STUDY OF MAJOR AND TRACE ELEMENT DEPOSITION IN GEORGIA USING THE MOSS BIOMONITORING TECHNIQUE

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Introduction

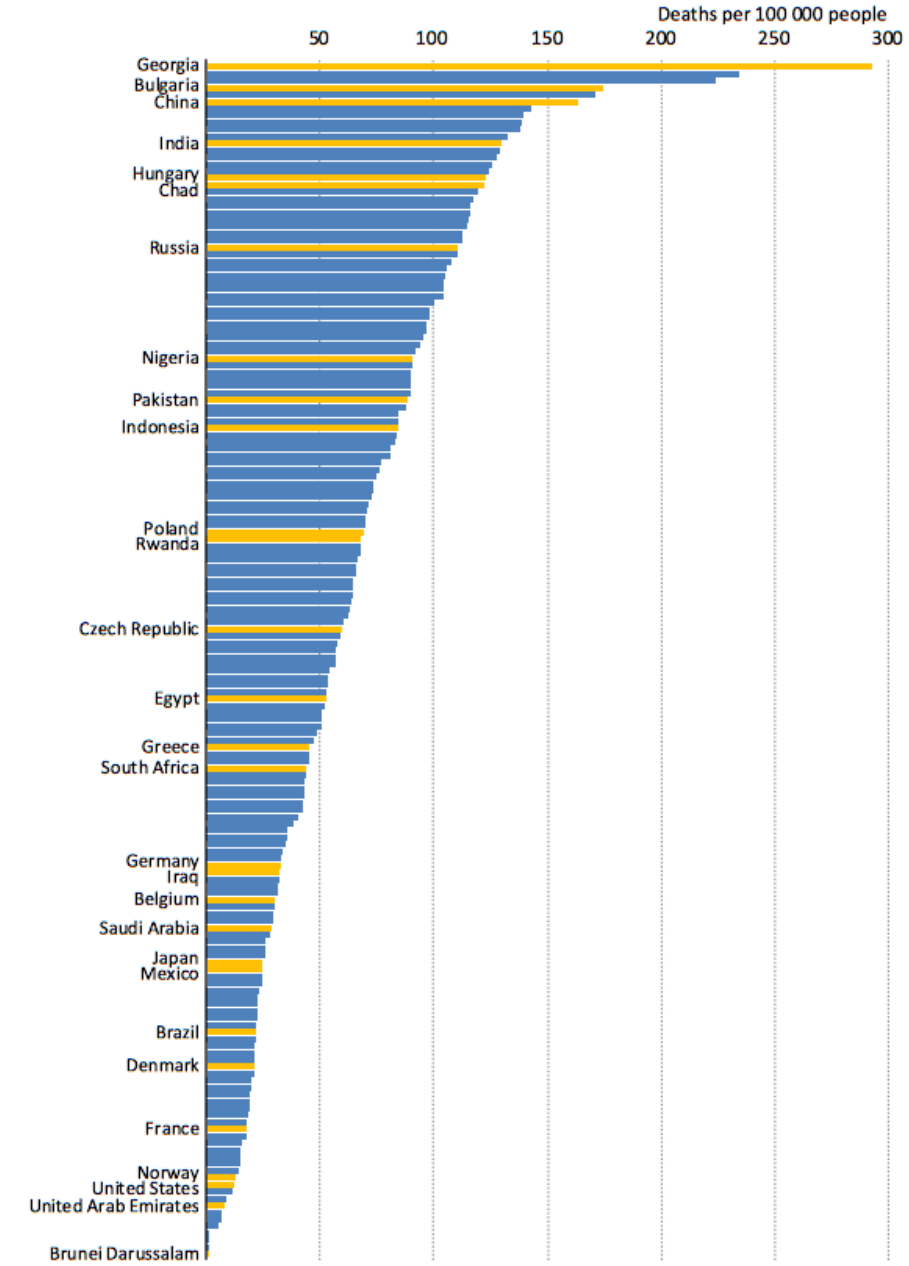
Georgia is a small country in the Caucasus region of Eurasia. Located at the crossroads of Western Asia and Eastern Europe.

Total area: 69,700 km^2
Population: 3.718 million

Introduction

Introduction

Figure 1.8 ▷ **Mortality rate attributed to air pollution (household and outdoor) by country, 2012**



Note: Only a selection of countries are highlighted.

Sources: WHO (2016b) and IEA analysis.

Introduction

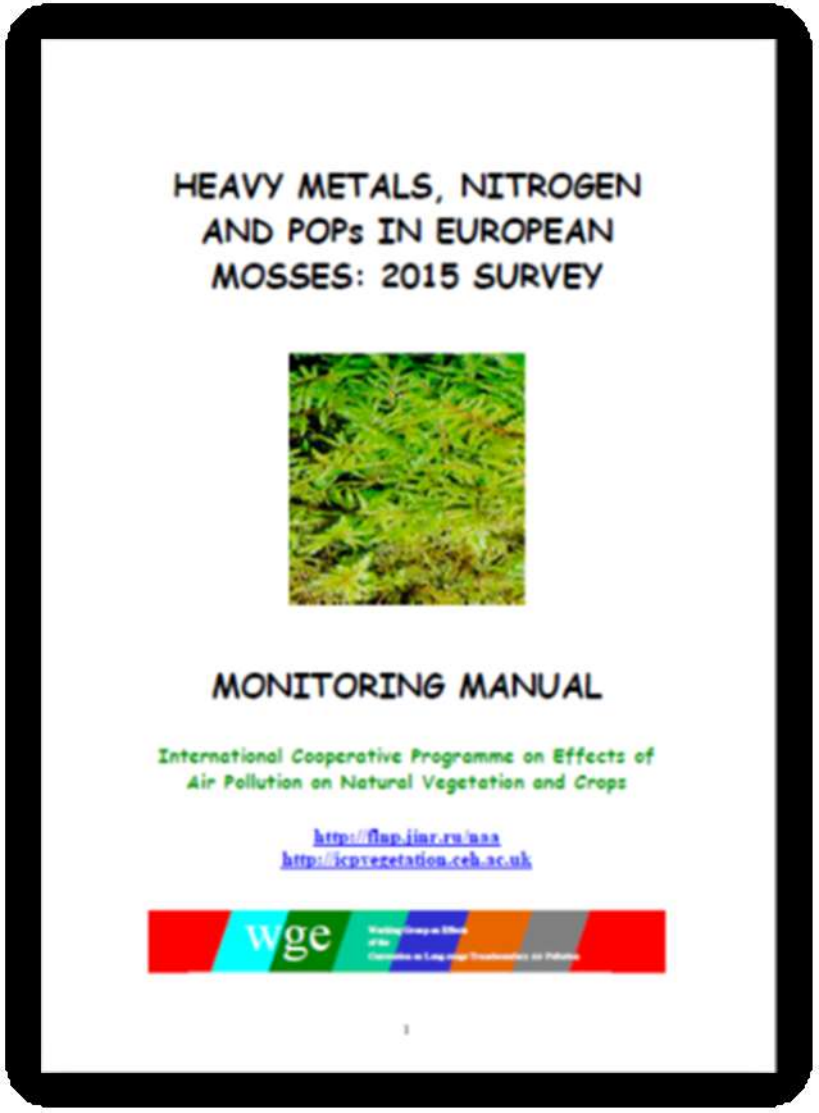
UNITED NATIONS
ECONOMIC COMMISSION
FOR EUROPE

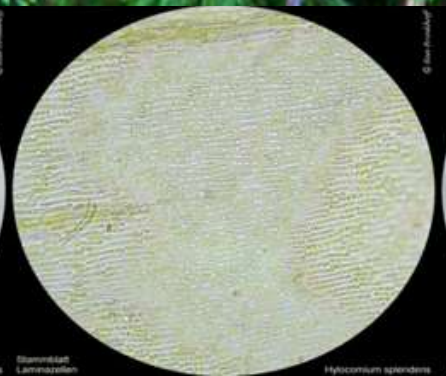
TFRN LRTAP
Long-range Transboundary Air Pollution

Since 2014 Georgia participates in the moss biomonotoring programme of the UNECE ICP Vegetation in the framework of the Convention on Long-Range Transboundary Air Pollution in Europe.

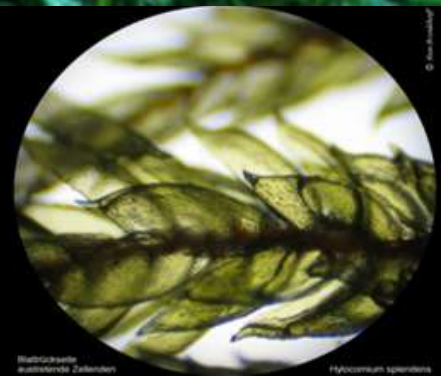
Sampling

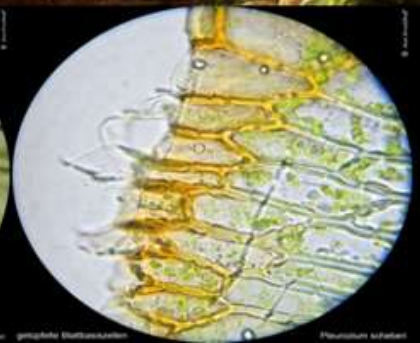
- Samples were collected during the period April – October.
- The sampling points were located at least 300 m from main roads (highways), villages and industries and at least 100 m away from smaller roads and houses.
- For each sampling site up to 10 sub-samples were taken in the area of 50 x 50m and combined into one collective sample.
- Each sampling point was situated at least 3 m away from the nearest projected tree canopy.
- Disposable plastic gloves were used when picking up the moss.
- Descriptions of all sites have been recorded along with the geographical coordinates determined by GPS



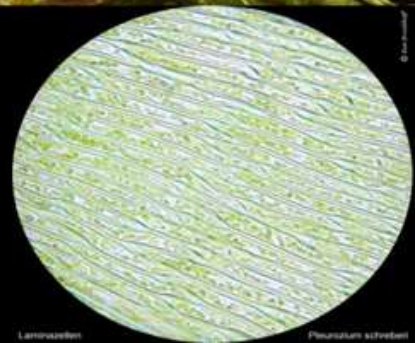


Hylocomium splendens
33 samples





Pleurozium schreberi
20 samples

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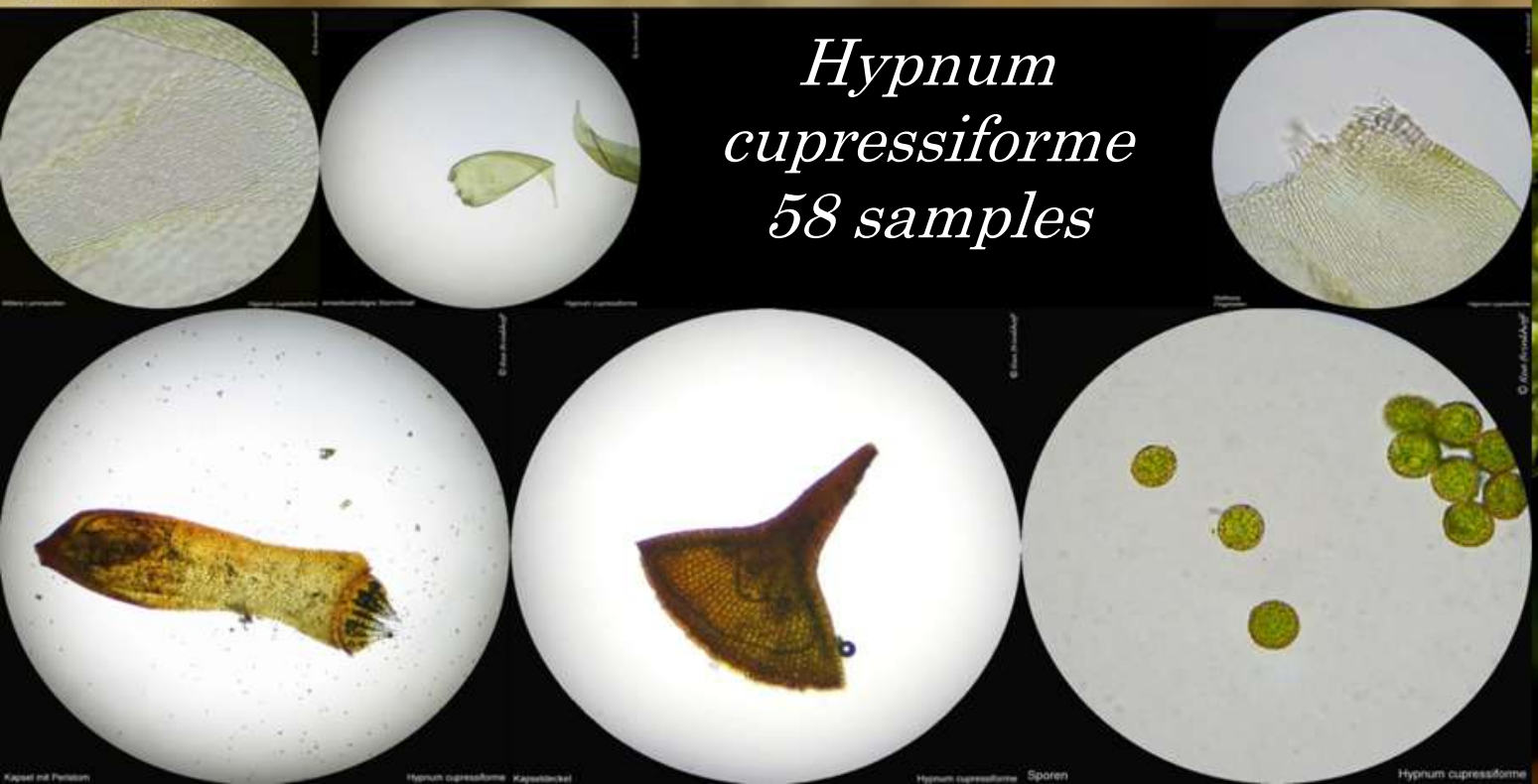
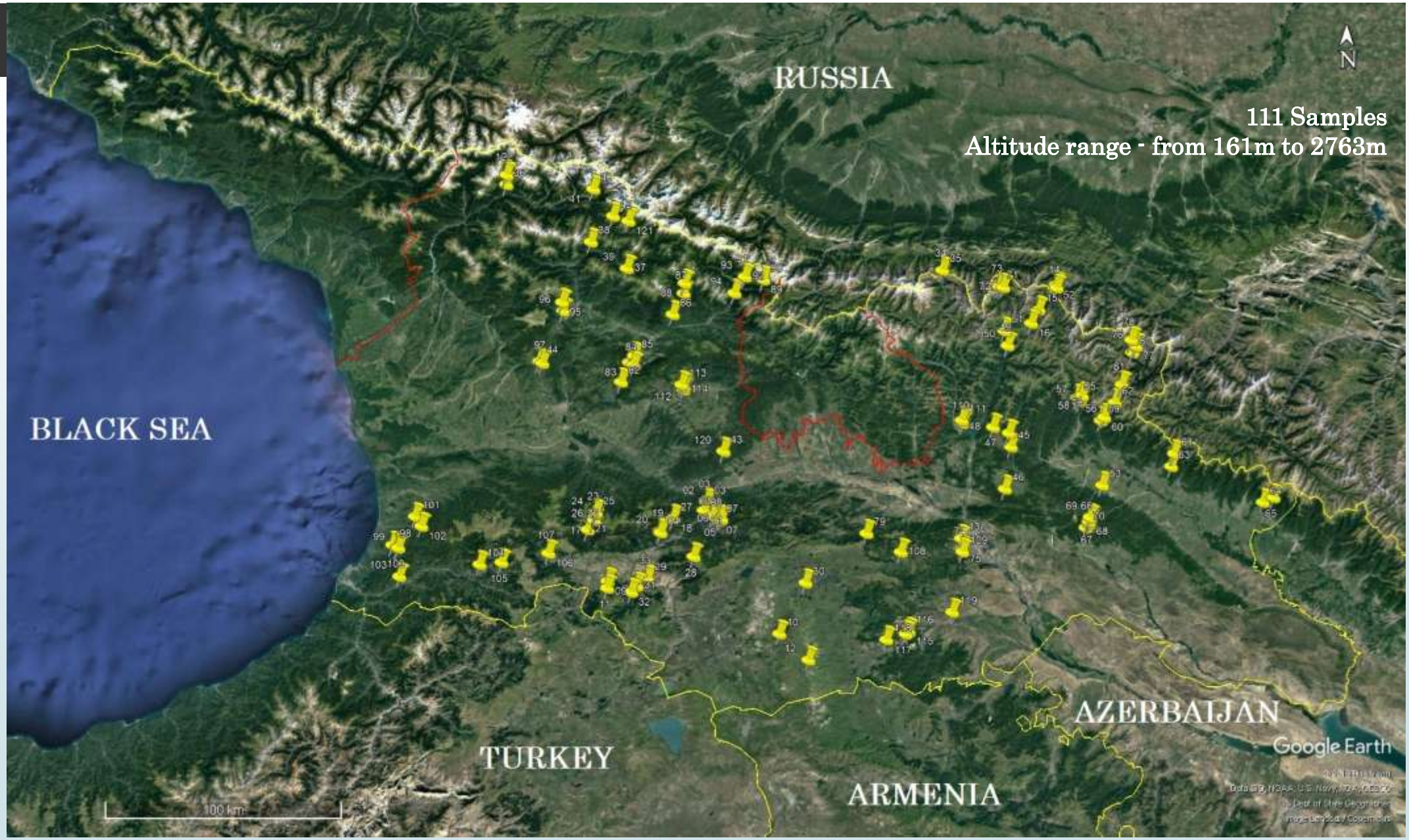
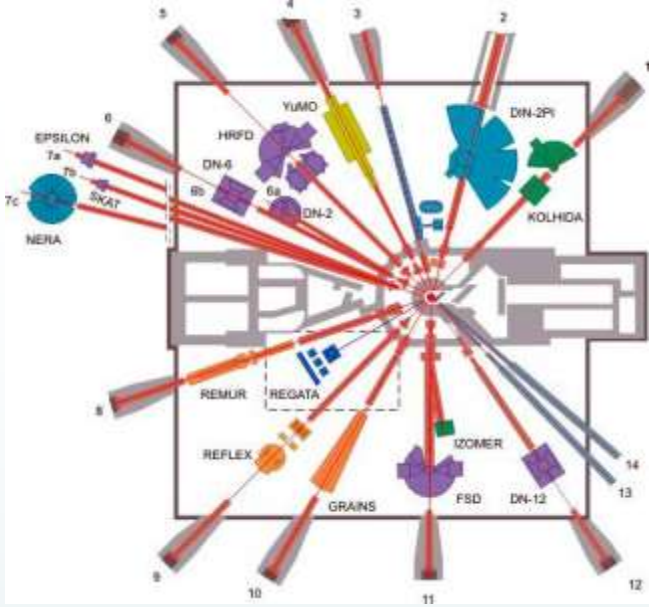

Hypnum
cupressiforme
58 samples

Sampling map 2014-2016



Analysis

- All the samples were dried to constant weight at 30–40° C for 48 hours.



ENAA

- They were not washed and not homogenized.
- About 0.3 g of mosses were pelletized in press-forms and packed for short-term and long-term irradiation.
- NAA of mosses samples was carried out using REGATA facility in the IBR-2 (JINR)
- The concentrations of 39 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Sr, Zr, Mo, Pb, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, W, Au, Th, and U) were determined based on relative method using the certified reference materials: Trace Elements in Pine Needles-1575a (NIST), Trace Elements in Coal-1632c (NIST), Montana Soil-2710 (NIST) and BCR-667 (Belgium).

Analysis

AAS

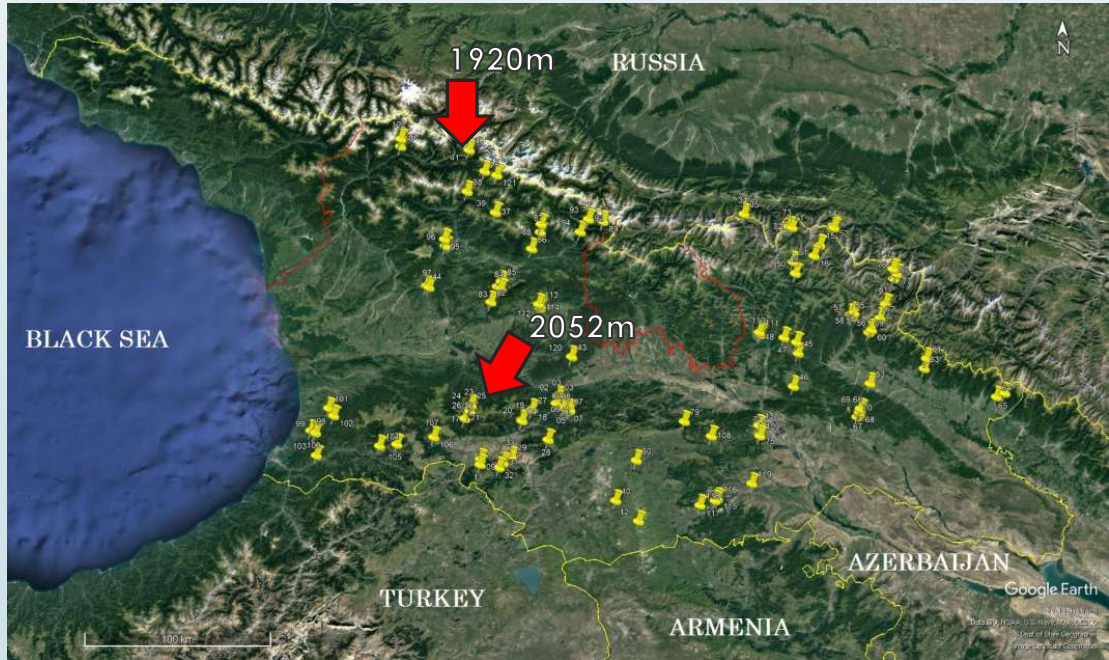
- Approximately 0.2 g of moss was placed in a Teflon vessel and treated with 3 mL of concentrated nitric acid (HNO_3) and 2 mL of hydrogen peroxide (H_2O_2).
- The moss material was introduced in a microwave digestion system (Mars; CEM, Matthews, NC, USA) for complete digestion.
- Digests were transferred to 100-mL calibrated flasks and made up to the volume with bi-distilled water.
- The amount of Cd, Cu and Pb in the moss samples was determined by means of a iCE 3300 AAS Atomic Absorption Spectrometer with electrothermal (graphite furnace) atomization (Thermo Fisher Scientiic, Waltham, MA, USA).
- The quality control was performed by using the NIST certified reference materials SRM 1570a (spinach leaves) and SRM 1575a (pine needles).

Analysis

SEM/EDX

The composition and morphology of the two samples from 2015 collection (No.24 Lesser Caucasus, Mescheti and No.41 Greater Caucasus, Lower Svaneti) from the mountainous regions of Caucasus were examined using a Scanning Electron Microscope "Tescan Vega II" with an energy dispersive spectrometer "Drycool" at the Borok Geophysical Observatory, a branch of the Institute of Physics of the Earth.

Samples were dispersed by ultrasound. The separated mineral particles were deposited on a double-sided adhesive coal tape.
The investigations were carried out at an accelerating voltage of 20 Kv and a current of 200 picoamperes



Statistical analysis and mapping

Statistical treatment STATISTICA 12.6

- Factor analysis (Varimax rotation with Kaiser normalization)

Geospatial mapping *ArcGIS 10.3*

- Spline interpolation

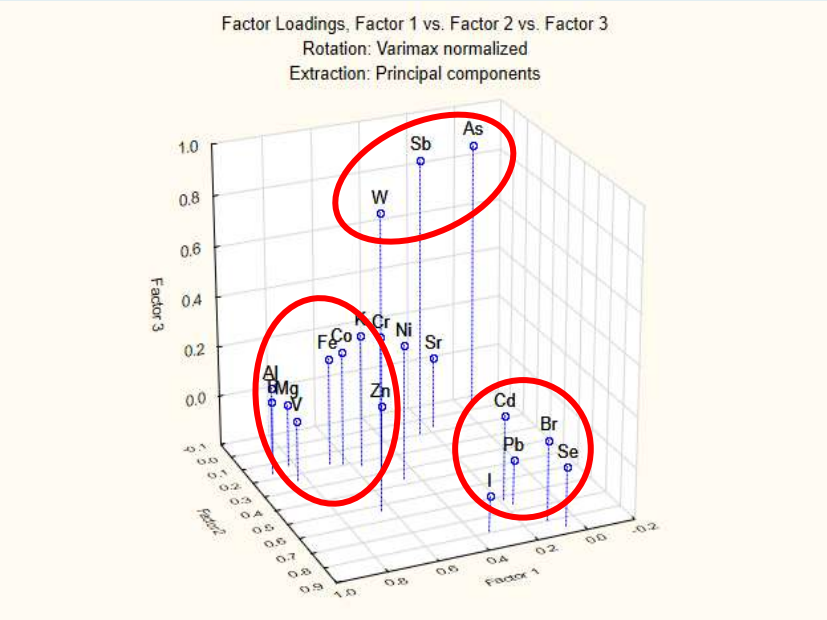
Results and discussion

Factor 1: Co (0.63), Fe (0.67), Al (0.89), V (0.84), Ti (0.90), Zn (0.64), Mg (0.82) – these elements obviously belong to light and heavy crust components;

Factor 2: I (0.79), Br (0.80), Se (0.86) most probably reflects a mixture of "marine elements";

Factor 3: As (0.87), W (0.75) and Sb (0.90) – is definitely a contamination by local mining industry;

Factor 4: Co (0.72), Cr (0.67), Fe (0.63) Ni (0.60) and Sr (0.79) is attributed to local industrial enterprises.

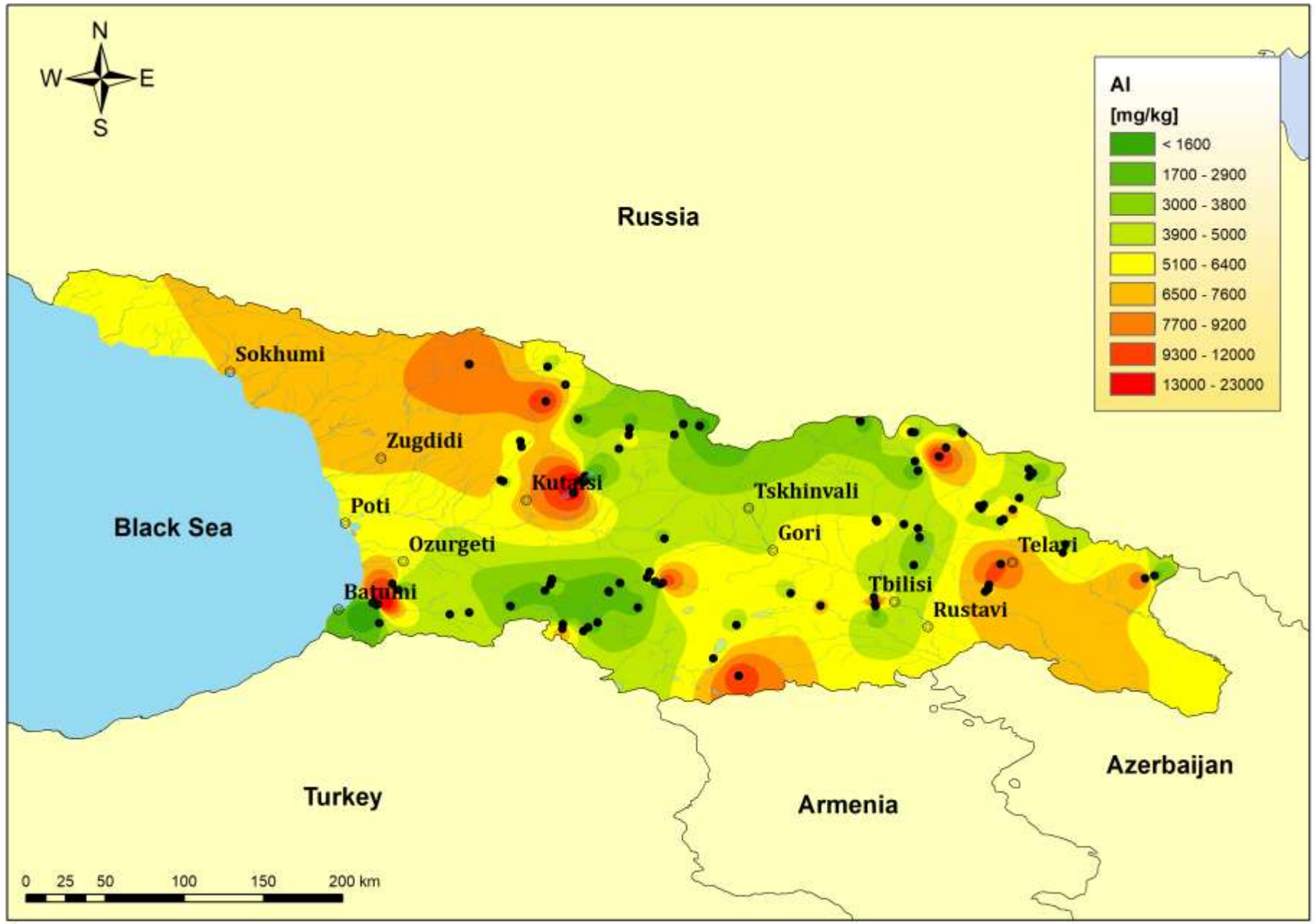


Matrix of Varimax rotated factor loadings (n=111, 19 selected elements)

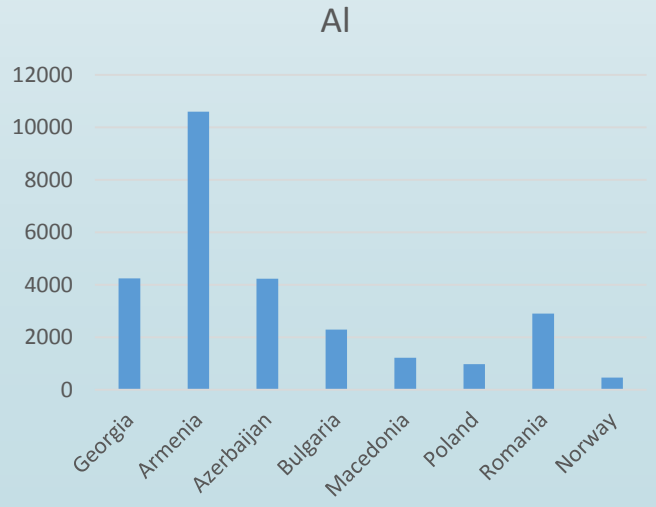
	Factor 1	Factor 2	Factor 3	Factor 4
As	-0.04	-0.04	**0.87**	0.06
W	0.44	0.15	**0.75**	0.31
Sb	0.25	0.09	**0.90**	0.16
Pb	0.17	**0.66**	-0.02	0.38
Cd	0.18	**0.62**	0.14	-0.35
Co	**0.63**	0.19	0.26	**0.65**
Cr	0.51	0.28	0.34	**0.67**
Fe	**0.67**	0.17	0.23	**0.63**
Ni	0.46	0.37	0.34	**0.60**
Al	**0.89**	0.13	0.12	0.34
Se	0.06	**0.86**	0.04	0.15
Br	0.11	**0.80**	0.12	0.19
I	0.34	**0.79**	-0.06	0.12
V	**0.84**	0.24	0.05	0.36
Ti	**0.90**	0.17	0.09	0.13
Sr	0.18	0.07	0.09	**0.79**
Zn	**0.64**	0.53	0.21	0.03
Mg	**0.82**	0.13	0.05	0.44
K	0.56	0.22	0.32	-0.10
Expl.Var	5.50	3.62	2.71	3.20
Prp.Totl	0.29	0.19	0.14	0.17

Aluminum (Al)

Factor 1

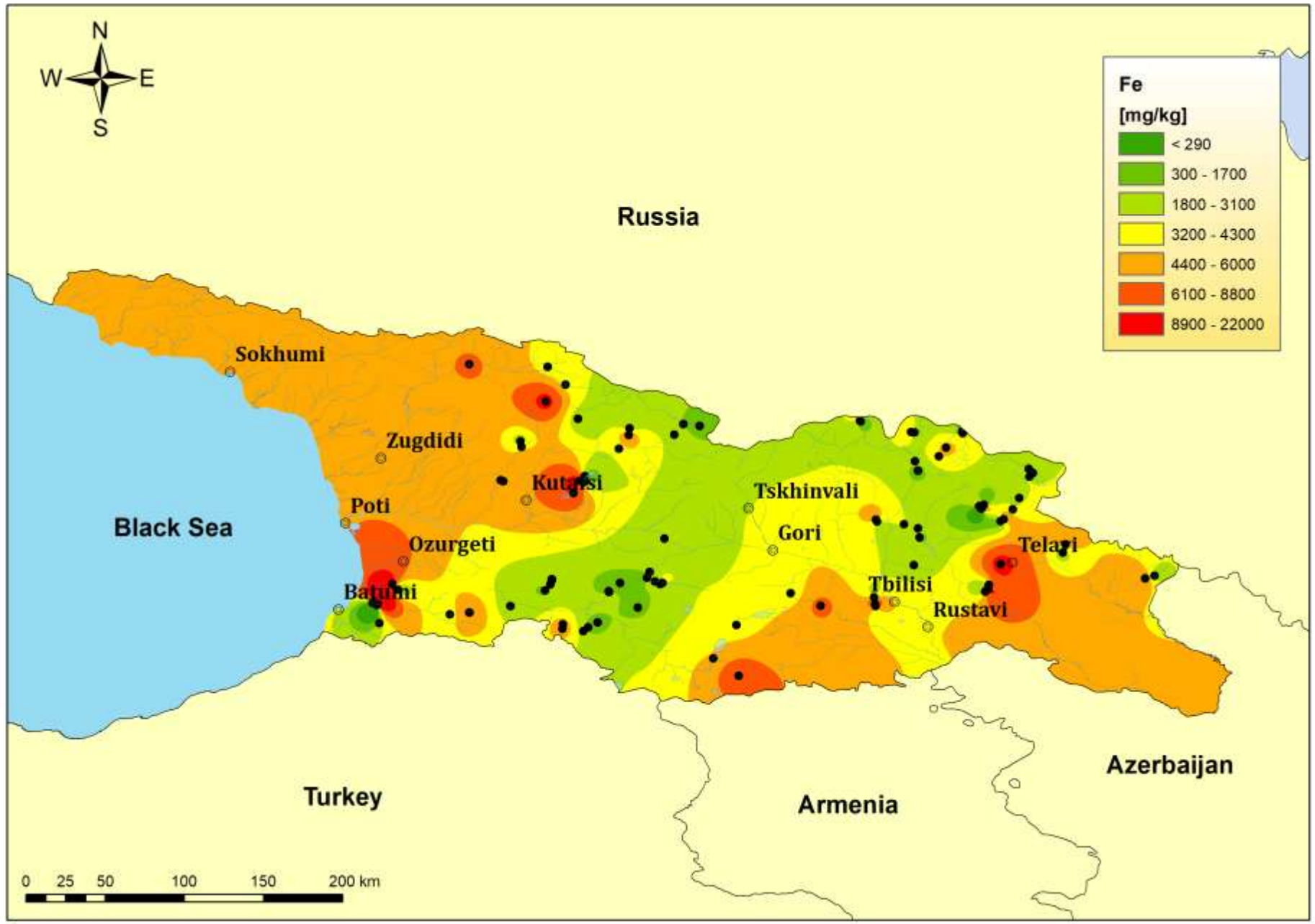


- Good indicator of mineral particles, mainly windblown soil dust
- Found in Earth's crust
- Connected with local sources: e.g metal industry

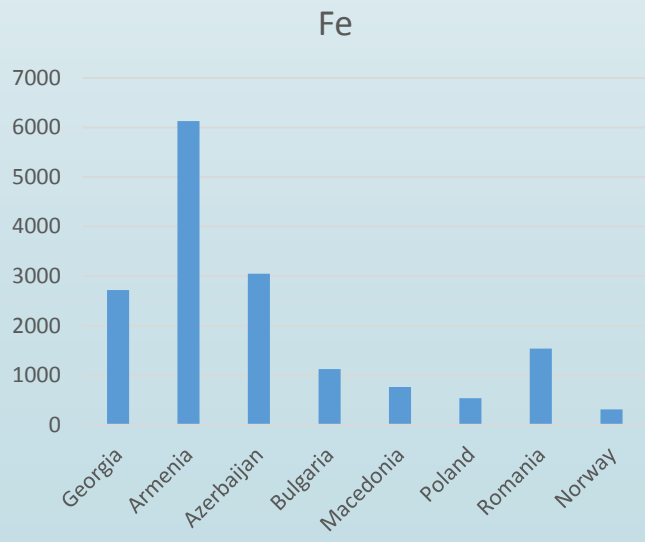


Iron (Fe)

Factor 1

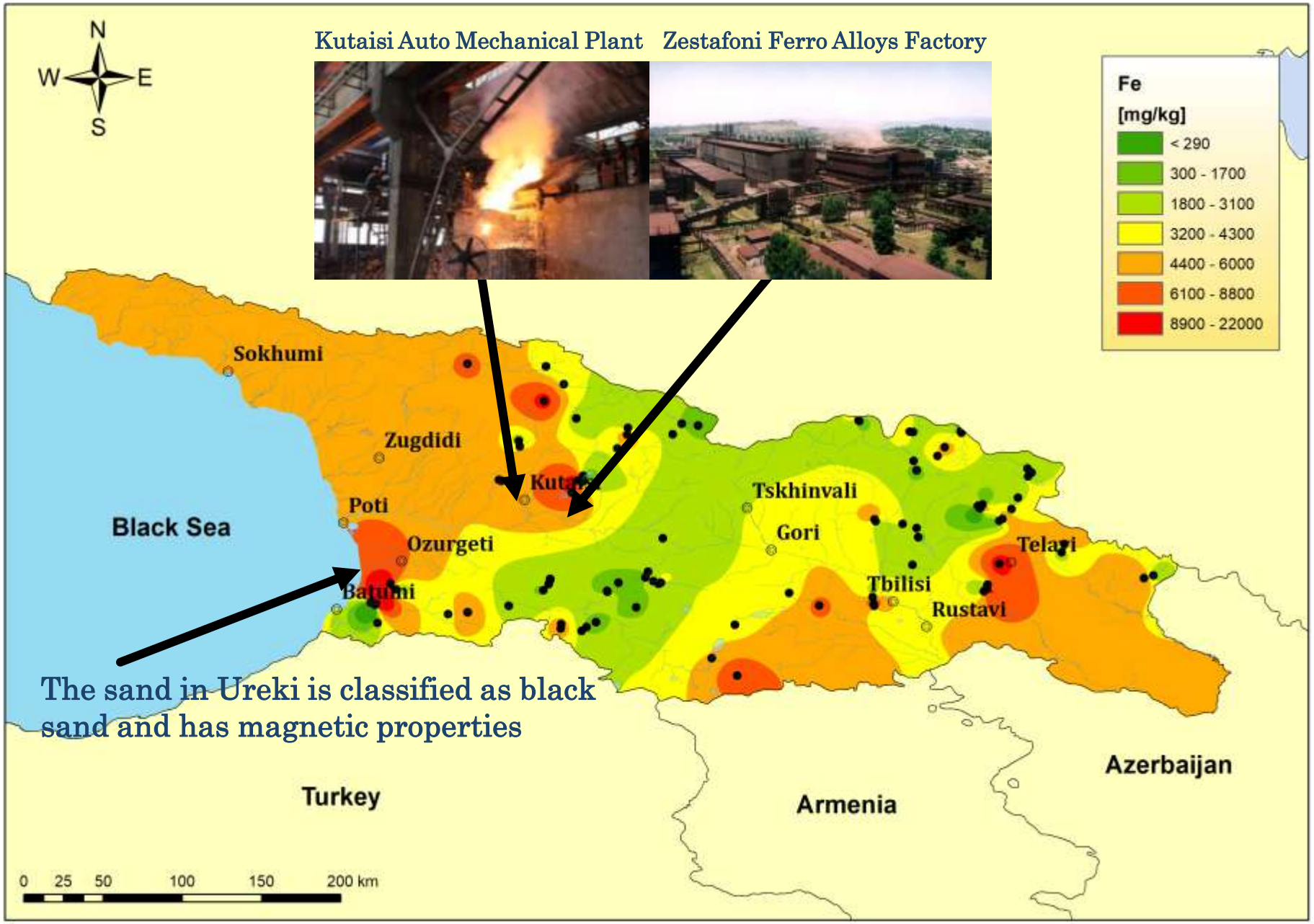


- Found in Earth's crust.
- Connected with local sources: e.g metal industry.



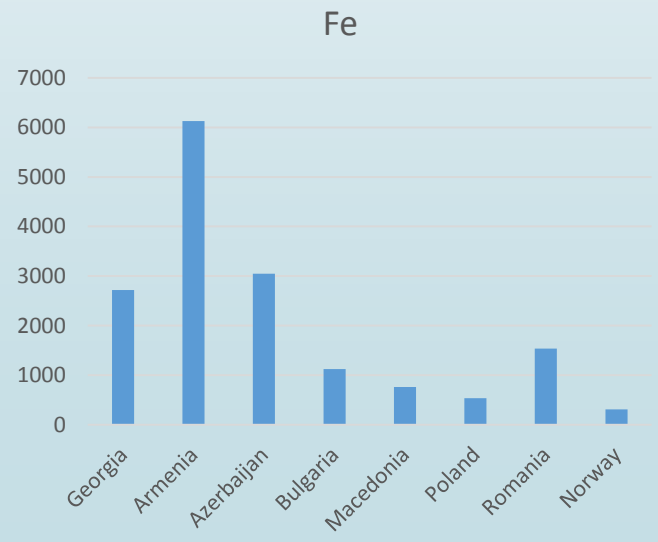
Iron (Fe)

Factor 1



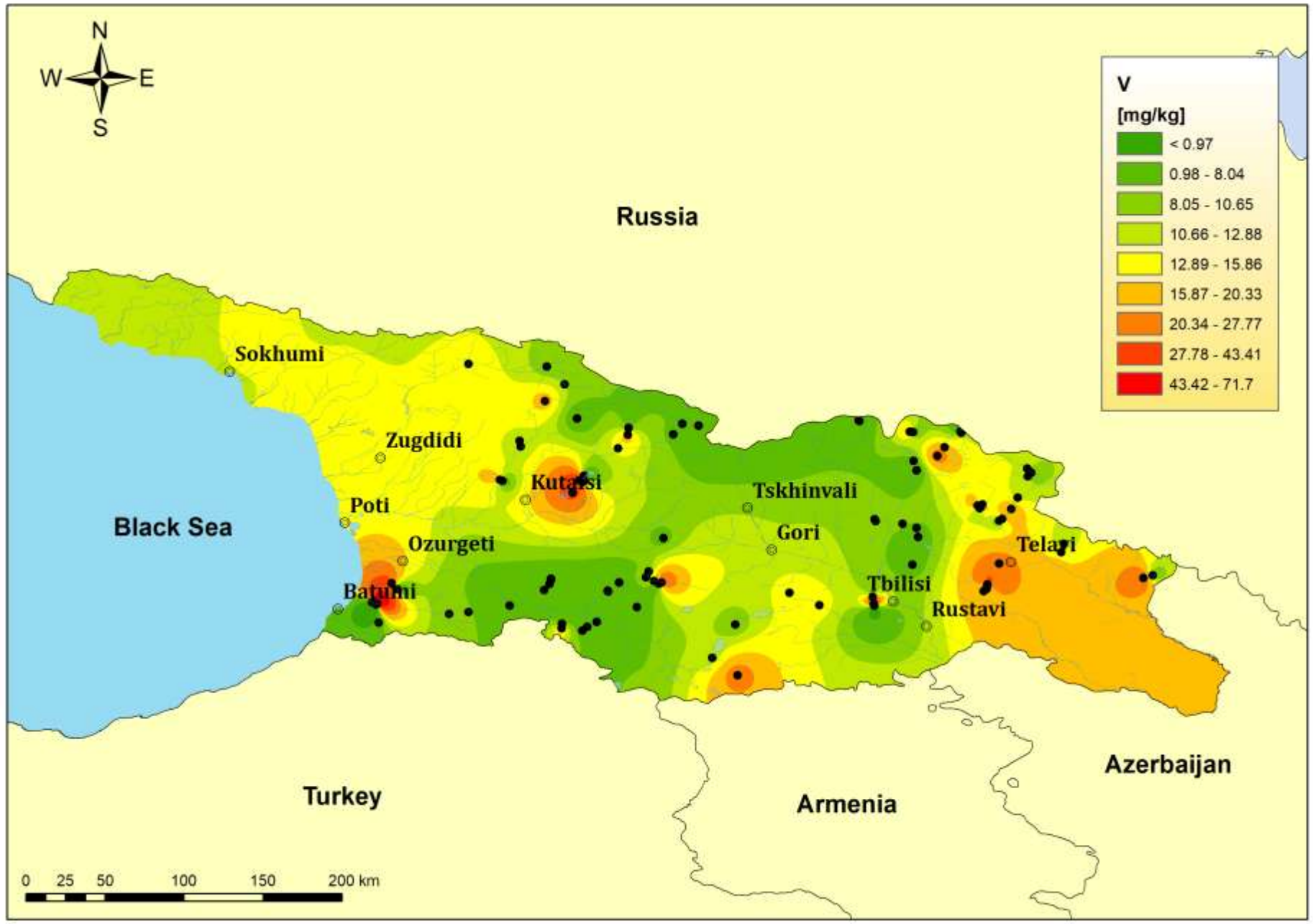
The sand in Ureki is classified as black sand and has magnetic properties

- Found in Earth's crust.
- Connected with local sources: e.g metal industry.

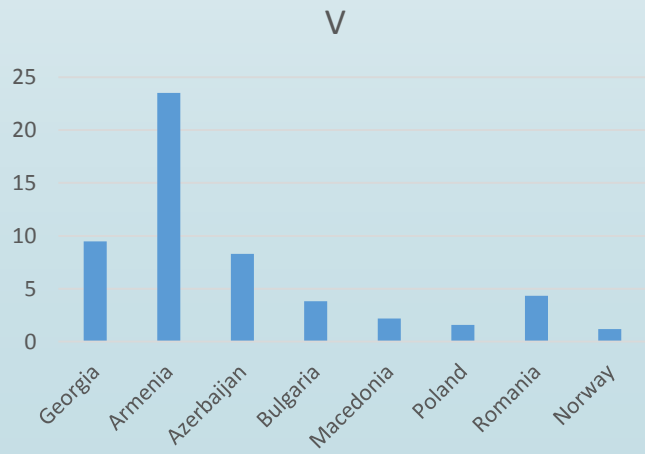


Vanadium (V)

Factor 1

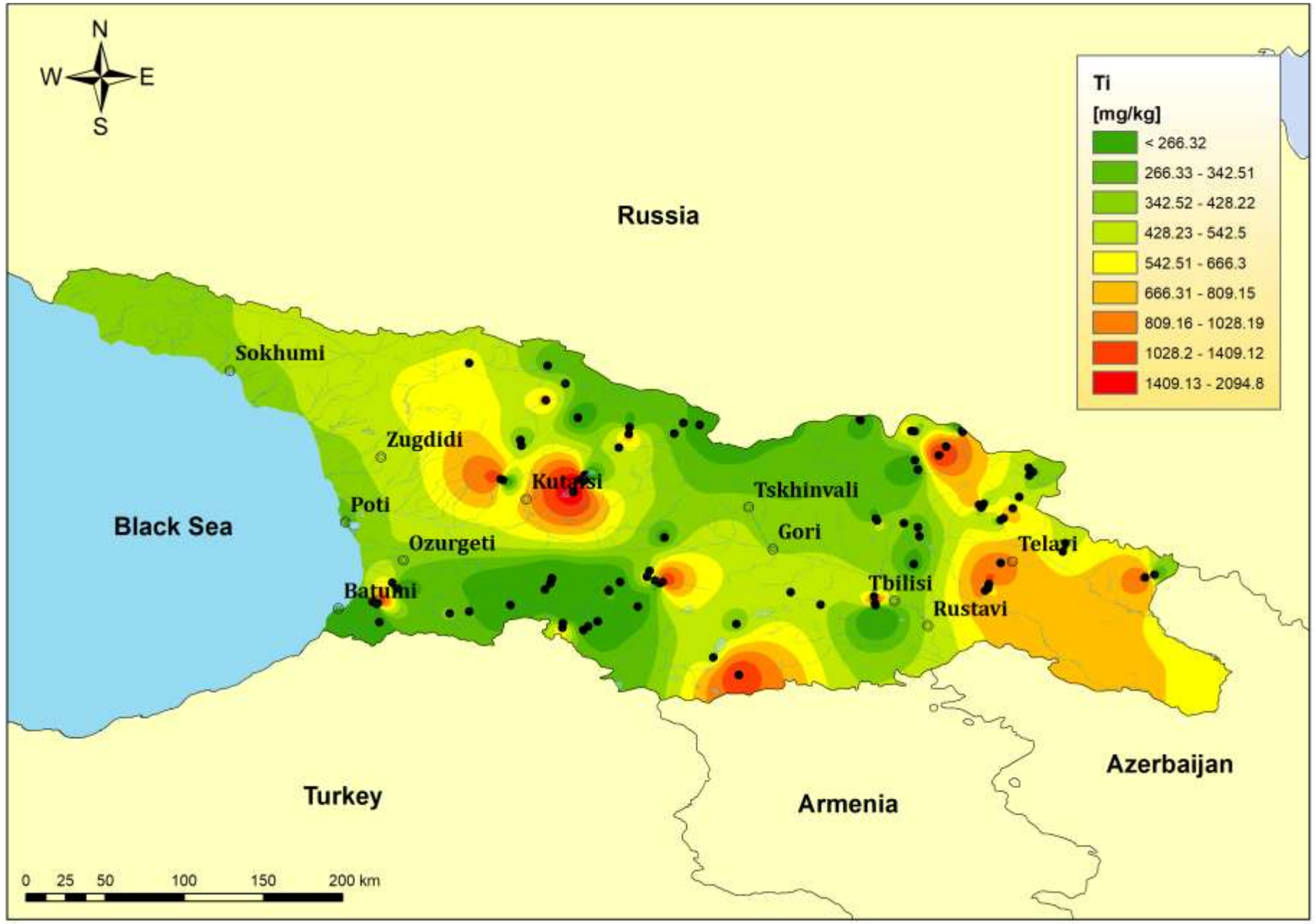


- Chemical similar to Ti, Fe, Al, U
- Due to industrial pollution
- Found in oil industry and petroleum refining

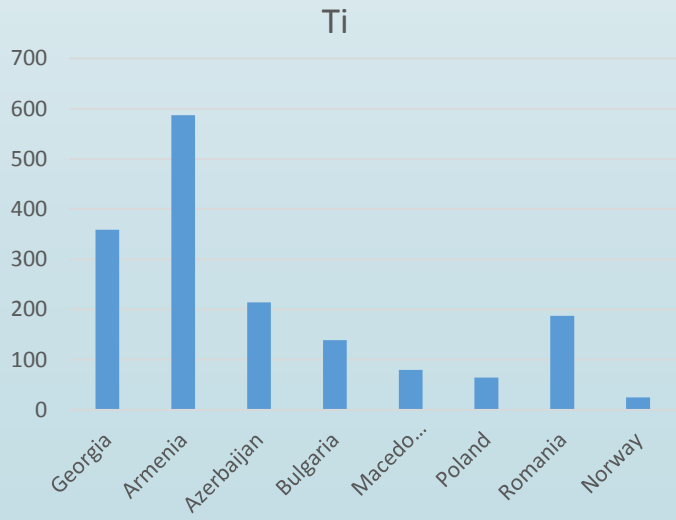


Titanium (Ti)

Factor 1

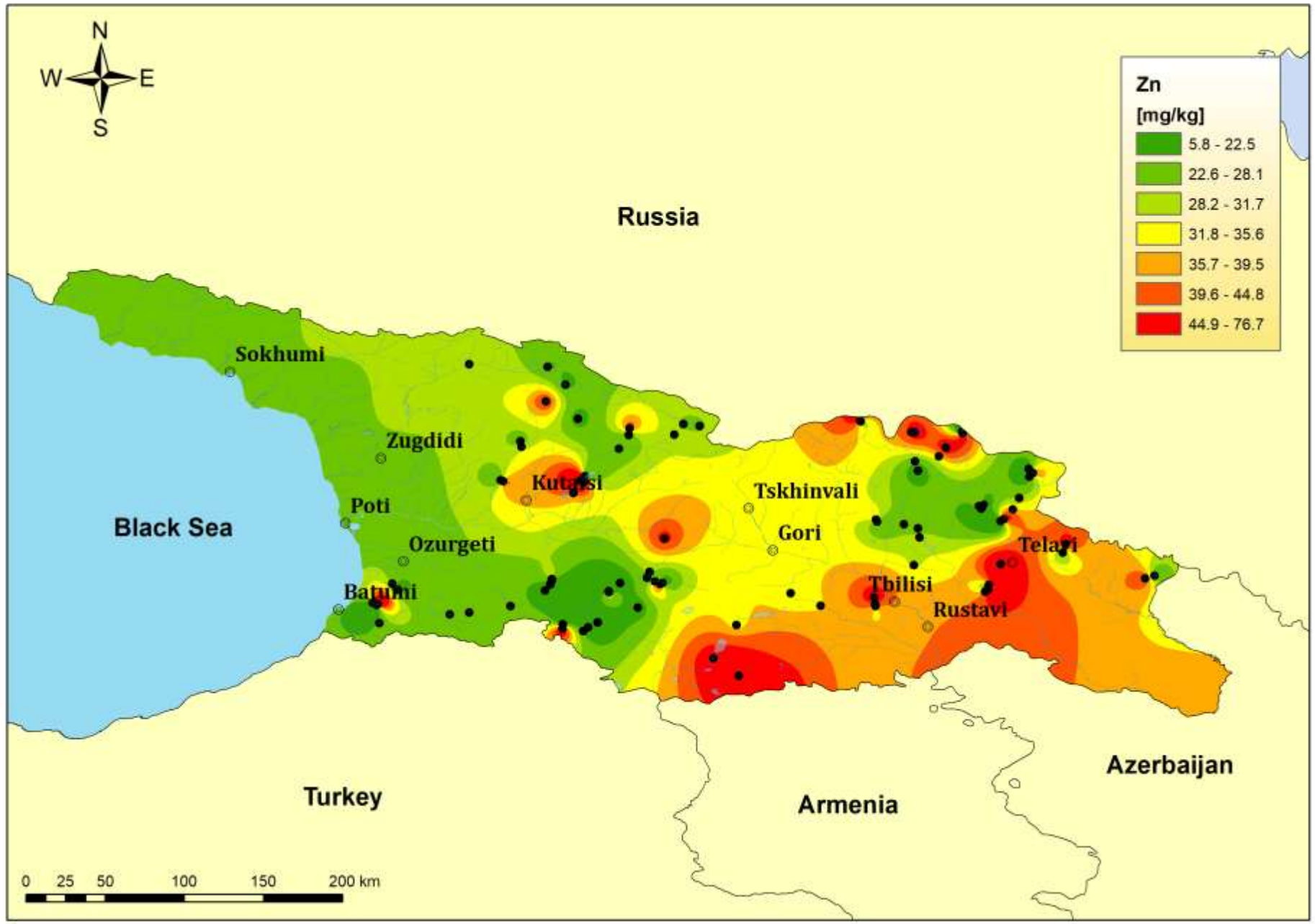


- Ti and V follow the same pattern in some areas

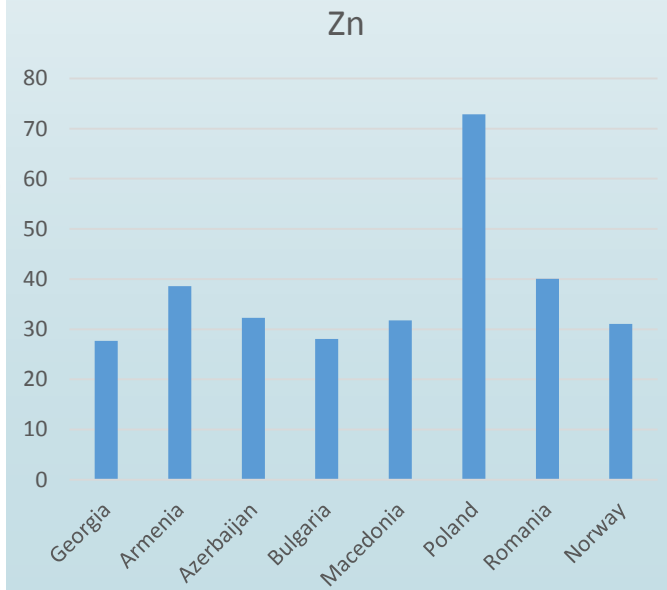


Zinc(Zn)

Factor 1

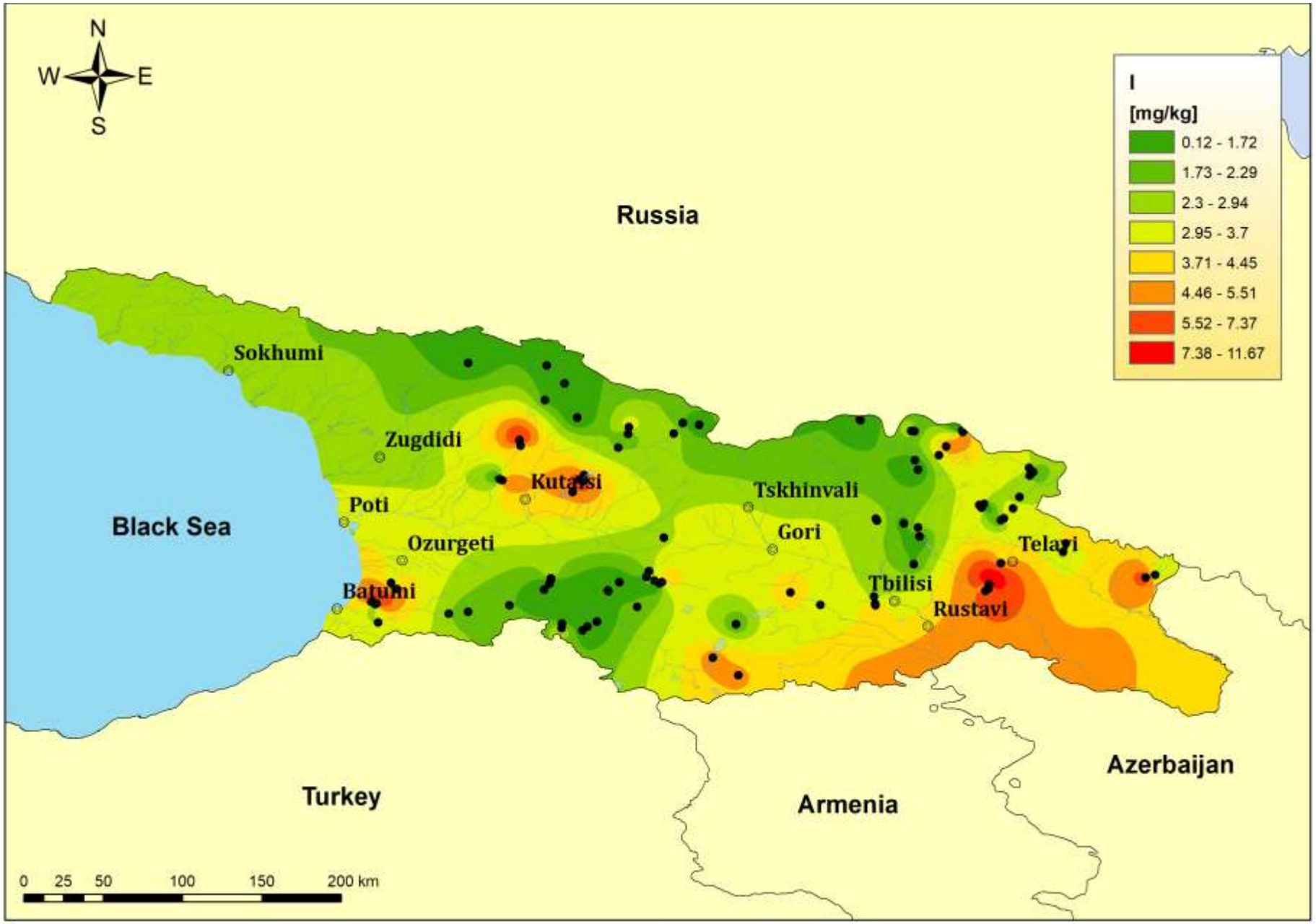


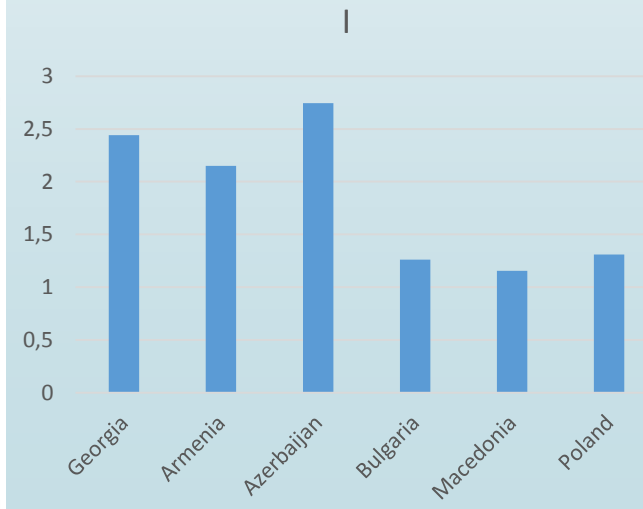
- Used in manufacture of rubbers, tires
- Traffic



Iodine (I)

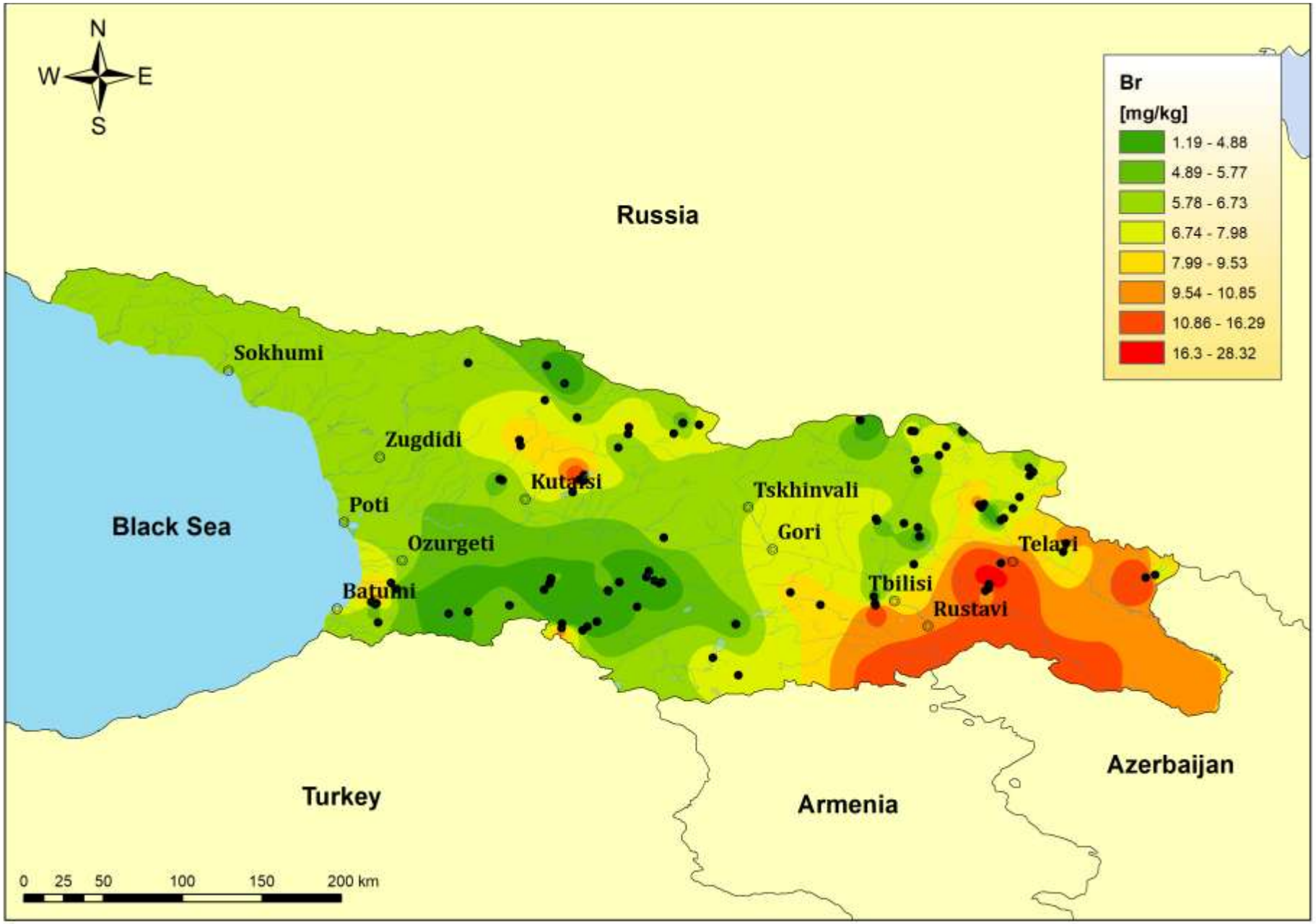
Factor2

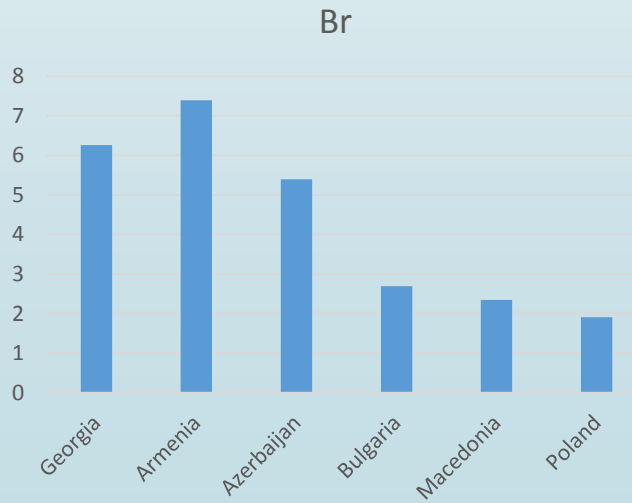


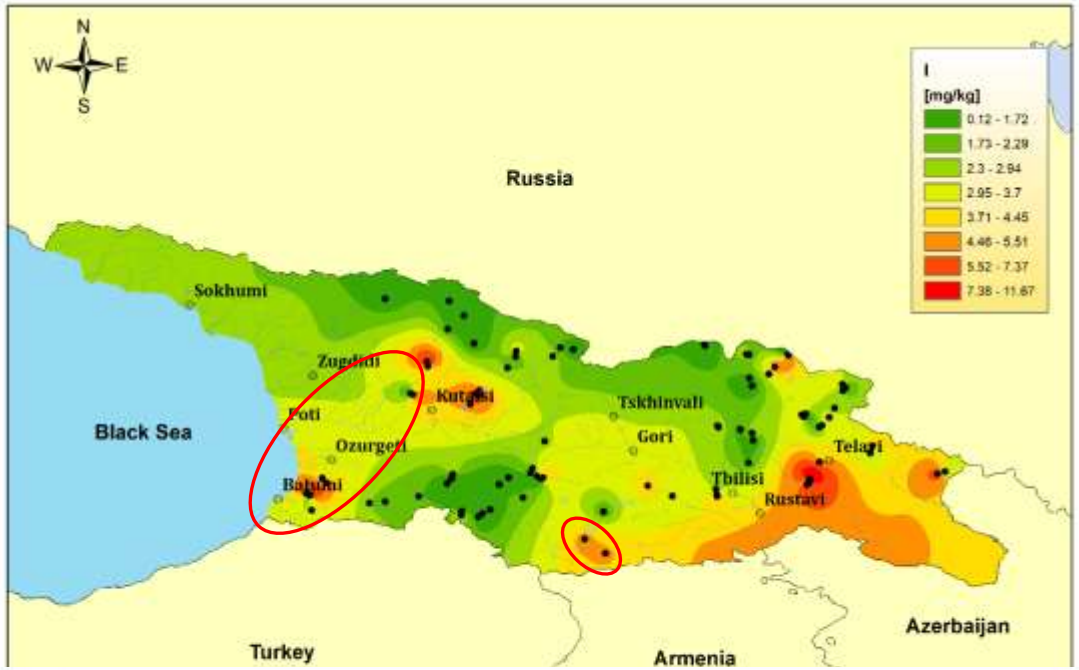


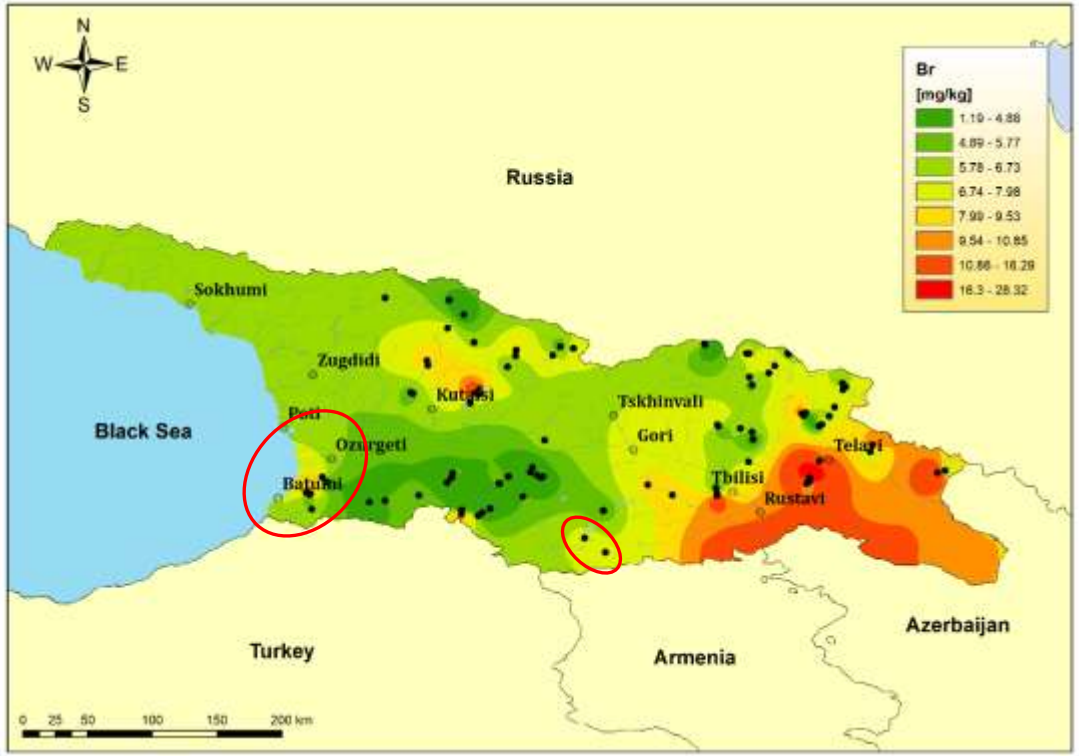
Bromine (Br)

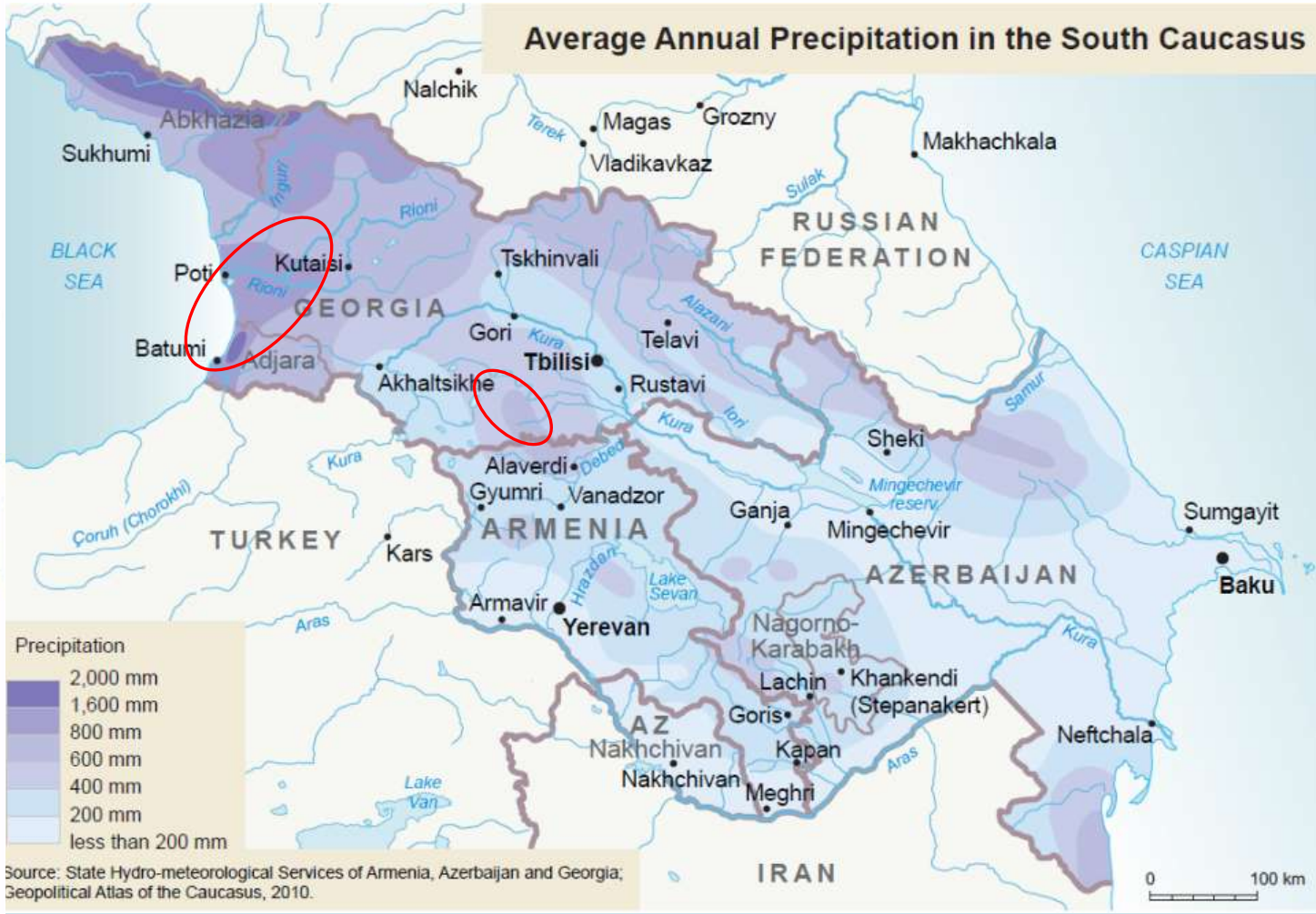
Factor2







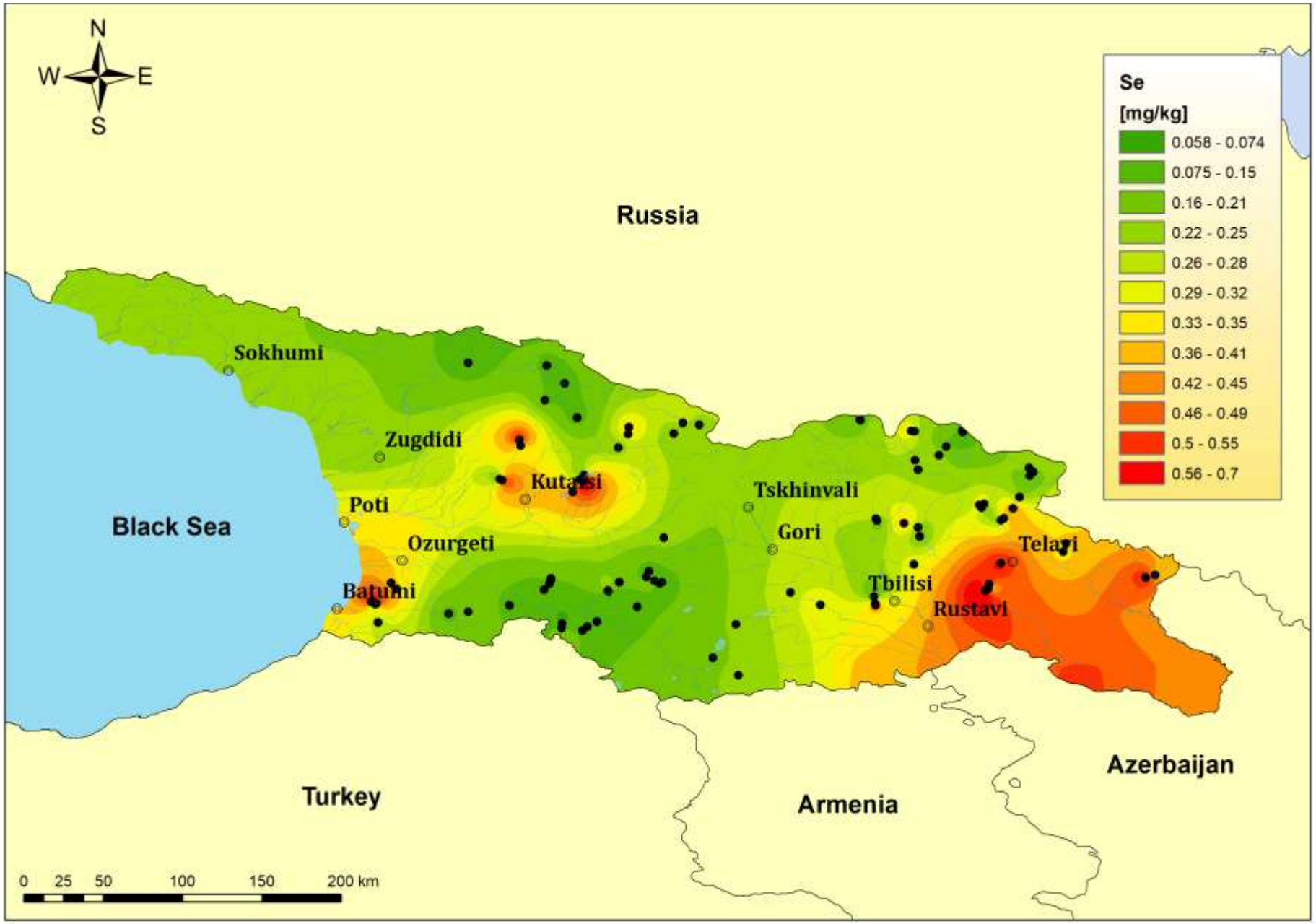




Source: State Hydro-meteorological Services of Armenia, Azerbaijan and Georgia; Geopolitical Atlas of the Caucasus, 2010.

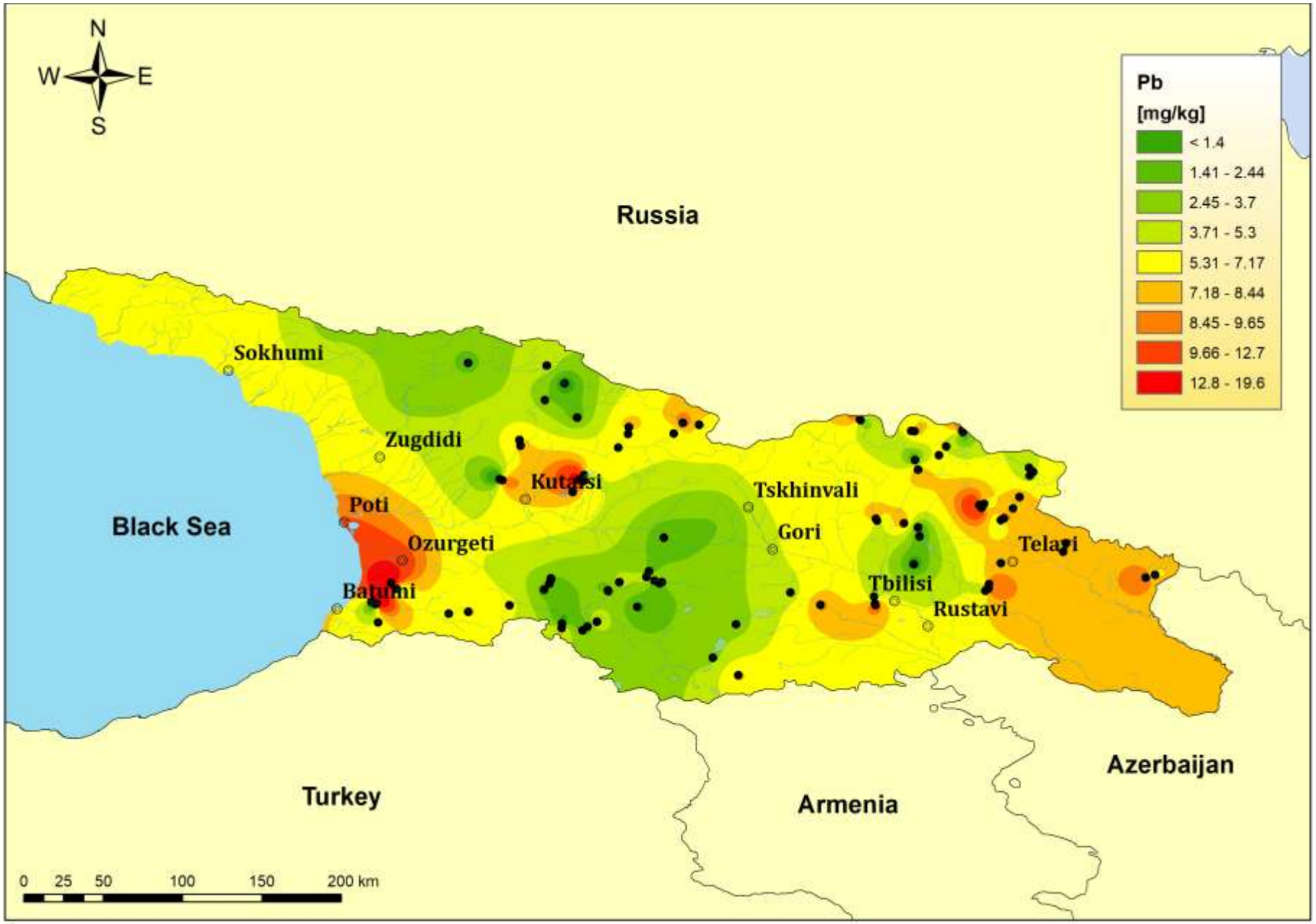
Selenium (Se)

Factor2

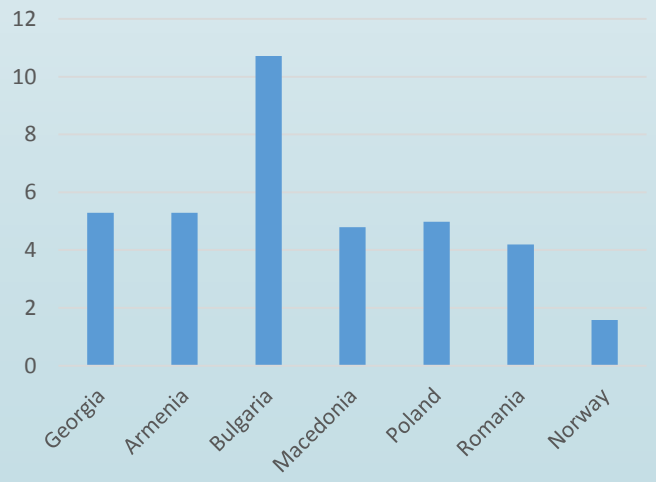


Lead (Pb)

Factor2

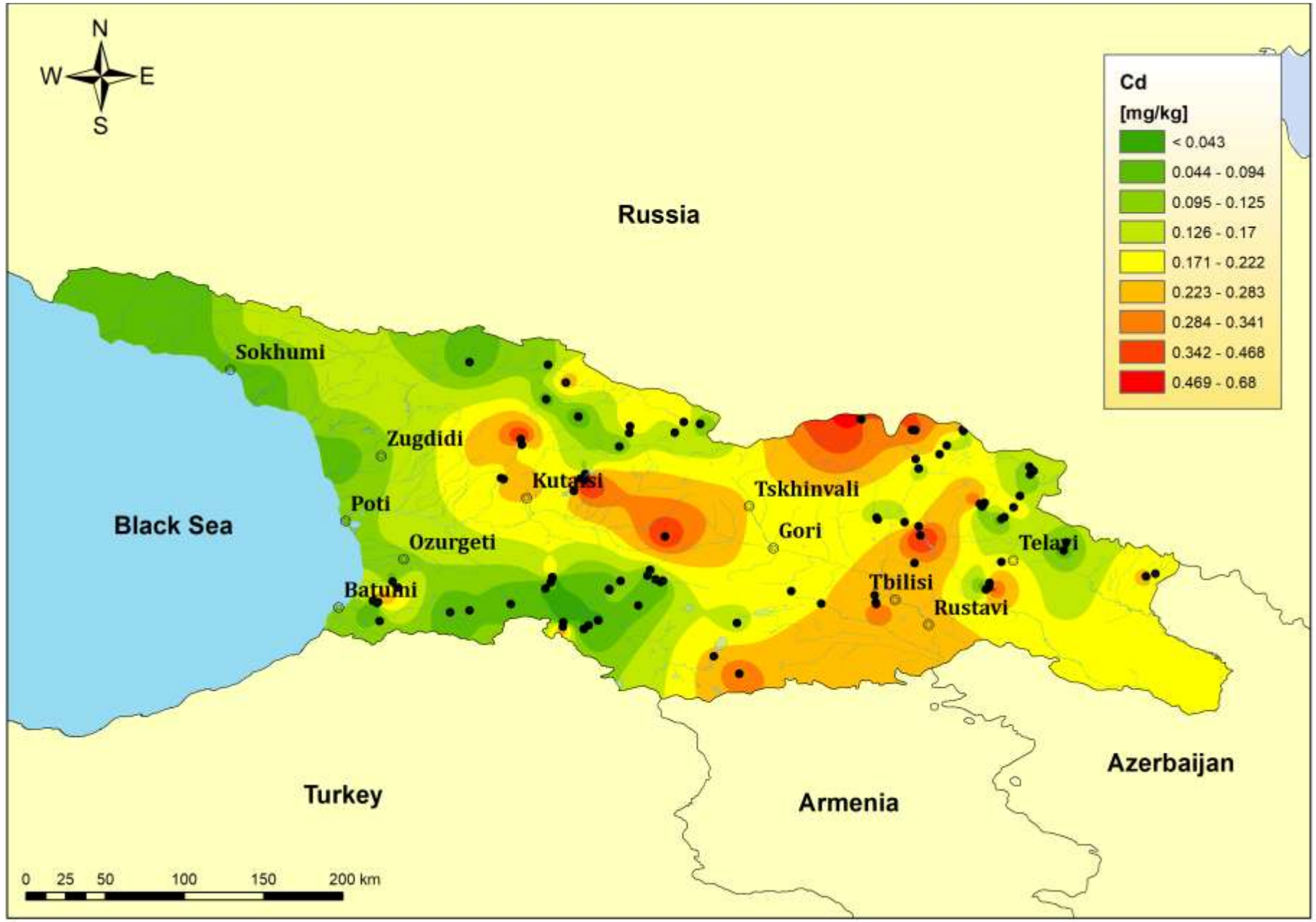


- Urban areas; industrial emissions,
- Lead and Marine elements follow the same pattern in some areas

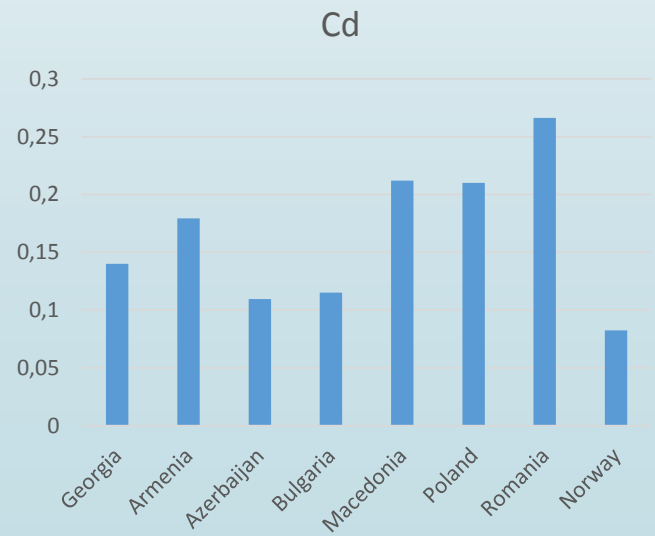


Cadmium (Cd)

Factor2

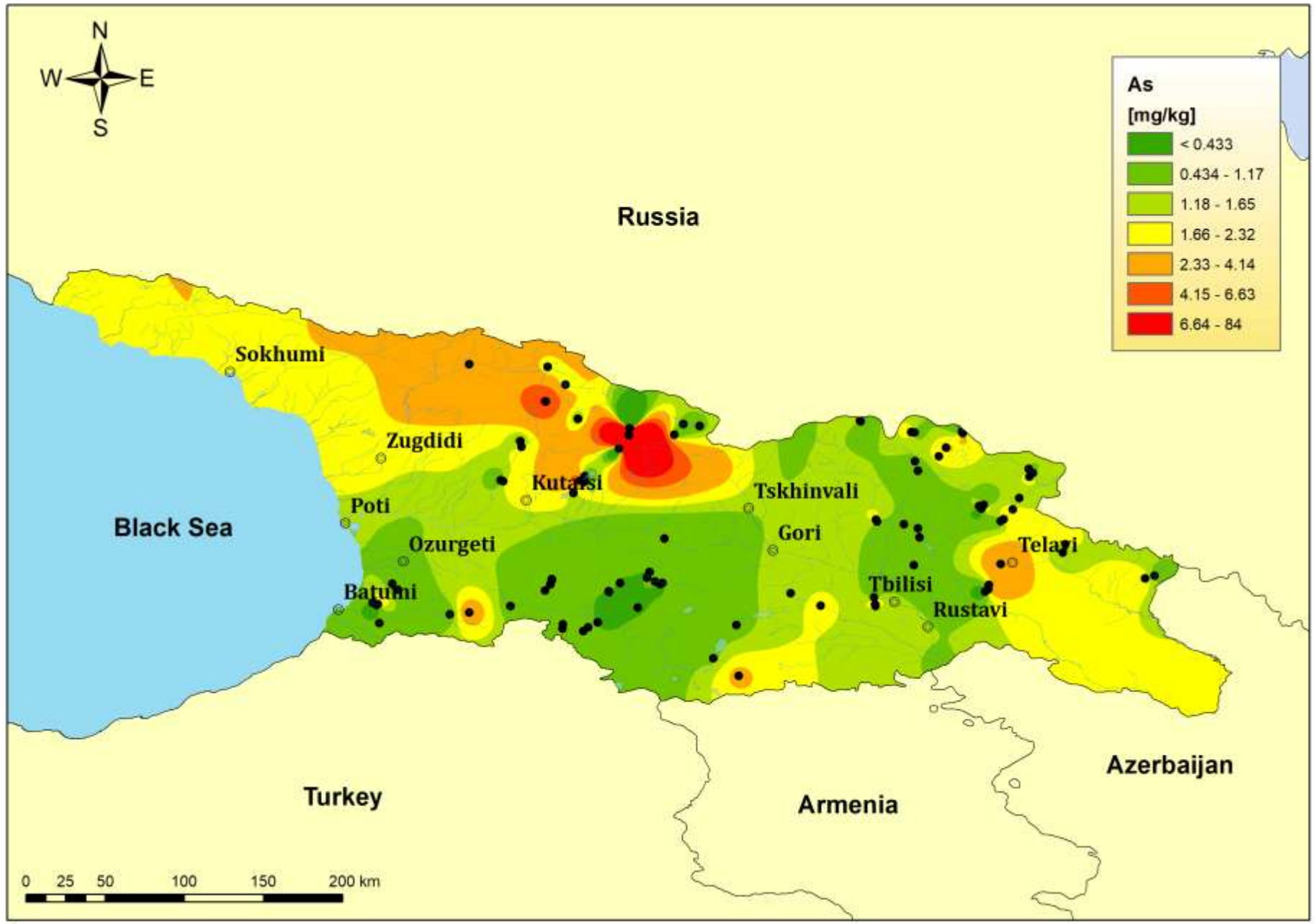


- Cadmium and Marine elements follow the same pattern in some areas



Arsenic (As)

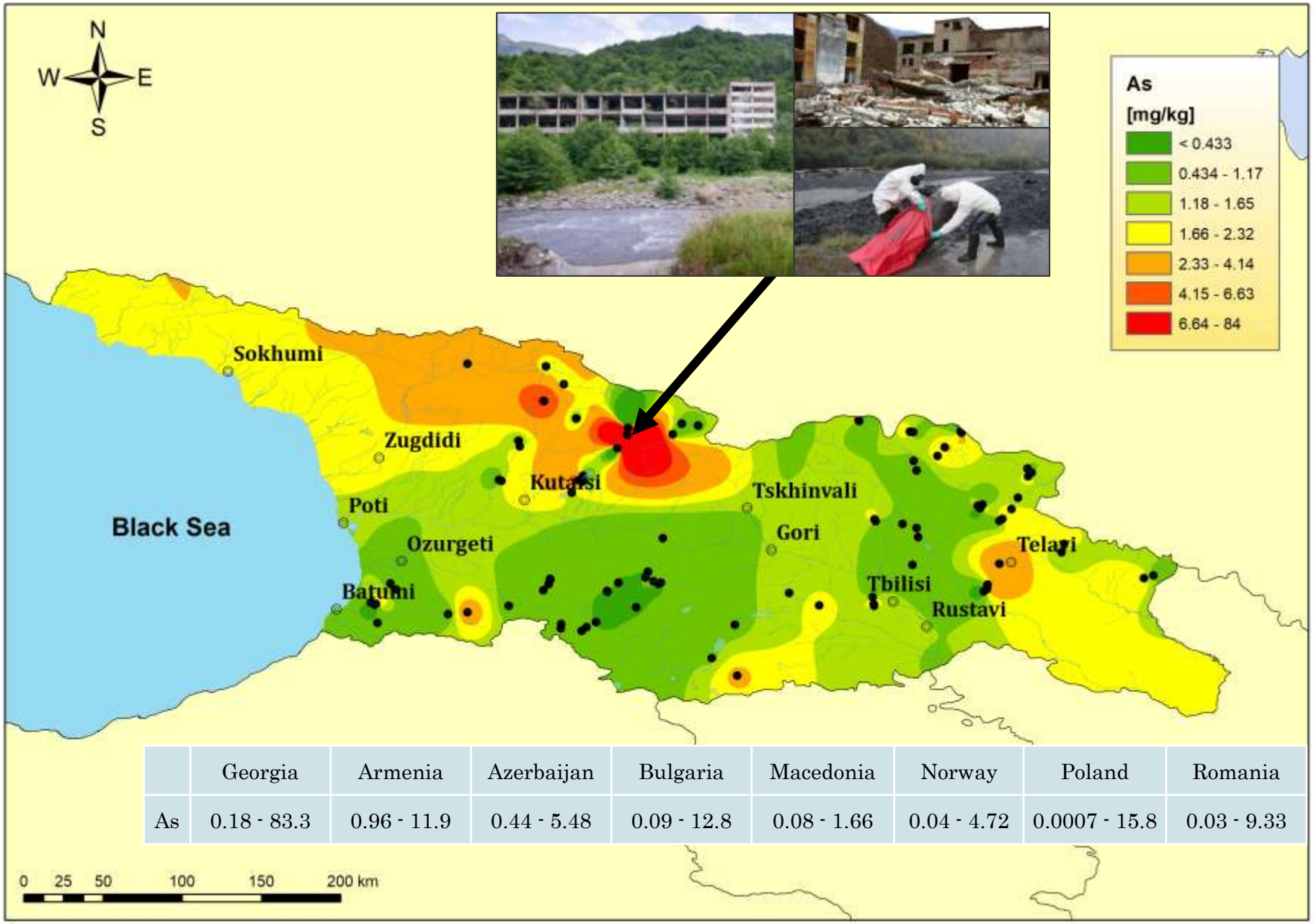
Factor3



- Poor condition of the old ore deposits of shut down plants and solid wastes in Uravi and Tsana.
- Other possible sources: Volcanic rocks, industrial activity

Arsenic (As)

Factor3

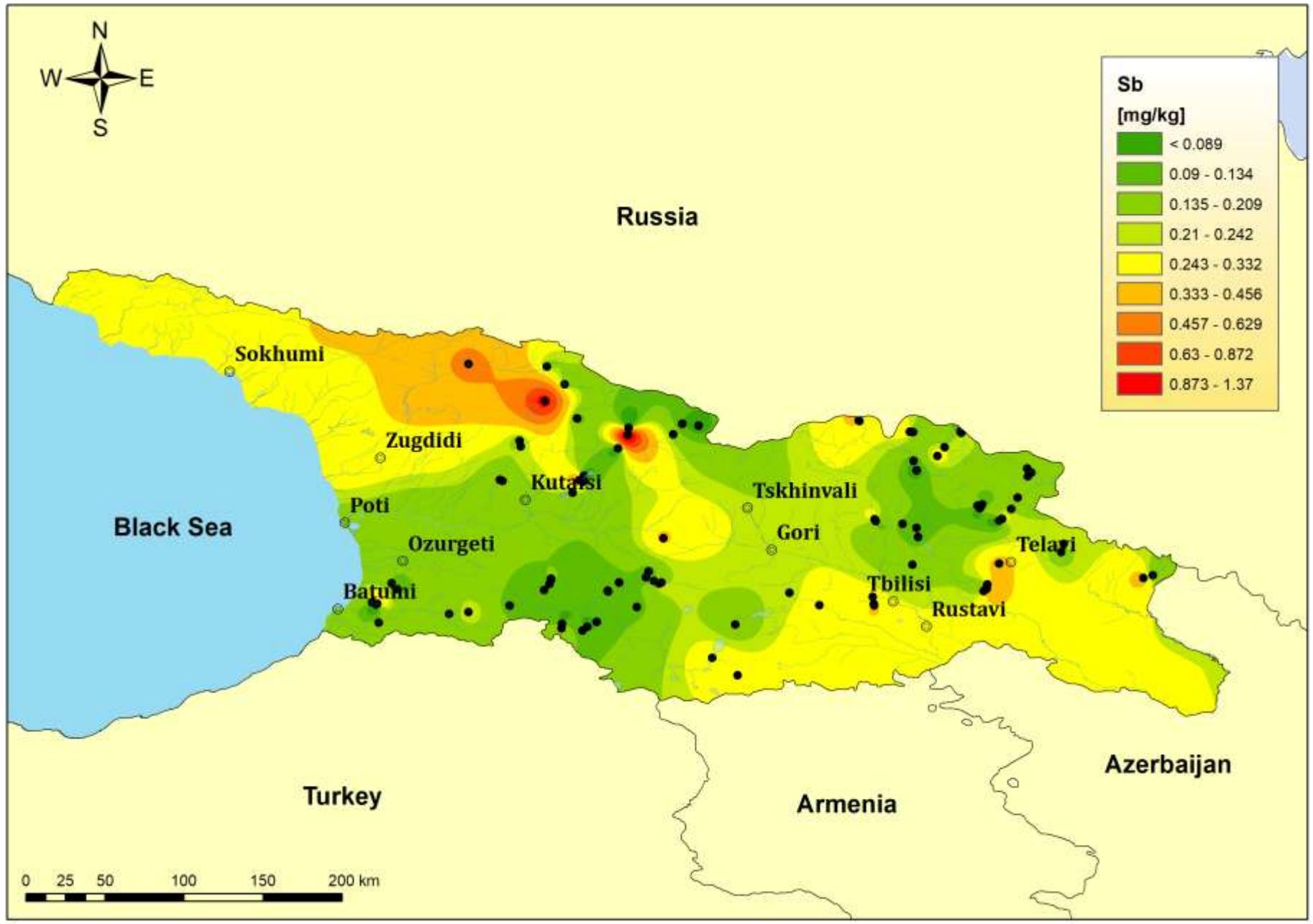


	Georgia	Armenia	Azerbaijan	Bulgaria	Macedonia	Norway	Poland	Romania
As	0.18 - 83.3	0.96 - 11.9	0.44 - 5.48	0.09 - 12.8	0.08 - 1.66	0.04 - 4.72	0.0007 - 15.8	0.03 - 9.33

- Poor condition of the old ore deposits of shut down plants and solid wastes in Uravi and Tsana.
- Other possible sources: Volcanic rocks, industrial activity
- Can be found abundantly in argillaceous sediments

Antimony (Sb)

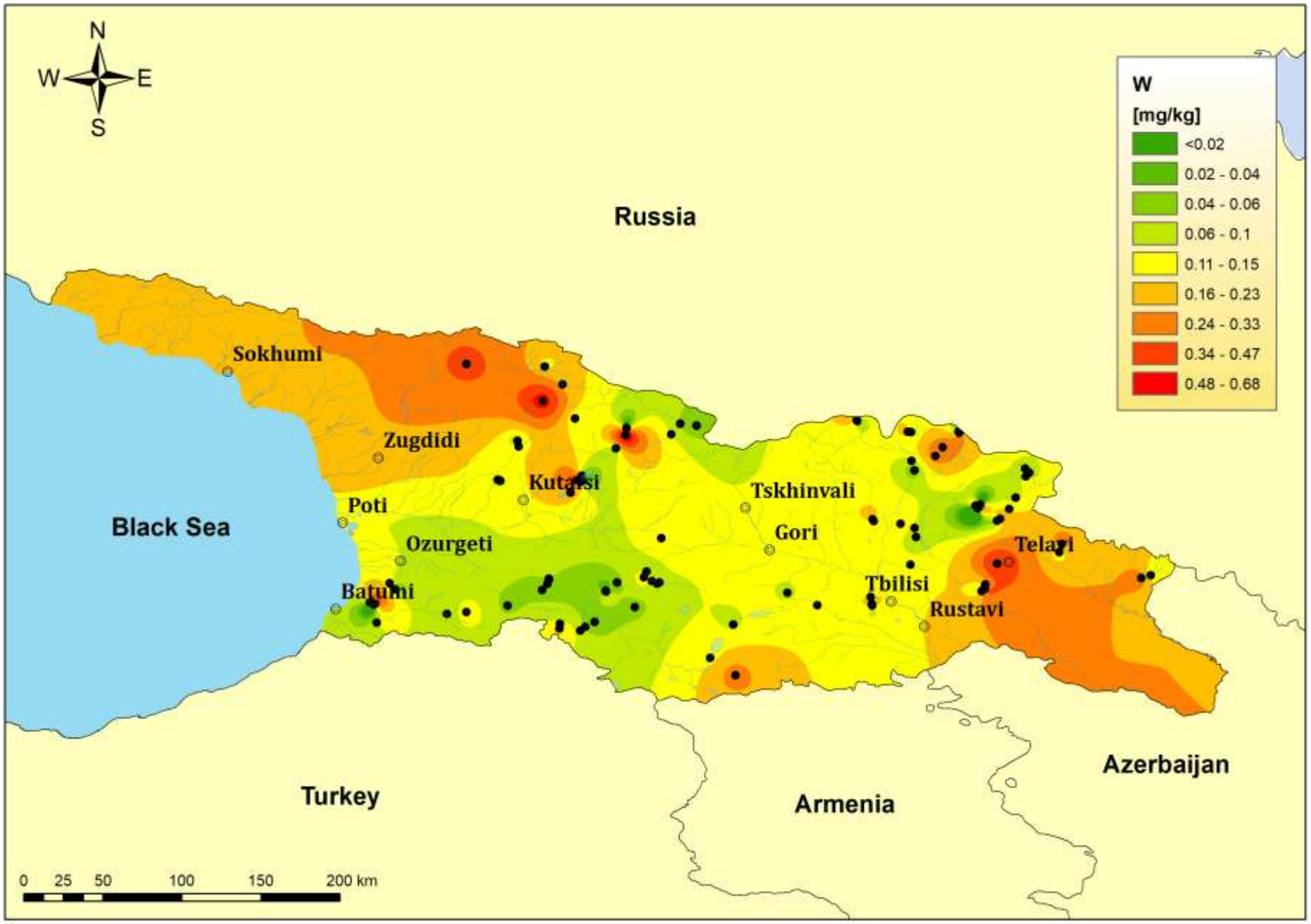
Factor3



- Arsenic and Antimony follow the same pattern in some areas.
- Can be found abundantly in argillaceous sediments

Tungsten (W)

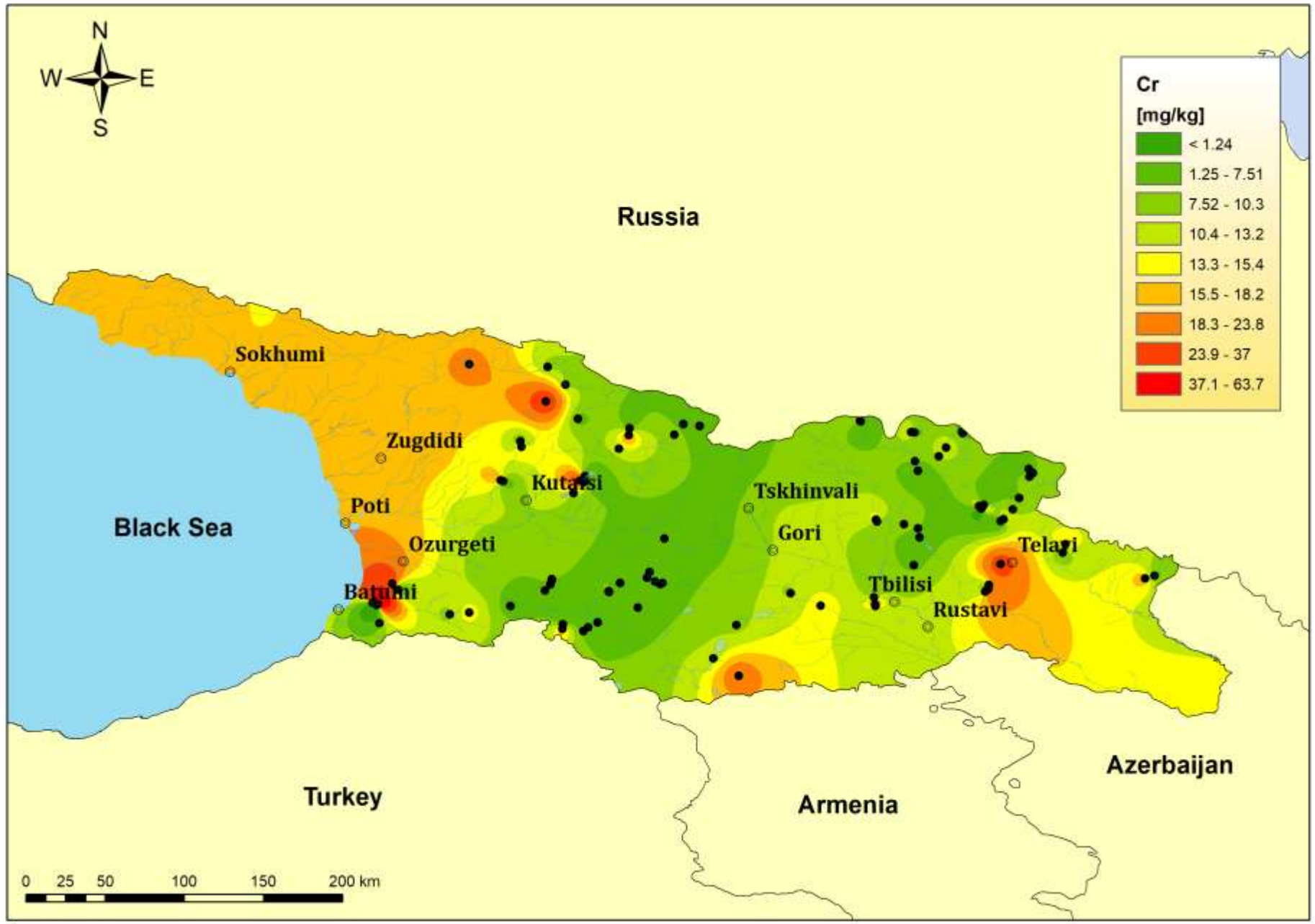
Factor3



- Tungsten, Arsenic and Antimony follow the same pattern in some areas.
- Possible sources: anthropogenic activities and different geological sediments (can be found abundantly in argillaceous sediments)

Chromium (Cr)

Factor 4

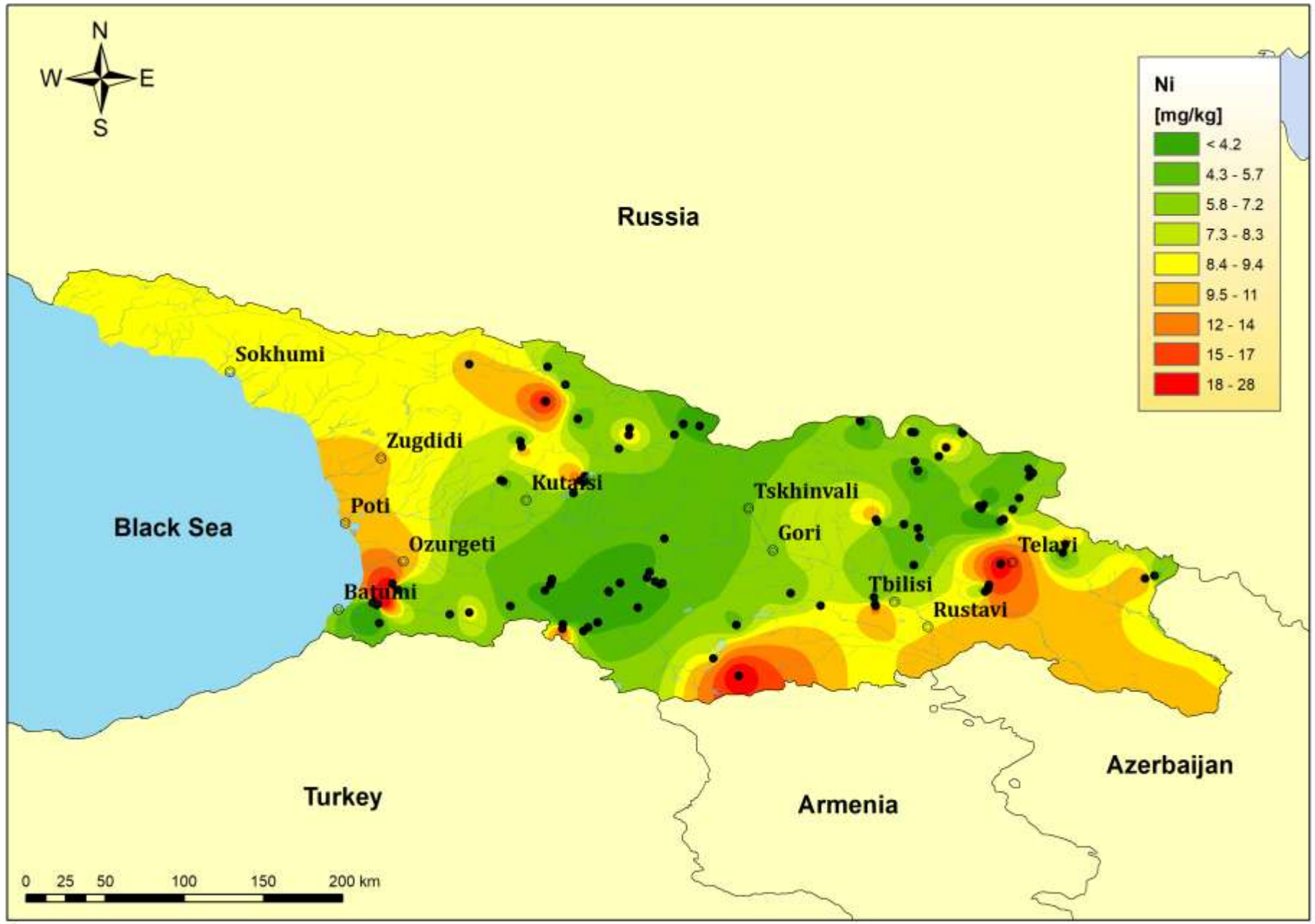


Maybe connected with:

- Ophiolites rocks
- Industrial activities

Nickel (Ni)

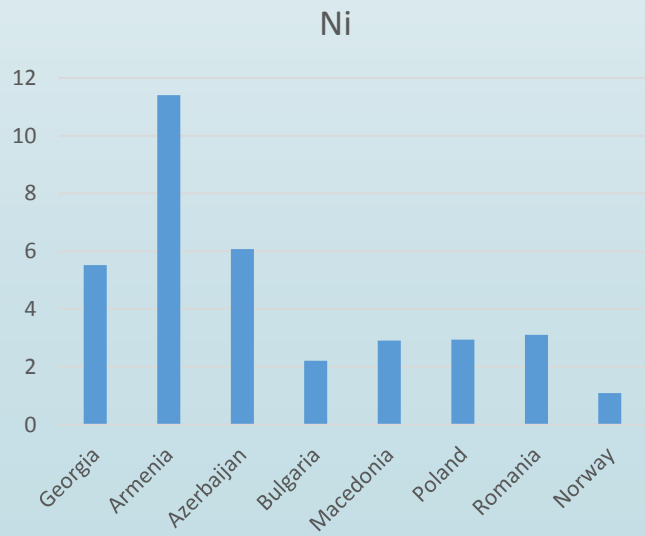
Factor 4



- Chemical similar to Fe, Co, Cu

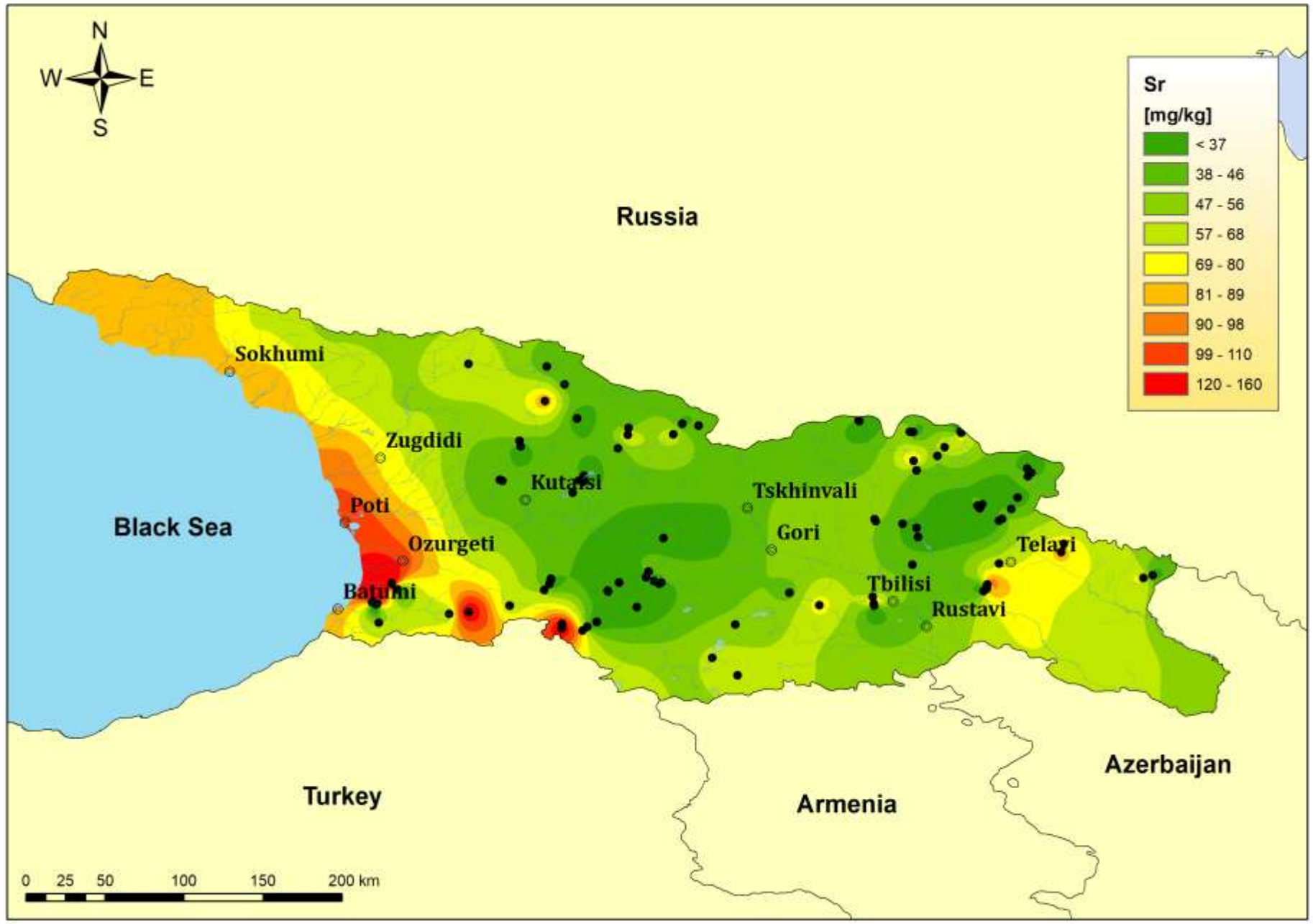
Possible sources:

- Oil combustion,
- Fe-Ni industry,
- Ophiolites rocks(Cr, Ni)

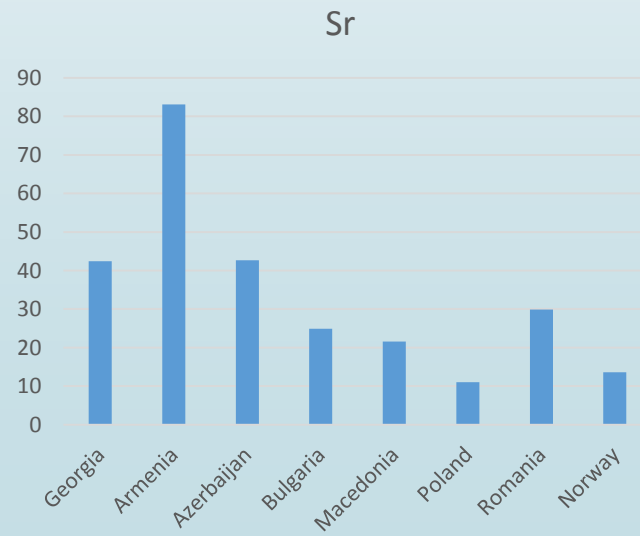


Strontium (Sr)

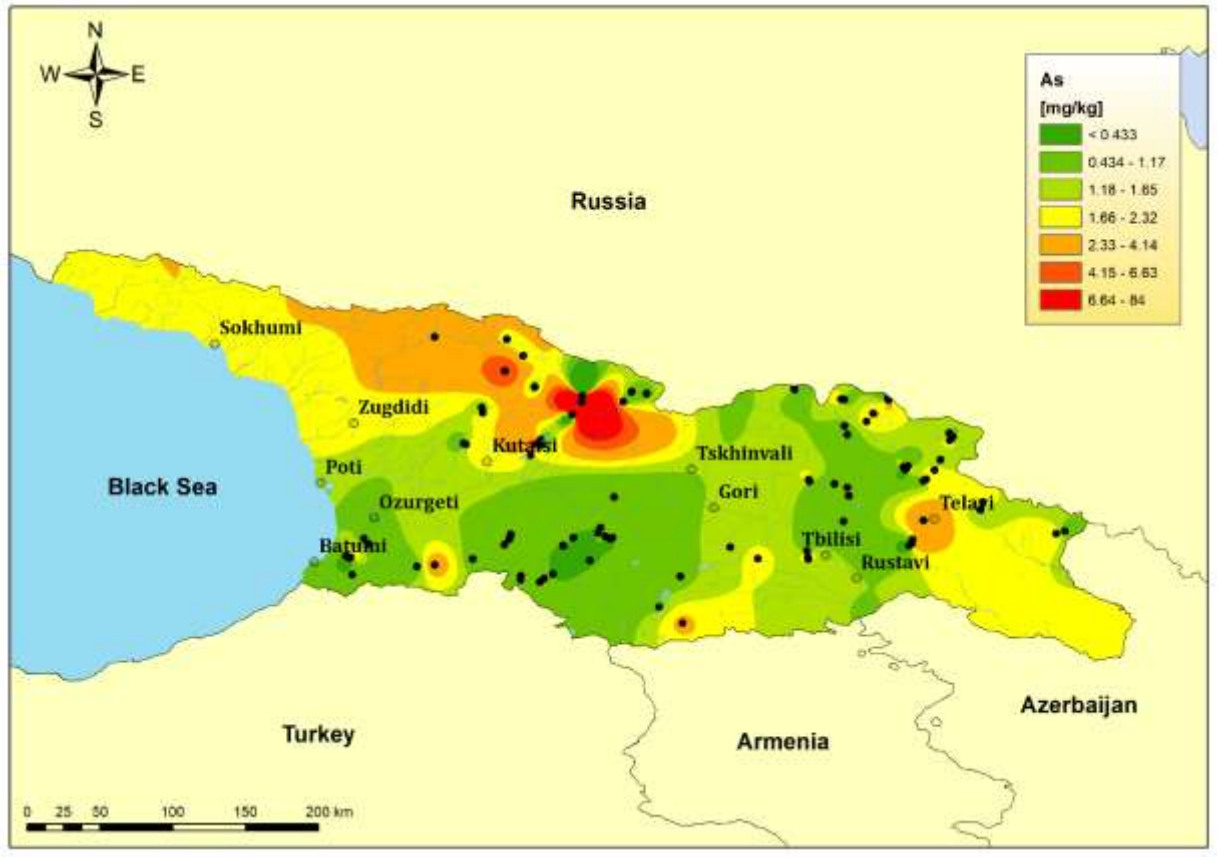
Factor 4

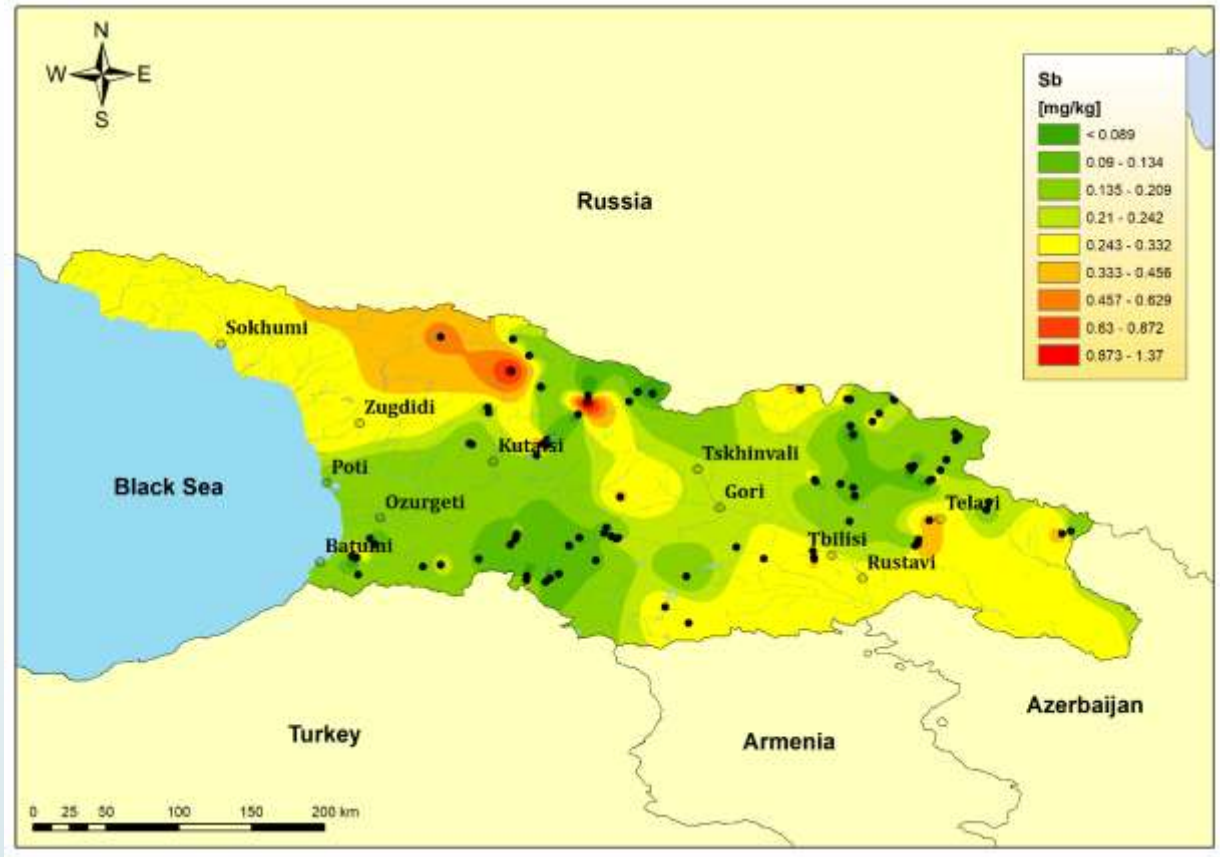


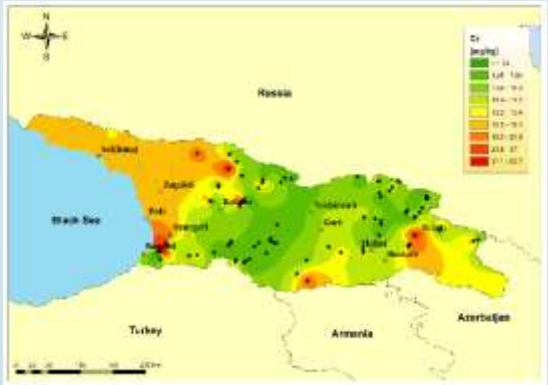
- Clay minerals have a large capacity to absorb Sr, and thus most argillaceous sediments are enriched in this element

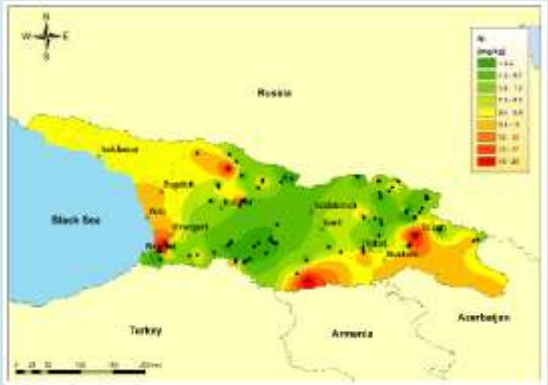


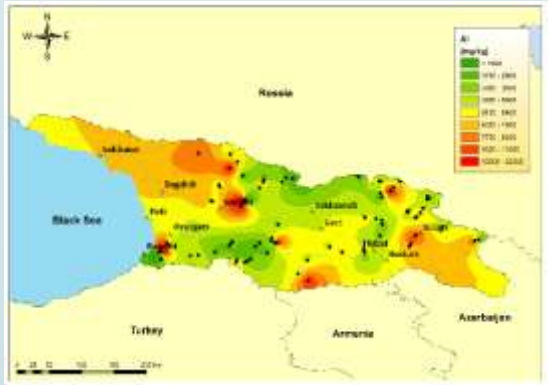
Results and discussion





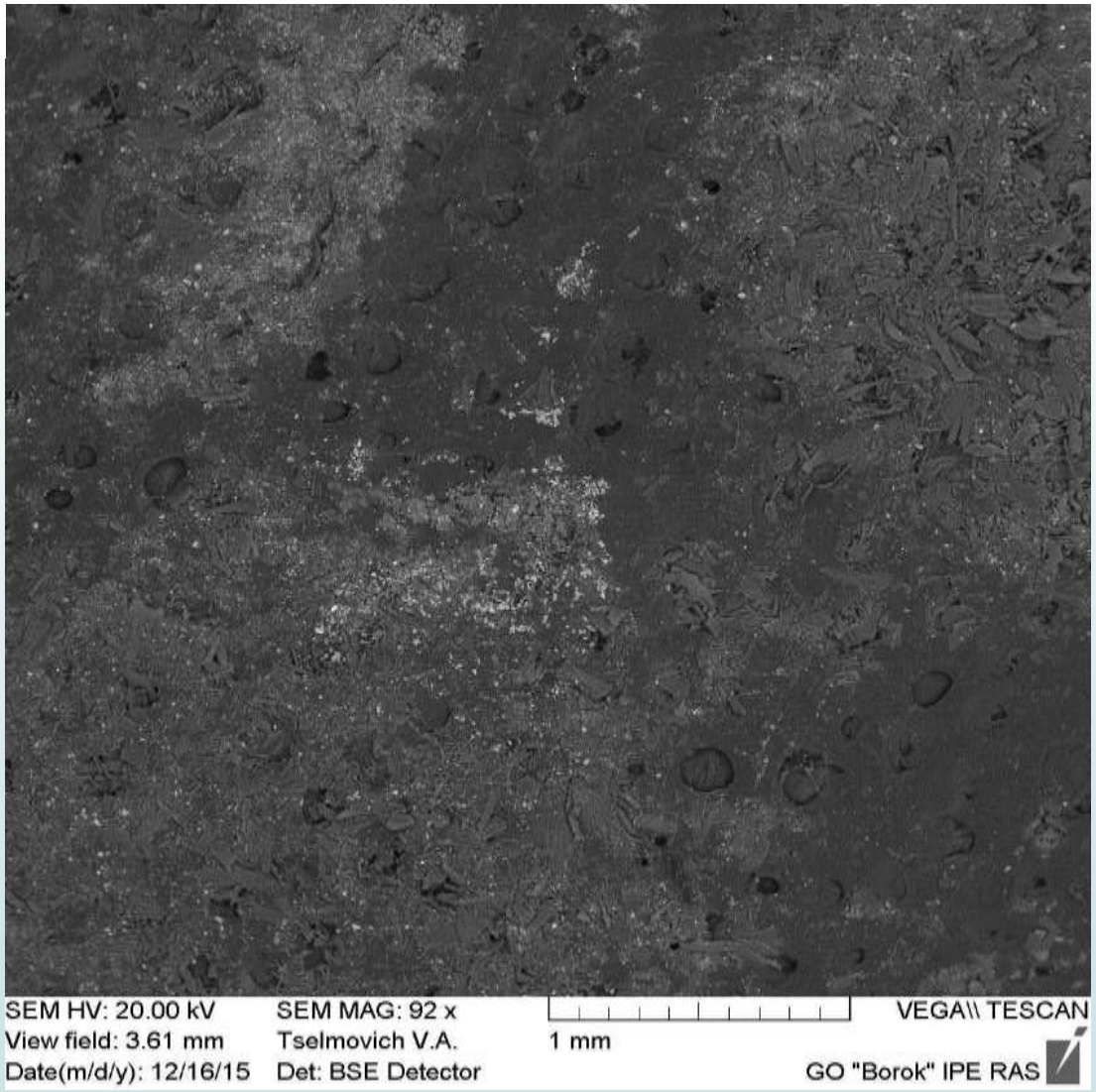




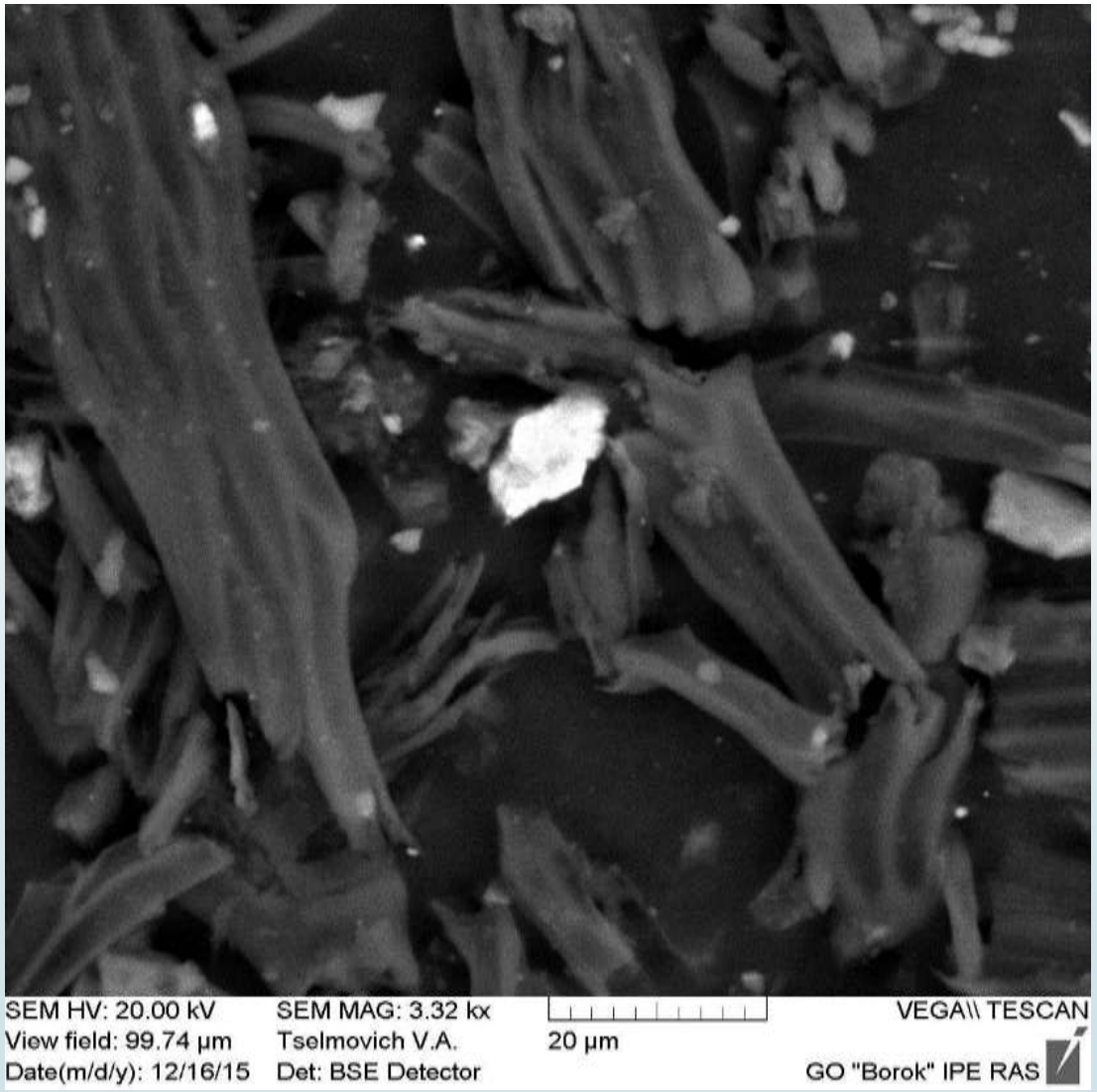


Results and discussion

The group of magnetic and paramagnetic particles, sample 41.

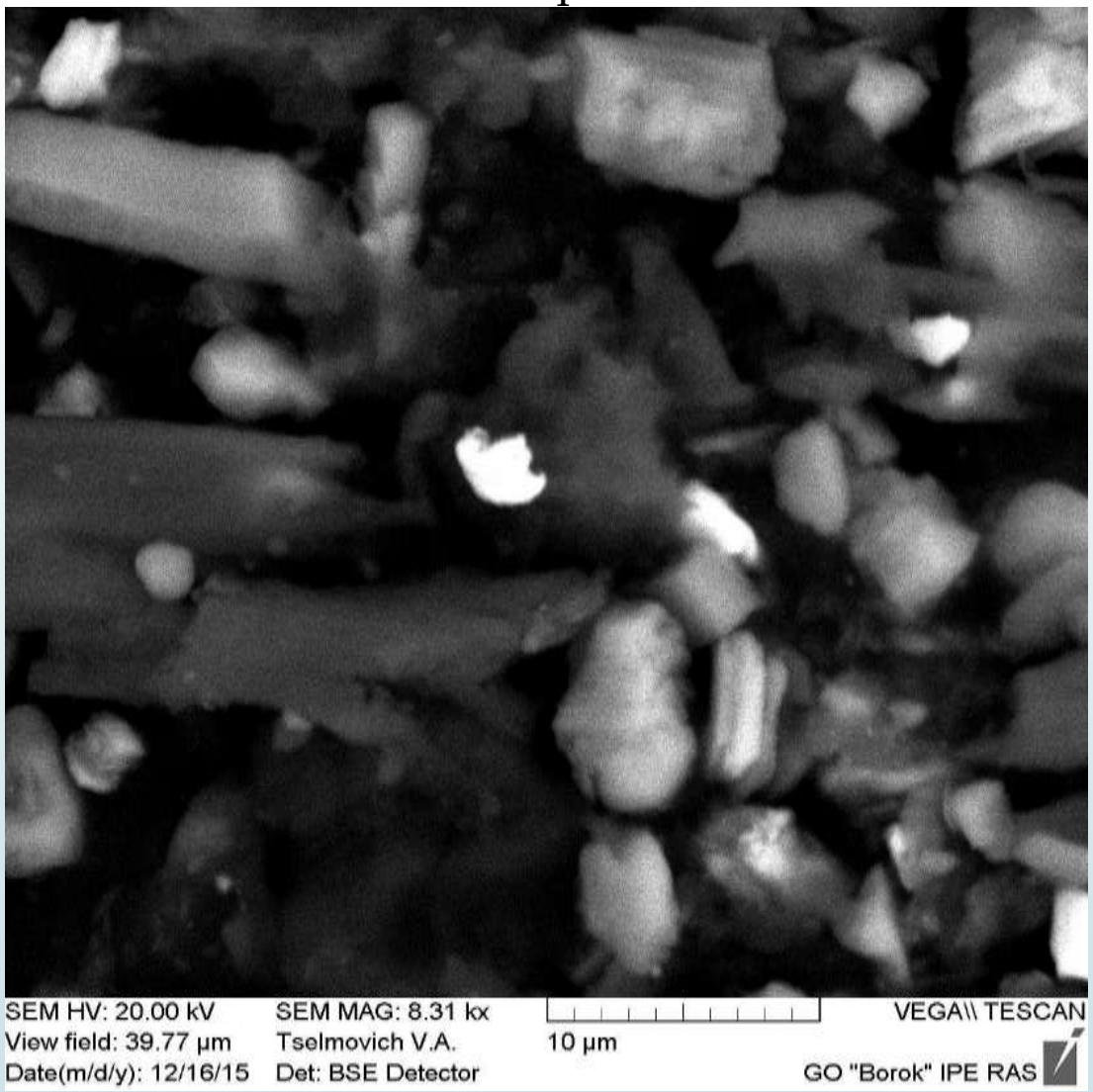


The terrigenous particle of titanomagnetite, sample 41.

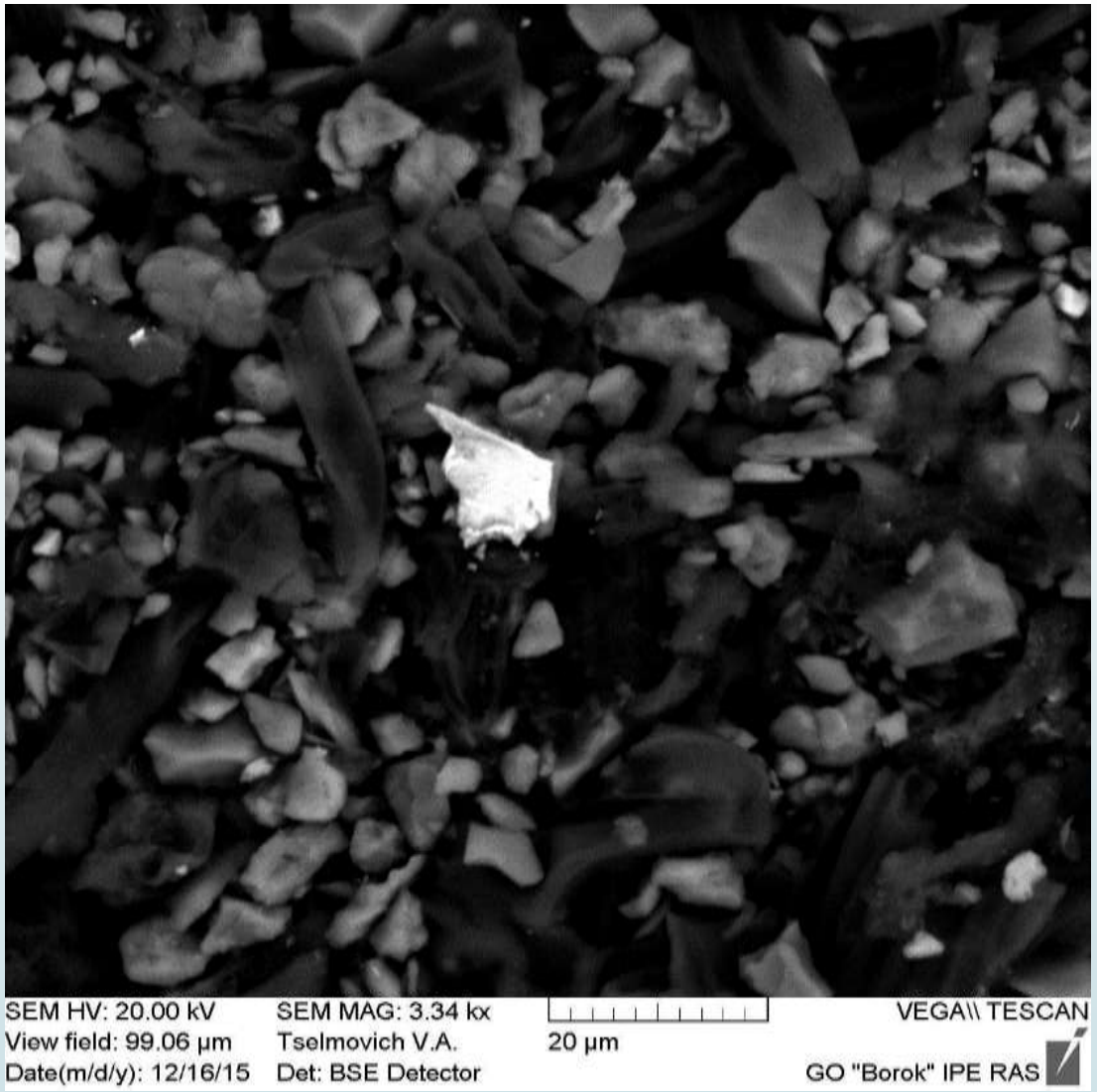


Results and discussion

The particles of native iron, size of 3x3 μm, sample 41

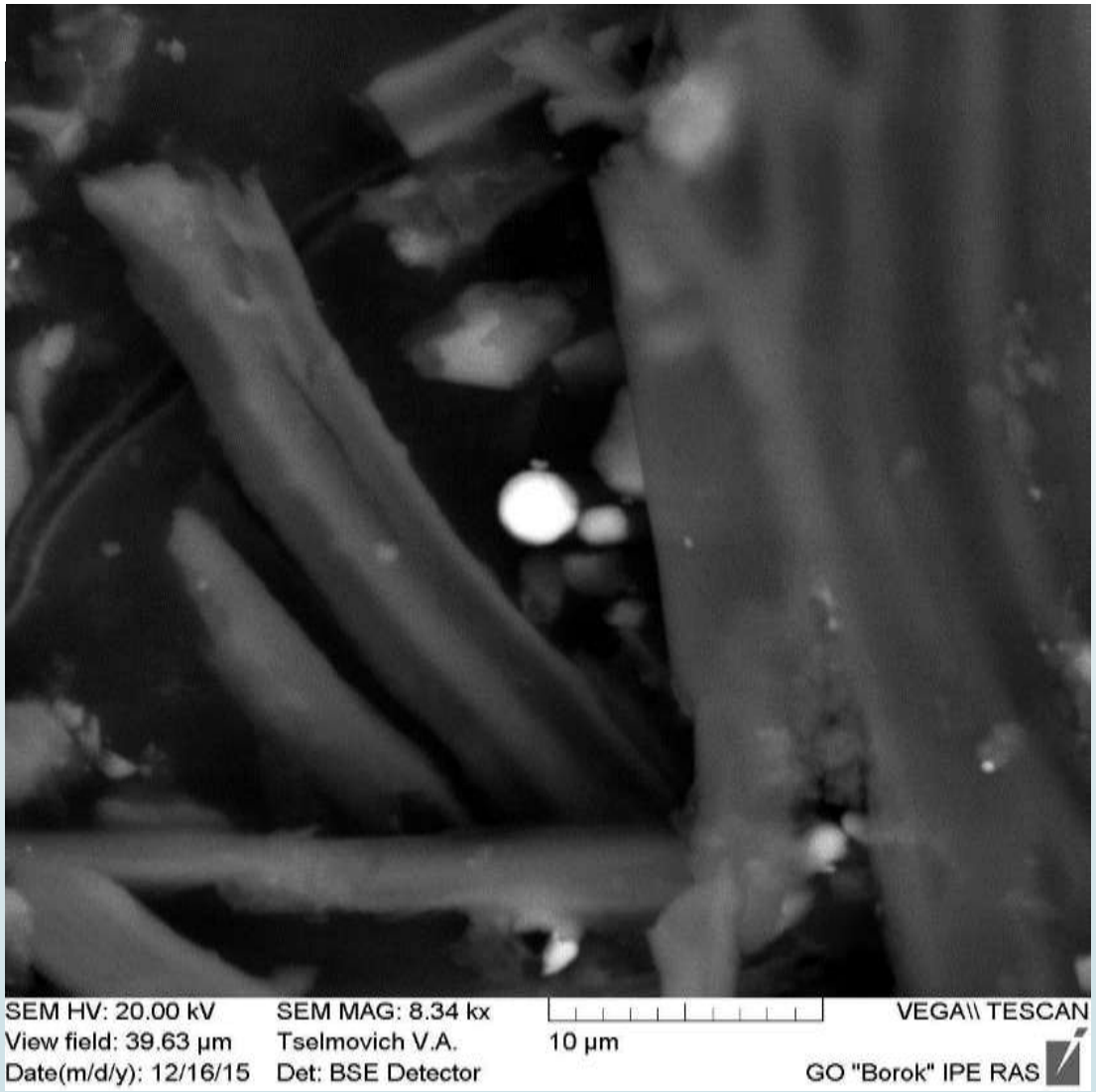


FeCr alloy particle (intermetallic compound), size of 10 x12 μm, sample 41

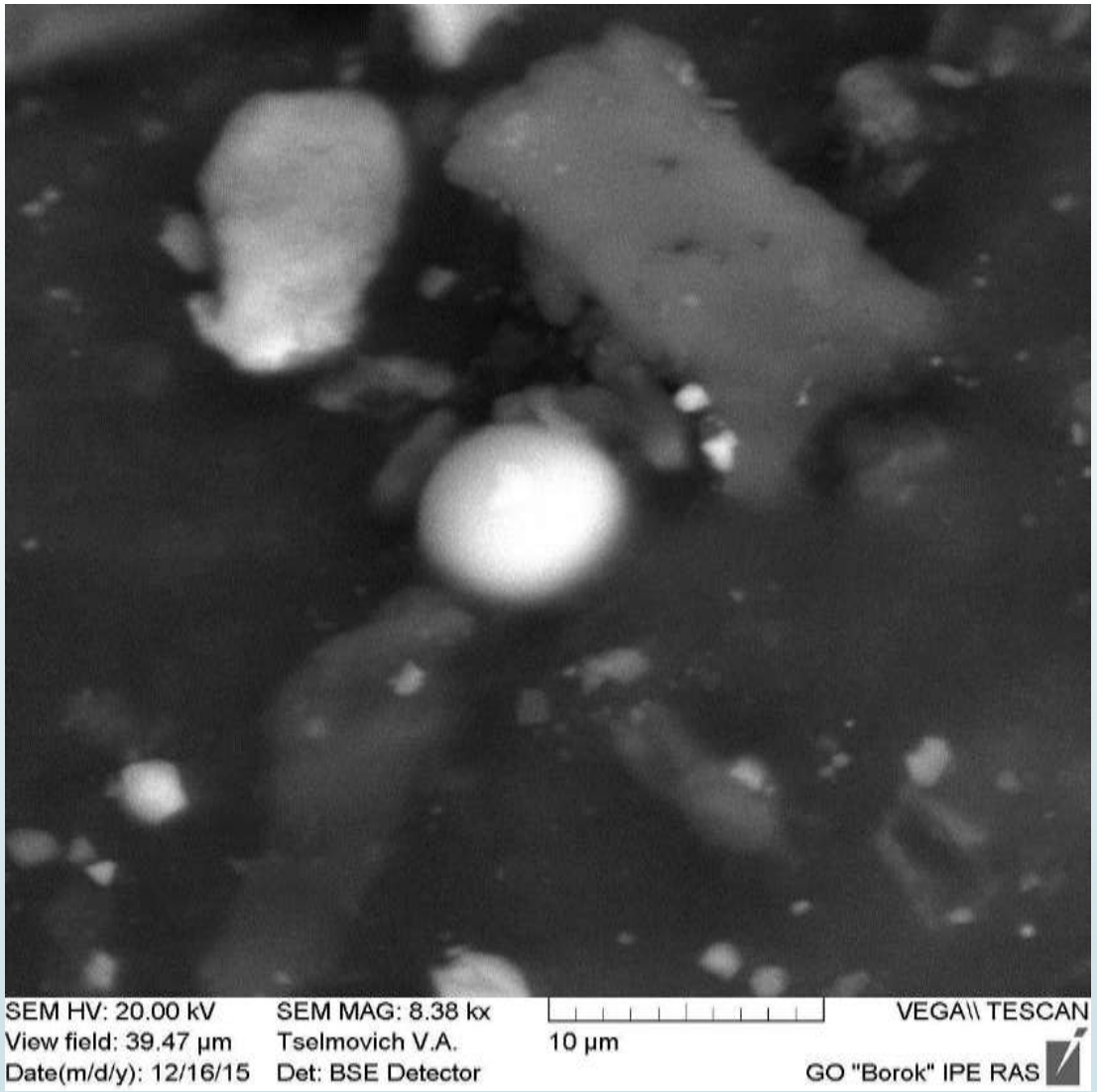


Results and discussion

Magnetite microsphere of cosmic dust, diameter 3 μm, sample 8



Aluminosilicate microsphere, presumably cosmic dust, diameter 6 μm, sample 8



Conclusions

- Moss biomonitoring provides a cheap and efficient method to deposition analysis for the identification of areas at risk from atmospheric deposition fluxes of heavy metals

- Microanalysis of moss samples show the presence of particles of various origins - clastic, anthropogenic and cosmogenic (cosmic dust).

- The northwest region of Georgia is characterized of high level of pollution as the majority of enterprises of the metallurgical and mining industries, like machine-building factory in Kutaisi, Zestaponi Ferroalloy Plant, old mining of arsenic which was performed until 1990, Chiatura mine complex, and other ones are located there. While the least polluted areas are located near Borjom-kharagauli National Park.

- The ecosystems and human health are still predicted to be at risk from adverse effects of heavy metals, the moss survey should be continued to monitor any future trends in heavy metal, The number of sampling points should be increase, trying to cover the whole country.

Thank you for attention!