THE EFFECT OF HEAVY INDUSTRY ON AIR POLLUTION STUDIED BY ACTIVE MOSS BIOMONITORING IN DONETSK REGION (UKRAINE)

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Heavy metals are one of the main environmental pollutants. A significant amount of heavy metals is released into the environment from mining and industrial activities (coal power plants, foundries, mines, smelters, agriculture, etc.), and agricultural practices.

Terrestrial mosses can be used as biomonitors in an effective active air quality biomonitoring method.

The ‘moss bag technique’ introduced by Goodman and Roberts (1971) is widely used for the assessment of levels of air pollution in urban areas.

The use of moss transplants overcomes many problems related to the lack of naturally growing mosses in paved and landscaped urban areas.

Hypnum cupressiforme

Sphagnum denticulatum

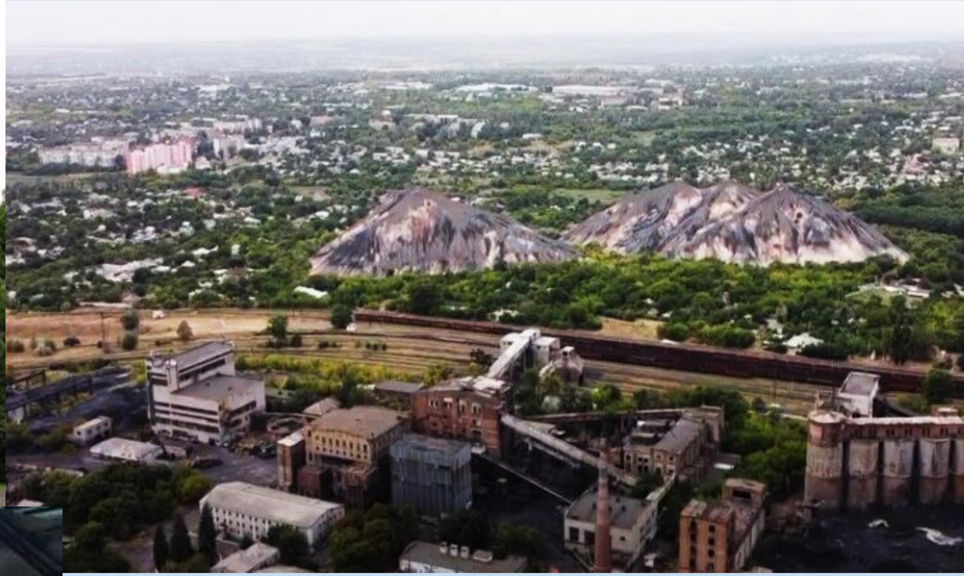
Pseudoscleropodium purum

Sphagnum girgensohnii

Nowadays, in the Donetsk region, the most developed industrial region of Ukraine, air pollution is among the most serious problems.

According to data reported by the Regional State of the Environment in the Donetsk region (2018), emissions from the coal industry constituted about 26.5 % of the total emissions.

The main cross-industry complexes in the region are power stations and facilities related to ferrous and non-ferrous metallurgy, machine-building, and chemical industries, as well as transport.


Nineteen coal mines are operated in the Donetsk region and tailings are stored in the immediate vicinity of residential areas.

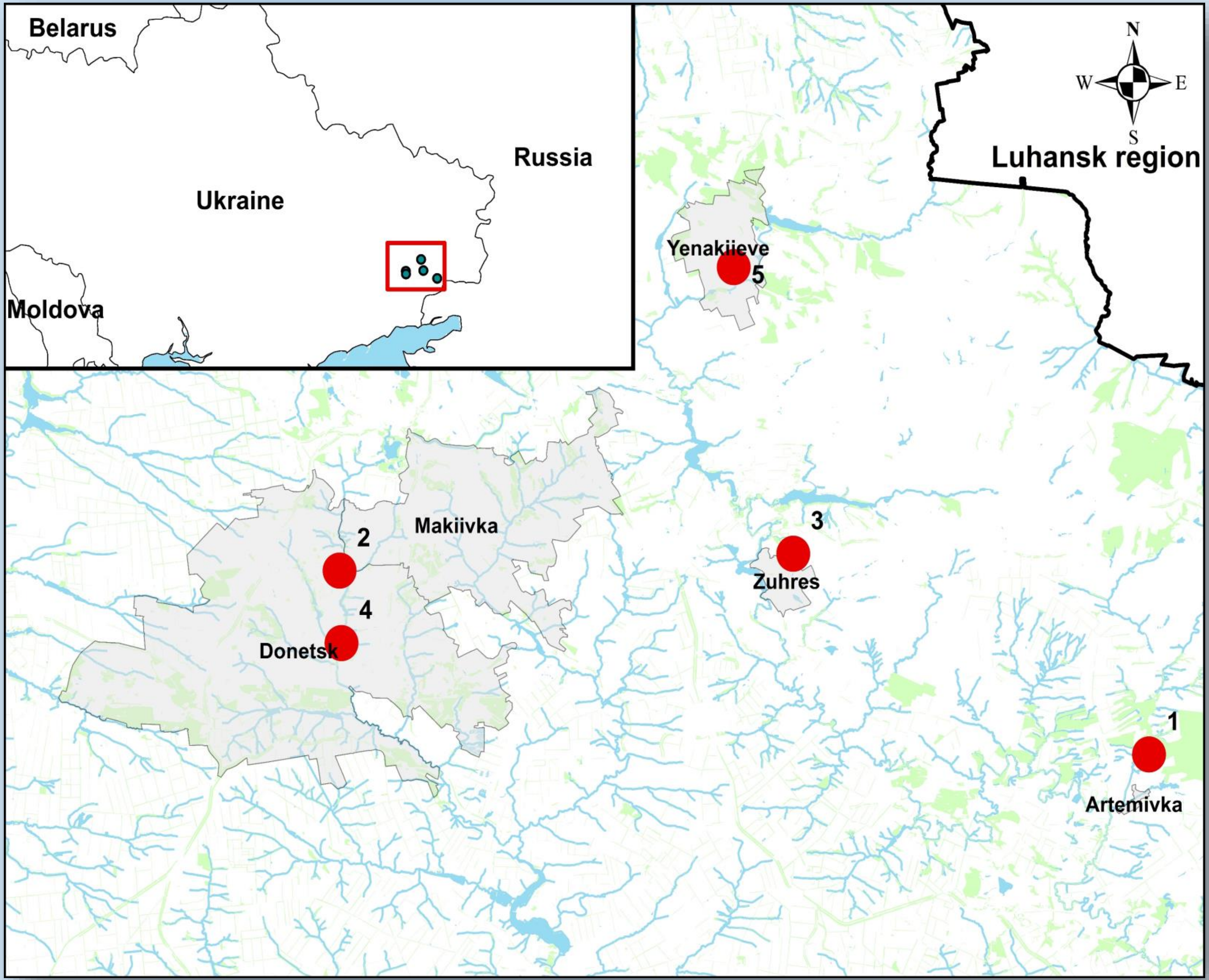
The Donetsk Metallurgical Plant is the largest metallurgical plant (ironworks) in the central part of the city.

Ceratodon purpureus

Brachythecium campestre

Moss samples were collected from the Ukrainian Steppe Nature Reserve (Khomytovs'ka steppe) located in the Donetsk region (about 68 km northeast from the nearest industrial zone) in 2018.

The collected mosses were cleaned from extraneous materials adhered to the surface of the samples, dried, and packed in special nylon net bags (10 × 10 cm^2 in size). Each moss-bag contained about 3 g of moss material. One sample of each moss species was kept in the laboratory and used as control.



Map of the exposure sites in the Donetsk urban area

Moss bags were exposed for six months at five different sites:

Site 1 - the landscape park "Doneckij Kryazh" considered as unpolluted;

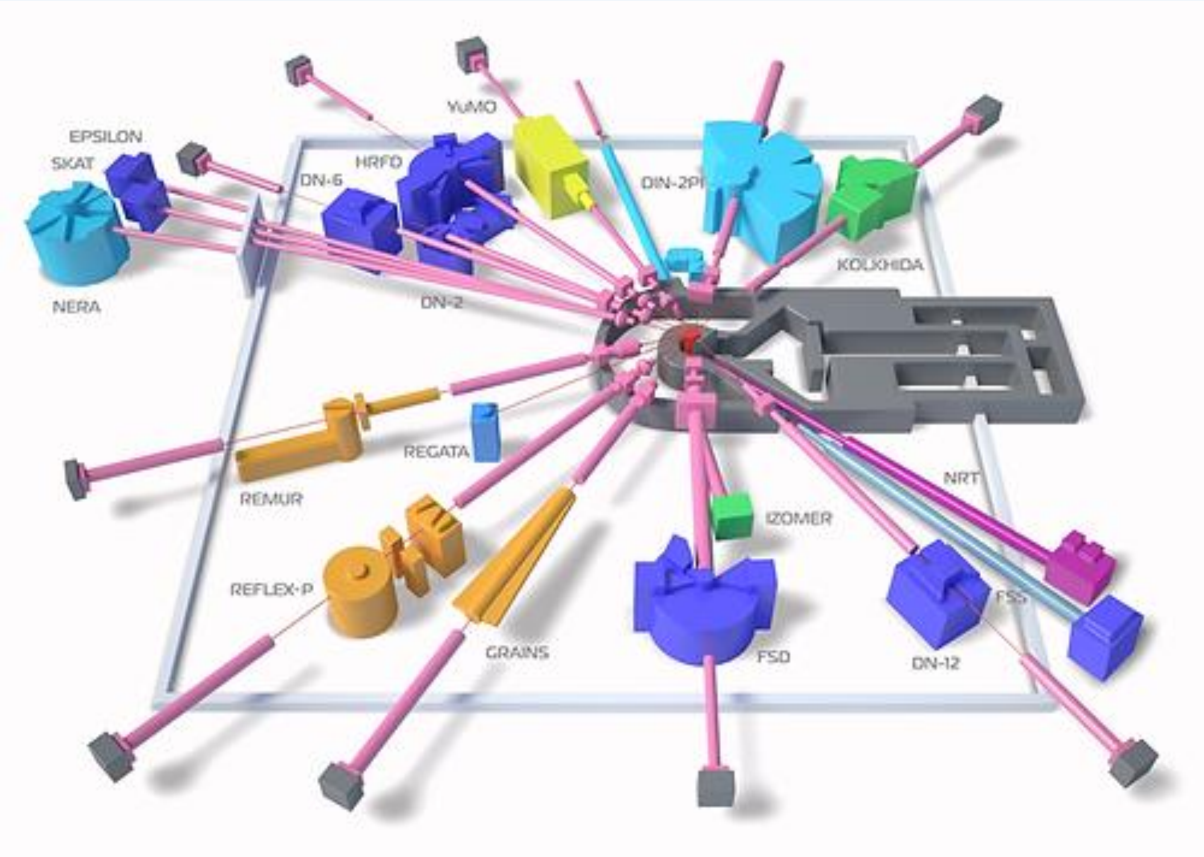
Site 2 - the Lenin Komsomol Park;

Site 3 - the Zuivska power station (Zuivska TES);

Site 4 - the Donetsk Metallurgical Plant;

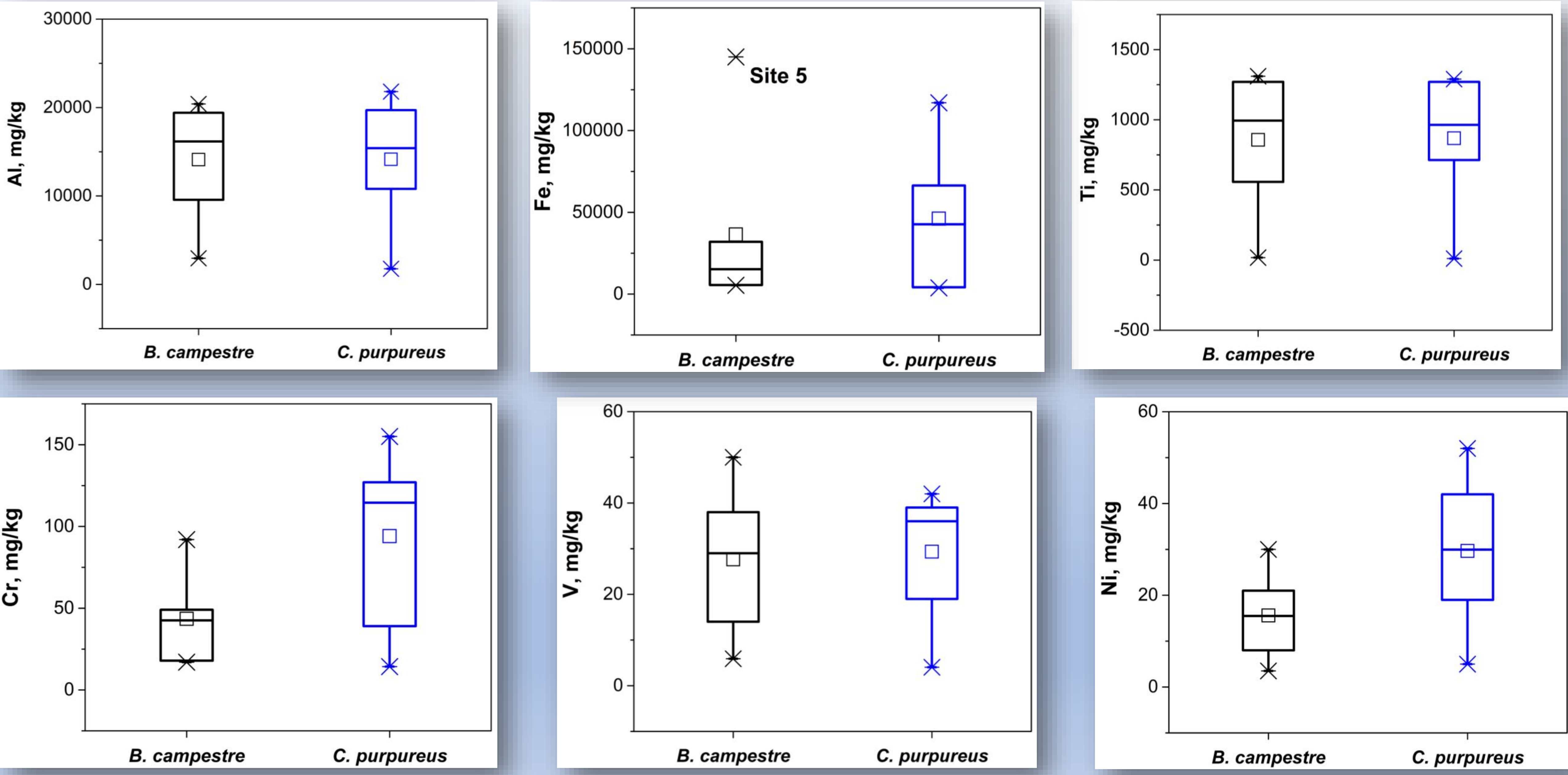
Site 5 - the Yenakiieve Iron and Steel Works.

A total of 16 elements (short-lived radionuclides: V, Mg, Ca, Al, K, Ti, and Mn; long-lived isotopes of Na, Cr, Fe, Co, Ni, Zn, Sr, Mo, and Ba) were determined in the moss samples by instrumental neutron activation analysis (INAA) at the high-flux pulsed reactor IBR-2 (FLNP, JINR, Dubna, Russia).

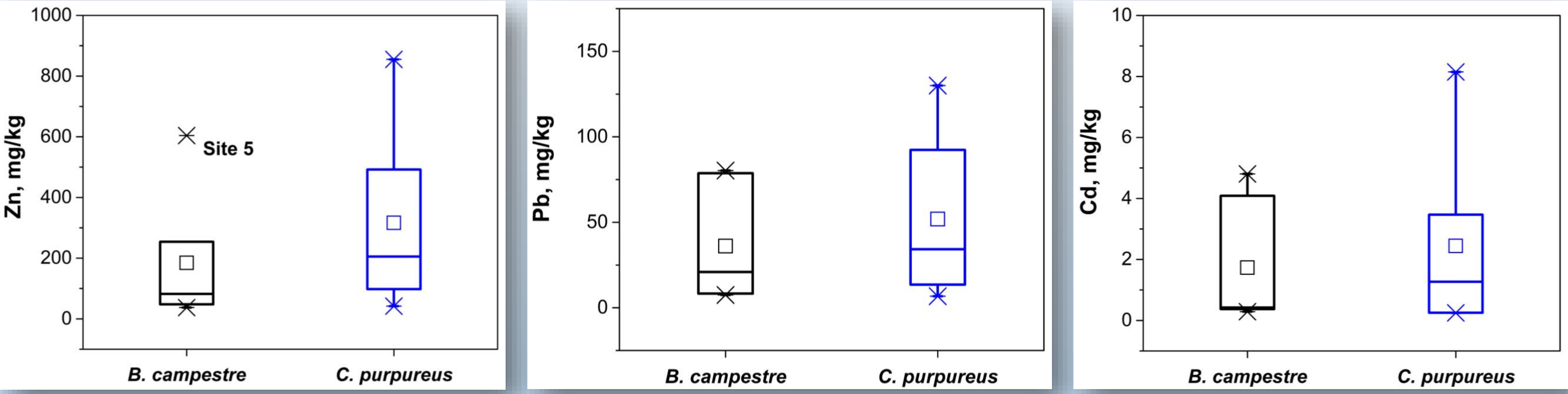


The concentrations of Cd, Cu, and Pb in the moss samples were determined using AA iCE 3000 Series Atomic Absorption Spectrometer with electrothermal (graphite furnace) atomization (Thermo Fisher Scientific).

Concentration of elements (mg·kg^{-1}) in both moss species at five exposure sites



Concentration of elements (mg·kg^{-1}) in both moss species at five exposure sites

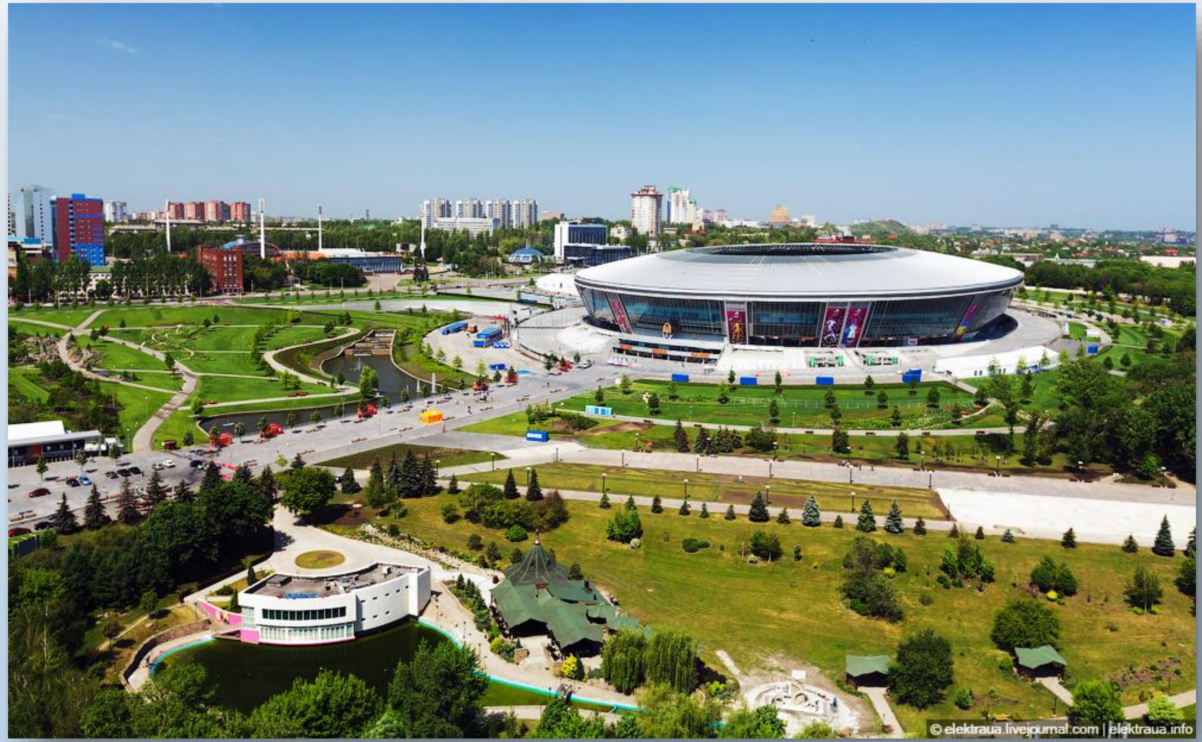


Site 1 - the landscape park "Doneckij Kryazh"

Al, Ba, Ti, Cr - soil dust input to the moss samples

Ti, Al, Ni, Cd, Zn, Ba, Cr can be emitted from brake wear, tyre wear, motor oil

Site 2 - the Lenin Komsomol Park



Ti, Al, Ni, Cd, Zn, Ba, Cr can be emitted from brake wear, tyre wear, motor oil

Al and Ti indicate contamination with soil dust

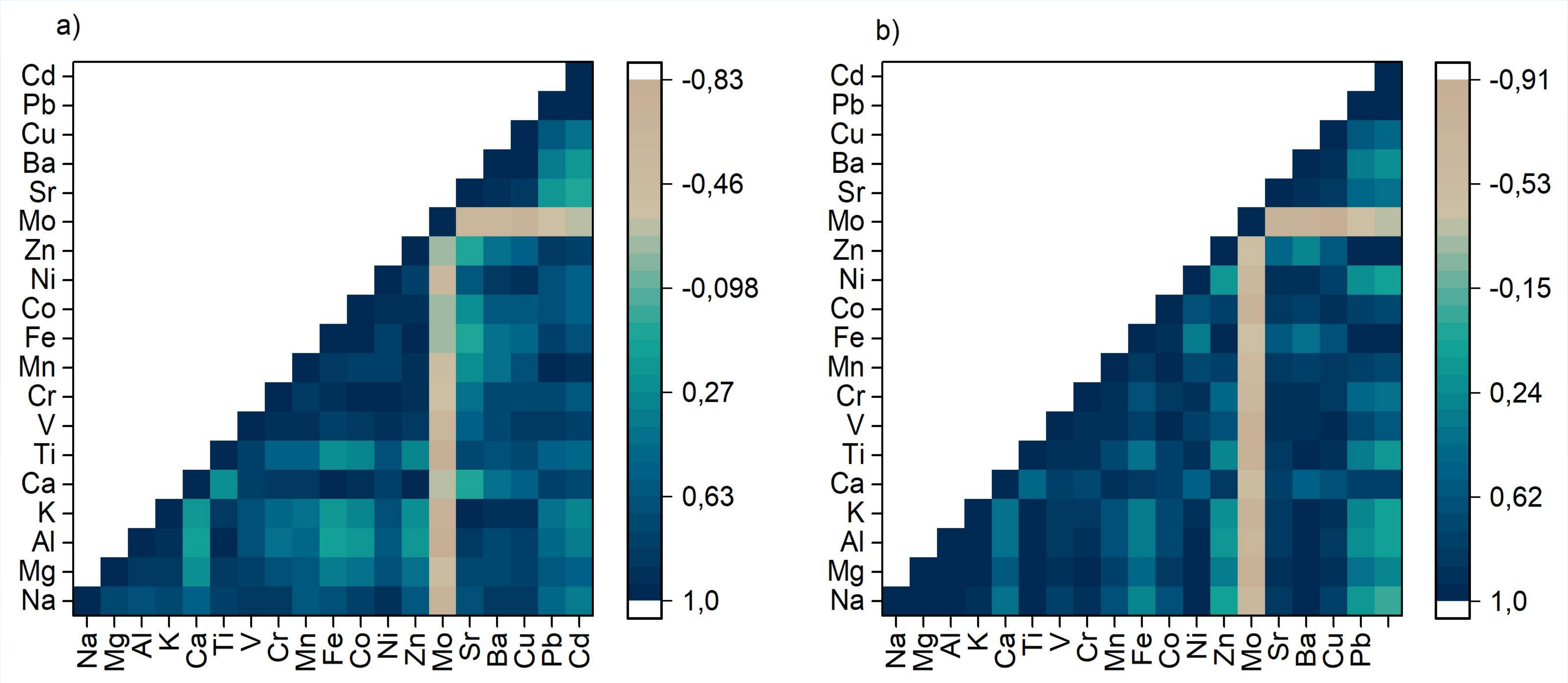
Site 3 – the Zuivska power station

Site 4 – the Donetsk Metallurgical Plant

Cr, Ni, V, Cd, and Pb associated with coal burning
Ni, Cd, Cu, and Mn are significantly related to fossil fuel combustion
Co, Ni, Cr may be released into the atmosphere from coal-fired power plants and incinerators
Substantial contributors to Cr emissions are metal processing, stainless steel welding, and the production of anti-corrosive coatings for boilers

Site 5 – the Yenakiieve Iron and Steel Works

Fe, Zn, Pb, Cd can be explained by emissions of steel production
Pb include mining and smelting of ores, and transport.
Zn is released into the atmosphere as the result of mining, purifying of Zn, Pb, and Cd ores processing during steel production.
Zn, Pb, Cd, and Cu are emitted into the air by waste incineration and disposal



Correlation matrices of the measured elements (a. *Brachythecium campestre* and b. *Ceratodon purpureus*)

Al-Ti, K-Sr, Ca-Fe, Ca-Zn, Cr-Co, Cr-Ni, Mn-Pb, Fe-Zn, Fe-Co, Co-Zn, Pb-Cd

Na-Mg, Na-Al, Na-Ni, Na-Ba, Mg-Al, Mg-K, Mg-Ba, Mg-Ti, Al-K, Al-Ti, Al-Ba, K-Ti, K-Ba, Ti-Ba, V-Co, V-Cu, Cr-Ni, Fe-Zn, Fe-Pb, Fe-Cd, Zn-Pb, Zn-Cd, Pb-Cd.

Median relative accumulation factor (RAF) values of elements

Moss	*Brachythecium campestre*	*Ceratodon purpureus*
Element	RAF_{median}	RAF_{median}
Na	**5.6**	**10**
Mg	n.d.	**3.3**
Al	**5.3**	**10**
K	0.66	0.93
Ca	0.23	0.67
Ti	**56**	**109**
V	**4.1**	**8.2**
Cr	**1.4**	**7.4**
Mn	0.75	**2.7**
Fe	**2.6**	**13**
Co	0.82	**4.8**
Ni	**3.6**	**6.4**
Zn	**1.3**	**6.3**
Mo	0	0
Sr	0.37	0.73
Ba	**2.6**	**6.6**
Cu	1	**1.2**
Pb	**2.5**	**5.6**
Cd	0.63	**7.9**

$$RAF_{median} = \frac{C_i - C_0}{C_0}$$

C_i is the element concentration (mg kg^{-1}) in the exposed moss sample,
C_0 is the initial element concentration (mg kg^{-1}) in moss before exposure.

RAF > 0.5 indicate insignificant elemental enrichment in the moss,
RAF > 1 indicate significant elemental enrichment

Contamination factors of elements at exposure sites

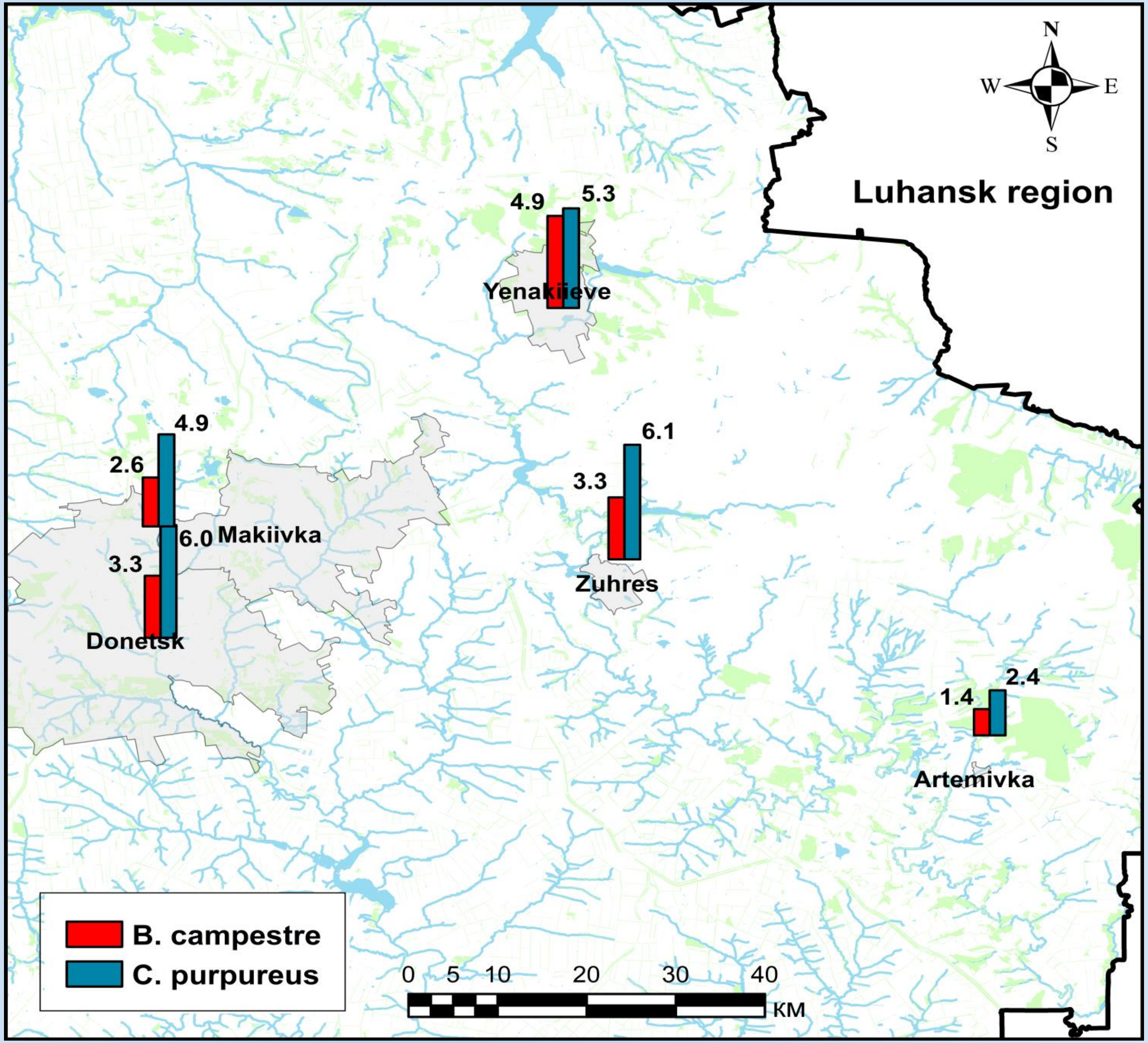
Element	Studied sites									
	Site 1		**Site 2**		**Site 3**		**Site 4**		**Site 5**	
	BC	**CP**	**BC**	**CP**	**BC**	**CP**	**BC**	**CP**	**BC**	**CP**
Ti	32	68	75	**124**	73	**110**	57	**122**	56	76
V	2.4	4.7	4.7	8.7	6.4	9.2	5.1	10.4	8.5	9.7
Cr	0.95	2.7	2.4	8.9	2.3	10.8	2.7	8.4	5.1	7.6
Mn	1.2	1.3	1.4	2.6	2.9	3.7	1.7	3.7	3.5	3.8
Fe	0.97	0.30	1.8	8.4	5.7	14.1	3.6	17.5	26	31
Co	0.70	2.9	1.8	5.3	1.8	5.8	2.5	5.8	6.6	7.3
Ni	2.3	3.8	4.6	8.4	4.3	10.4	6.0	7.4	8.6	4.6
Zn	0.78	2.3	1.1	2.5	5.3	7.3	2.3	11.7	12.6	20.4
Mo	0.07	0.14	0.08	0.25	0.1	0.25	0.13	0.22	0.13	0.18
Cu	1.4	1.8	1.8	2.2	2.0	2.1	2.6	2.3	2.3	2.2
Pb	1.1	2.0	2.1	3.5	10.5	6.5	3.5	13.6	10.7	19.5
Cd	1.3	1.0	1.3	1.3	16.6	8.8	1.6	14.0	14.1	33

$$CF_i = \frac{C_i}{C_{i\ \mathrm{background}}}$$

C_i - measured concentration
$C_{i\ \mathrm{background}}$ - the background value of metal *i*

$CF_i < 1$ – no contamination;
$1 \leq CF_i < 2$ - suspected contamination;
$2 \leq CF_i < 3.5$ – slight contamination;
$3.5 \leq CF_i < 8$ – moderate contamination;
$8 \leq CF_i < 27$ - severe contamination;
$CF_i \geq 27$ - extreme contamination

Pollution load index of exposure sites in two moss species



$$PLI = \sqrt[n]{\prod_{i=1}^{n} \mathrm{CF}_i}$$

PLI > 1 implies pollution

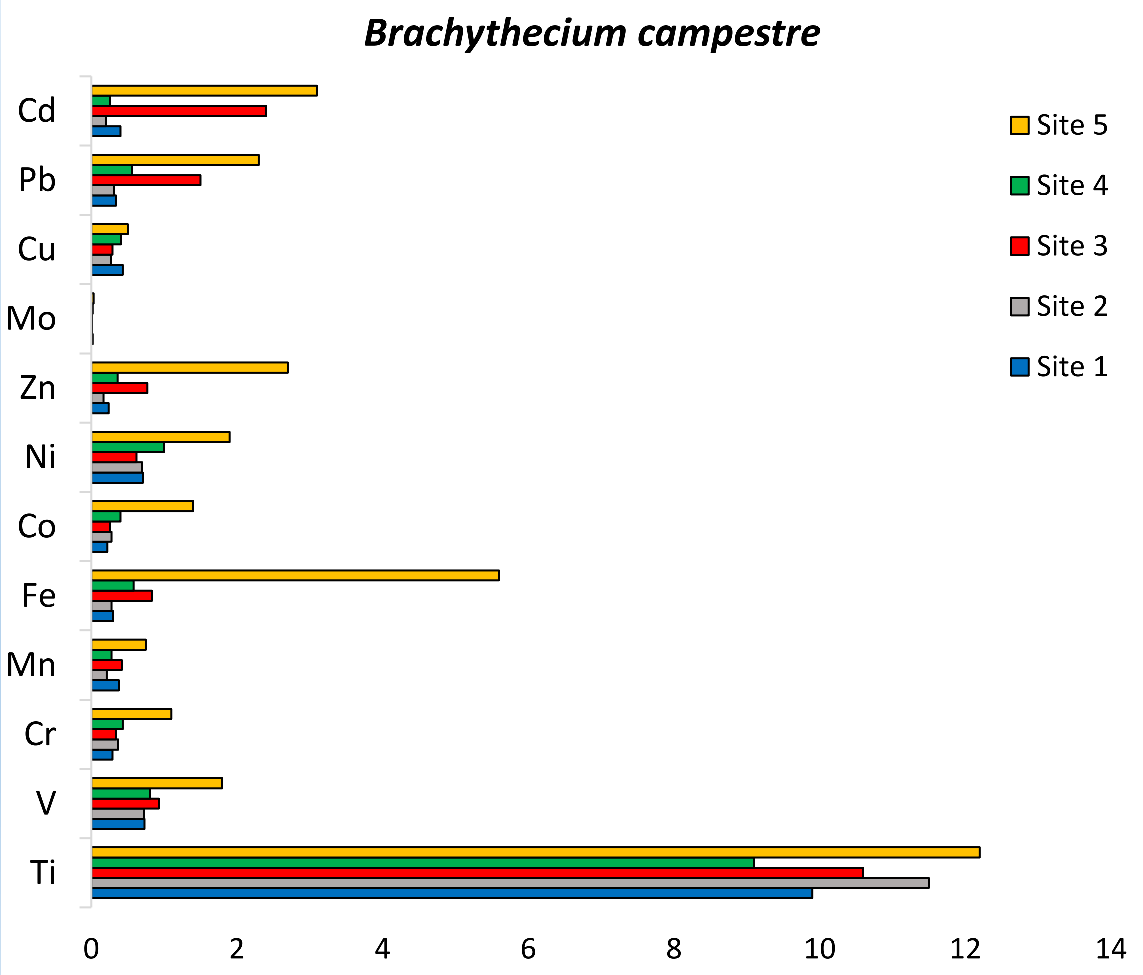
PLI < 1 means no contamination

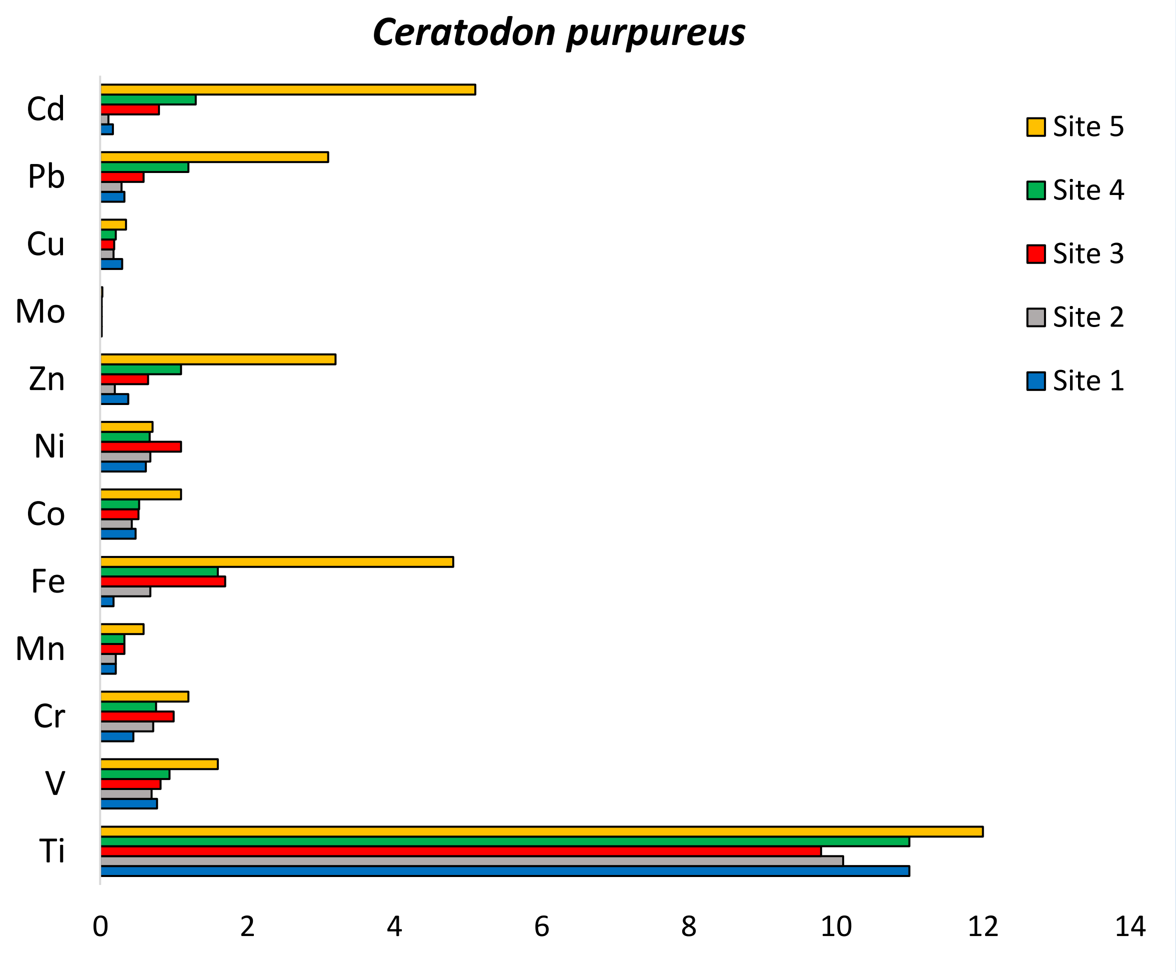
Enrichment factor of elements at exposure sites

$$EF = \frac{(C_M/C_x)\ moss}{(C_M/C_x)\ background}$$

C_x - Al as the reference element

EF < 1 no enrichment
1 < EF < 3 minor enrichment
3 < EF < 5 moderate enrichment
5 < EF < 10 moderately severe enrichment
10 < EF < 25 severe enrichment
25 < EF < 50 very severe enrichment
EF > 50 extremely severe enrichment





Potential ecological risk index

$$RI = \sum \left(T_i \frac{C_i}{C_{i\,background}} \right)$$

T_i – the toxic-response factor for a given substance (Cr = 2, Mn = Zn = 1, Co = Ni = Cu = Pb = 5, As =10, Cd =30)
C_i and $C_{i\,background}$ – the measured concentration and the background value

RI ≤ 150 low pollution
The Landscape park "Doneckij Kryazh" and the Lenin Komsomol park
In general, the air pollution level is the lowest in the Landscape park "Doneckij Kryazh".

300 < RI < 600 considerable pollution
The Zuivska power station and the Donetsk Metallurgical Plant

RI > 600 high pollution
At the Yenakiieve Iron and Steel Works, the RI values of 605 and 1196 in *Brachythecium campestre* and *Ceratodon purpureus*, respectively

Conclusions

- **For the first time active moss biomonitoring was used to assess trace element deposition in the Donetsk region.**
- **The distinct morphology of acrocarpous and pleurocarpous mosses implies differences in the concentrations of elements in moss.**
- The significant accumulation of elements in the *Ceratodon purpureus* moss bags indicated that this moss species is an efficient accumulator in urban settings.
- The RAF values obtained for *Ceratodon purpureus* were two times higher than for *Brachythecium campestre*.
- The PLI values for both moss species revealed a highly polluted status of the studied sites.
- According to the high EF values obtained for Ti, Fe, Zn, Pb, and Cd, the most significant anthropogenic sources of air pollution in the Donetsk region are coal burning, steel production (metallurgical plants, and power station), and transport.
- The RI indicated high pollution levels at the Yenakiieve Iron and Steel Works.
- **The obtained results showed high levels of heavy metal accumulation in the moss samples and provide strong evidence for poor air quality in the Donetsk region.**
- **The *Ceratodon purpureus* moss species could be used for biomonitoring of atmospheric trace element pollution in urban areas.**

Thank you for attention!