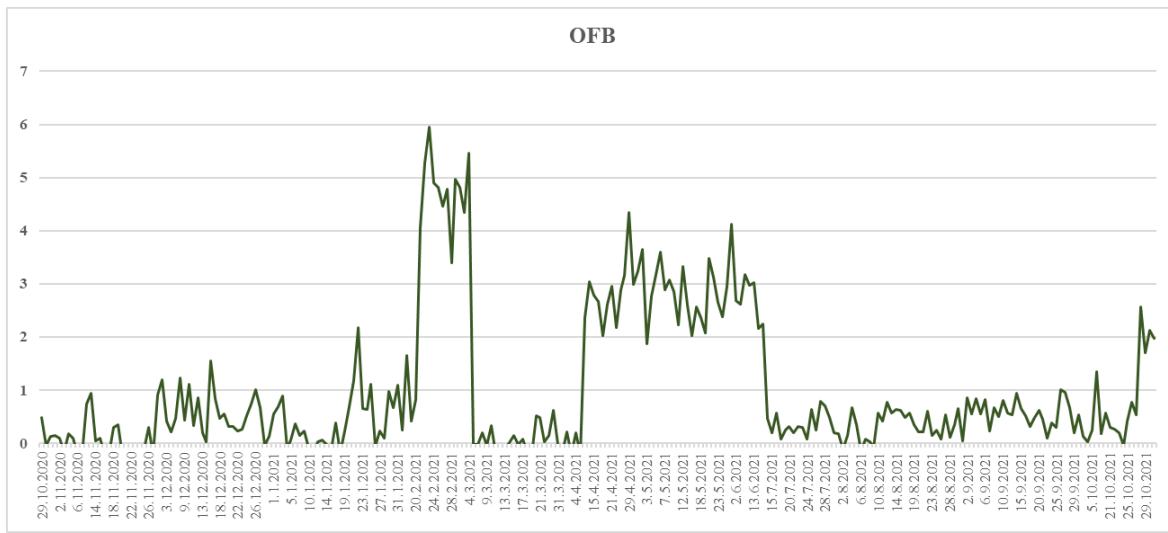


Figure C12. Open fire burning profiles and temporal distribution – Novo Lische urban exposed site

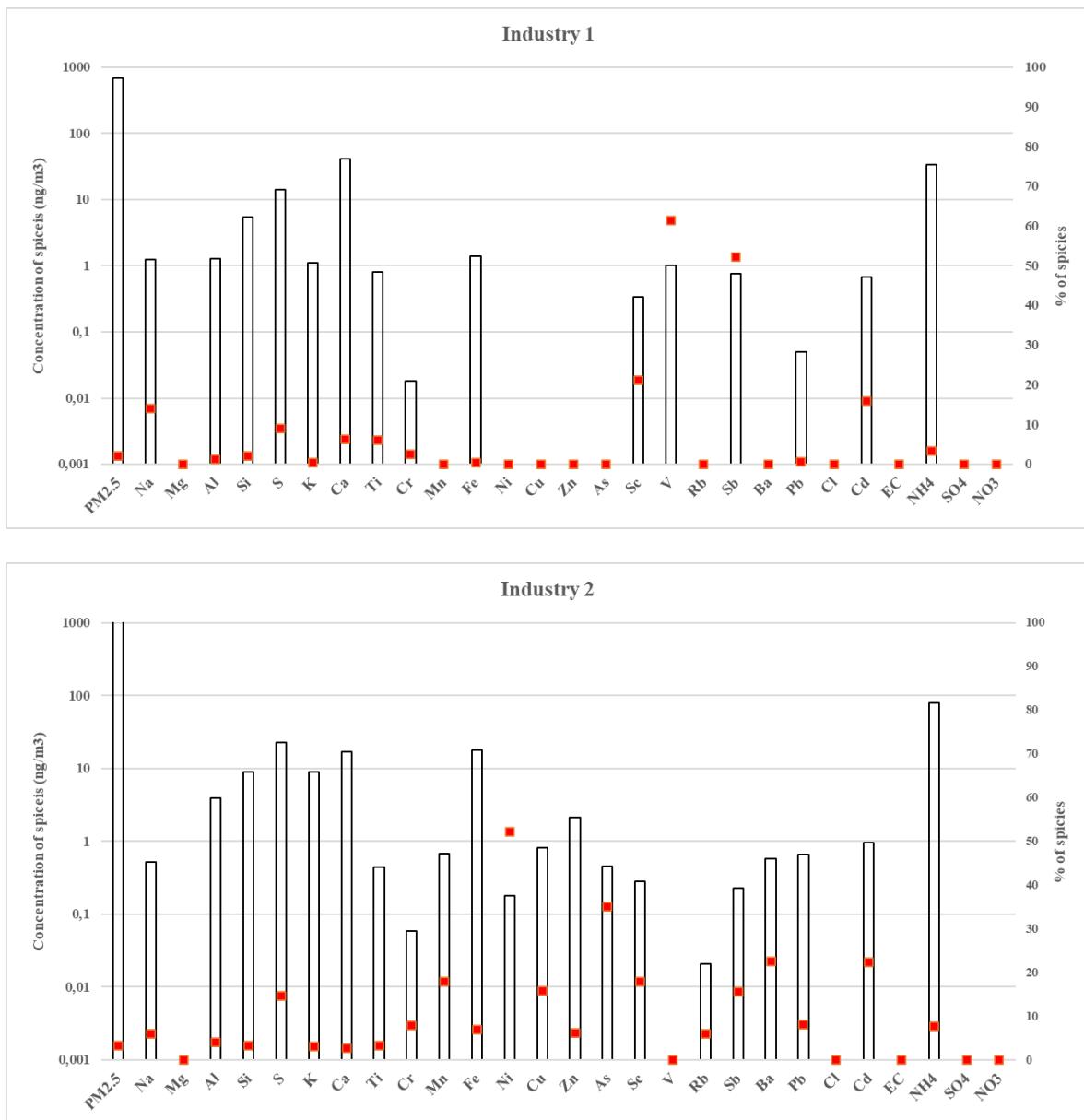


Figure C13. Industry related profiles – Karposh urban background site

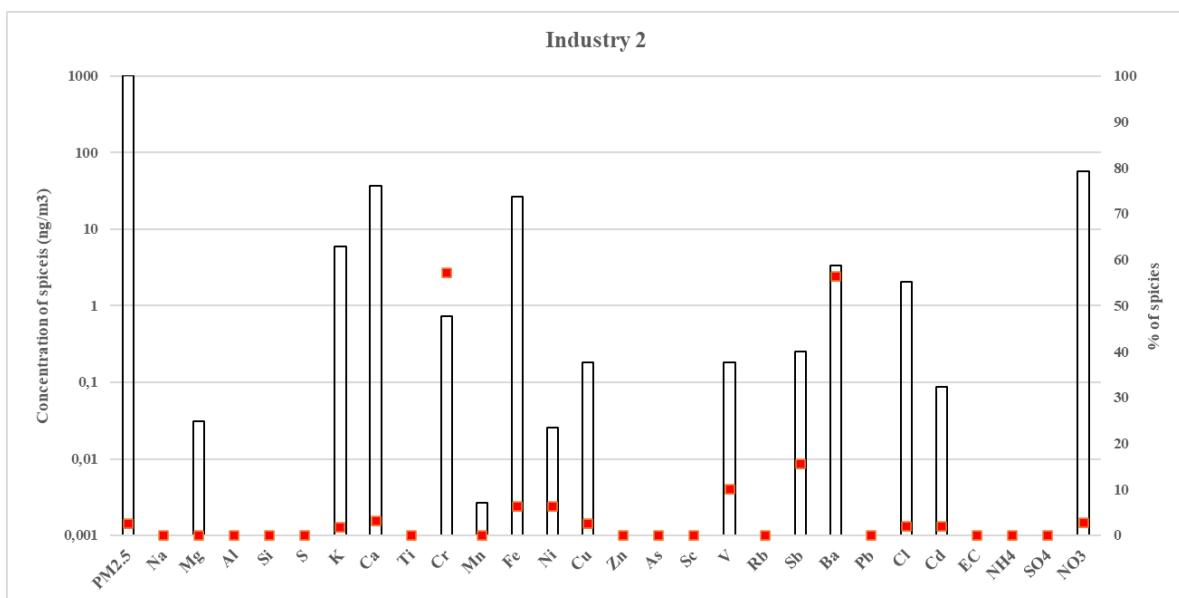
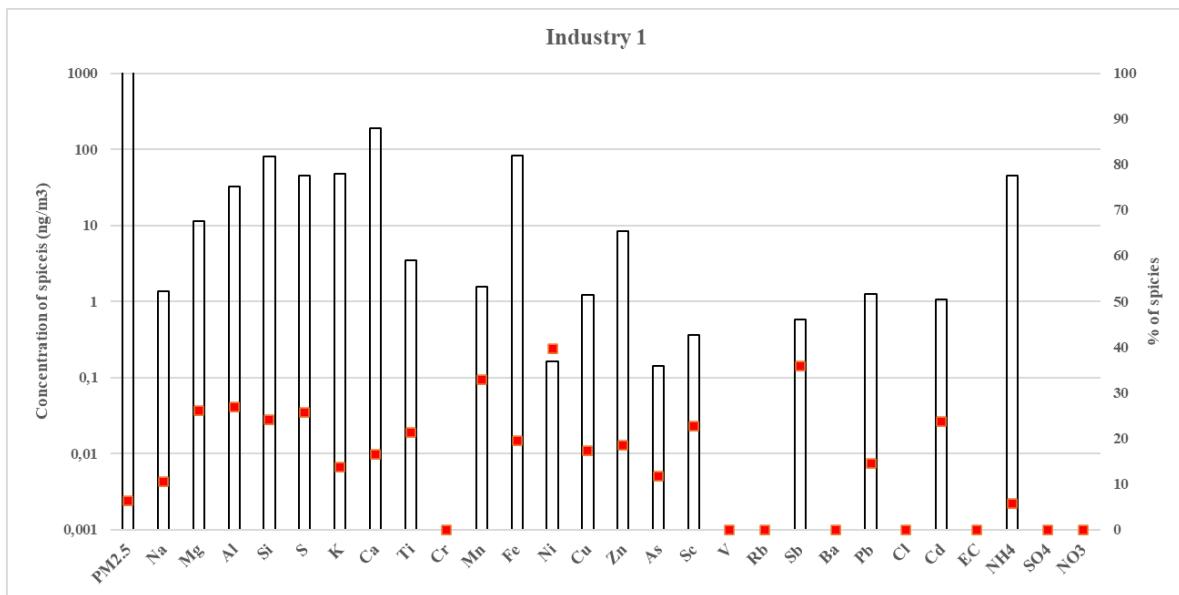


Figure C14. Traffic related profiles – Novo Lisiche urban exposed site

Appendix D: Sources Contribution

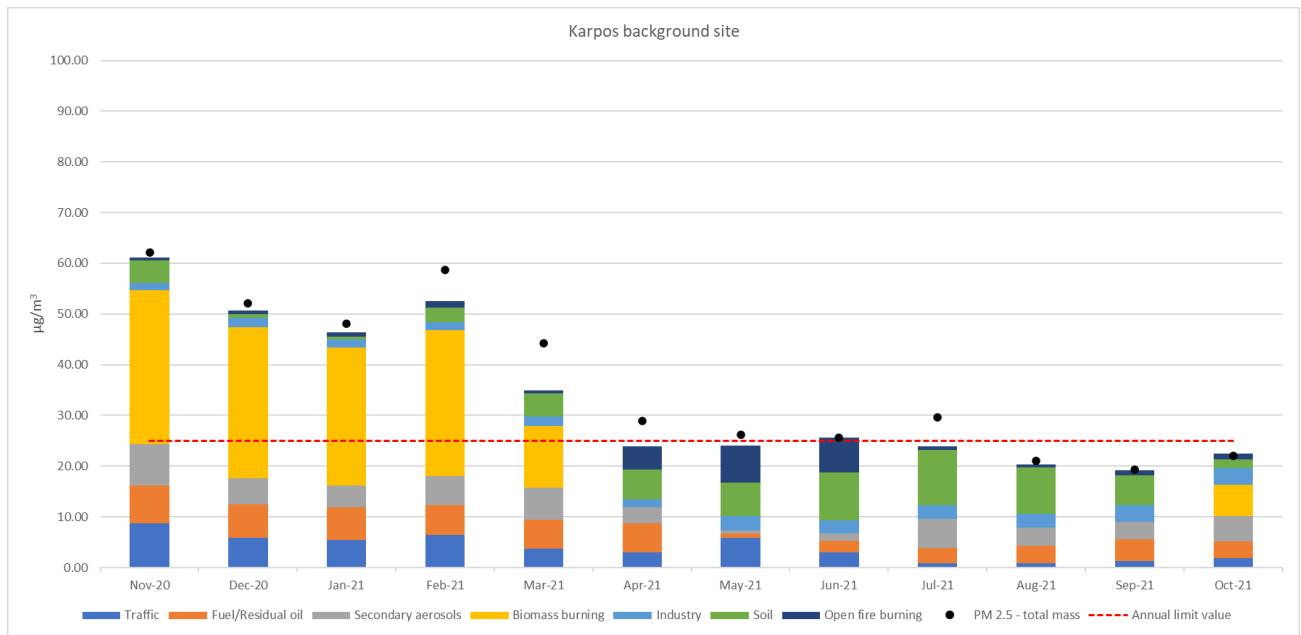


Figure D1. Average monthly contributions to total particulate mass (PM 2.5) – Karposh urban background site

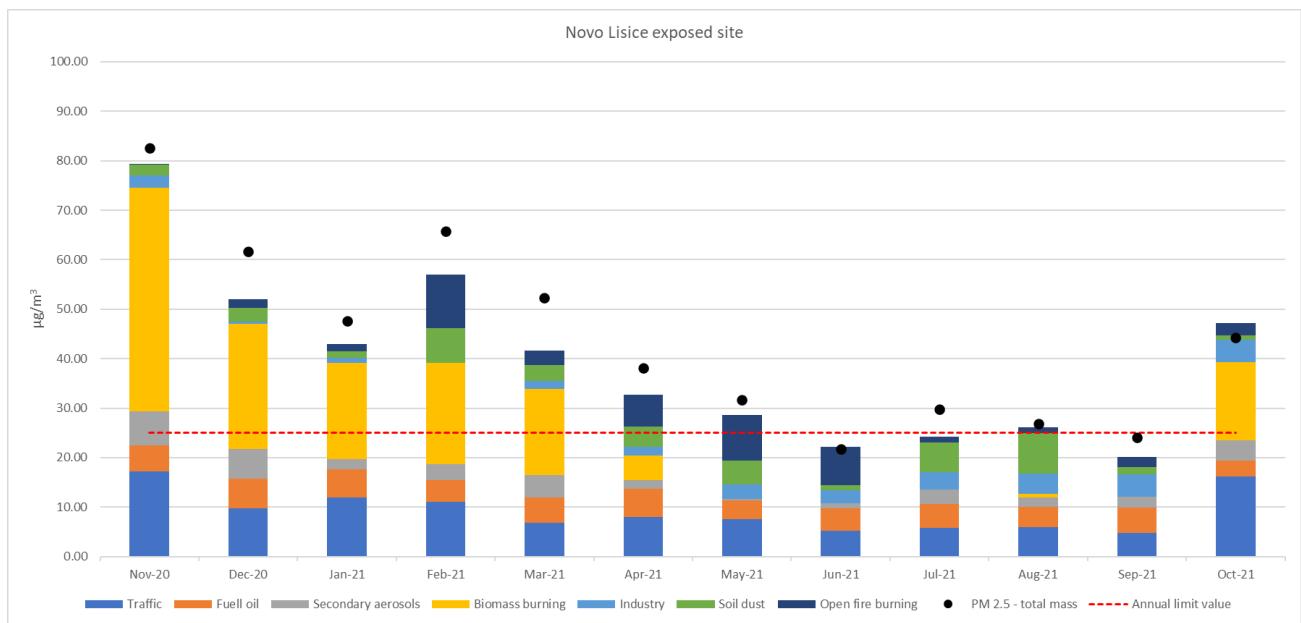


Figure D2. Monthly contributions to total particulate mass (PM 2.5) – Novo Lisiche urban traffic exposed site

Appendix E: PMF Analysis

Table E1. Summary of the identified factors and associated key species (% of the species > 30)

Sources	Key species	
	Novo Lisiche urban exposed	Karposh urban background
Biomass burning	K, Rb, Cl and NO ₃ ⁻	K, Cl and NO ₃ ⁻
Traffic	Na, S, Ca, Cr, Mn, Fe, Cu, Zn, V, Ba, Pb, Cl, EC and SO ₄	Cr, Cu, Ba and Cl
Industry	Ni, Mn and Sb	Mn, Ni, Zn, As, Sc, V, Sb, Pb and Cd
Fuel oil	EC, V, Cd, Sc and As	EC, V, Cd and Ba
Secondary aerosol	S, NH ₄ and SO ₄	S, NH ₄ and SO ₄
Open fire burning	Ni, Cu, As and Rb	Ni, Cu, As and Rb
Soil dust	Mg, Al, Si, Ca, Ti, Cr and Fe	Mg, Al, Si, Ca, Ti, Mn and Fe

Table E.2. Bootstrap (BS) and Displacement (DIS) results summary.

		Karosh urban bacground	Novo Lisiche urban exposed
BS	Reproducibility Range	91-100	86-100
BS	Unmapped	0	0
BS	Lowest reporducability	Industry 2	Road Dust
DIS	Swaps	0	0
DIS	dQ%	0	-0.01