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GEOCHEMICAL MAPS OF TRACE ELEMENTS IN MOSS AROUND TIKVEŠ LAKE NEAR KAVADARCI, REPUBLIC OF MACEDONIA

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A b s t r a c t: In this paper the geochemical maps of distribution of elements Li, Be, B, Na, Mg, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Sr, Mo, Cd, Cs, Ba, Tl, Pb, Bi, Th, U in the moss from the sort *Campothecium lutescens* near the brake of the Tikveš Lake are presented,. The close surrounding of the factory for production of ferronickel to the researched area as well as the direction of the air masses, contribute to higher concentrations of the elements NI, Fe, Co, Cr, Pb, Zn, As which define this area as a hot spot in terms of the air quality.

Key words: moss; geochemical map; nickel

INTRODUCTION

During the determining of the level of air pollution of some region, some organisms are often used as indicators. These methods of usage of some organisms as indicators of the air-pollution are often practiced today due to their fast application. The mosses together with the lichen are often used as bio-indicators of the air-pollution and determination of the air quality (Natho, 1964; Skye, 1968; Kunze, 1972; Diamantopoulos et al., 1993; Vokou et al., 1999; Stafilov et al., 2008, 2010; Bačeva et al., 2011, Frontasyeva et al., 2004). On the quality of the air in an environment, the production and the consumption of the various energy resources have a great impact, among them, mostly the coal. With the burning of coal, in particularly the lignite, large quantities of ashes are produced in the atmosphere and large quantity of sulphur and nitric compounds are erupted. The traffic, especially the road one, has a great impact on the air quality, then the industry for metal processing (smelter) as well as the usage of protection in the agriculture.

The usage of mosses in determination of the level of air-pollution is classified in the so called biological methods of monitoring of the air quality. These methods involve 4 registrations and following of the changes made under influence of the pollutants over some living biological organisms. The advantages of the biological indication in relation to the physical-chemical are in that the living organisms could point to the cumulative effect of the pollution substances.

MATERIALS AND METHOD

Study area

The researched area is in the surrounding of the brake of the Tikveš Lake, some 10 km west from the town of Kavadarci and 3 km west from the metallurgic factory for production of ferronickel FENI INDUSTRY (Fig. 1). The Tikveš Lake is a man-made water accumulation built at the end of the 1970 on Crna Reka river. This is one of the largest man-made water accumulations in Republic of Macedonia, with a length of 30 km and a capacity of 500 million cubic meters of water. The research area is near the metallurgic factory for production of ferronickel FENI INDUSTRY.

A factory for nickel production was built in the Tikveš area in 1980. It processes 1 500 000 tons laterite types of nickel ore. By 2005, the complete amount of nickel ore originated from the Ržanovo mine, from the south parts of the Tikveš valley, the Kožuf mountain, and after 2005 ores from Albania, Turkey and Indonesia start to be reprocessed.

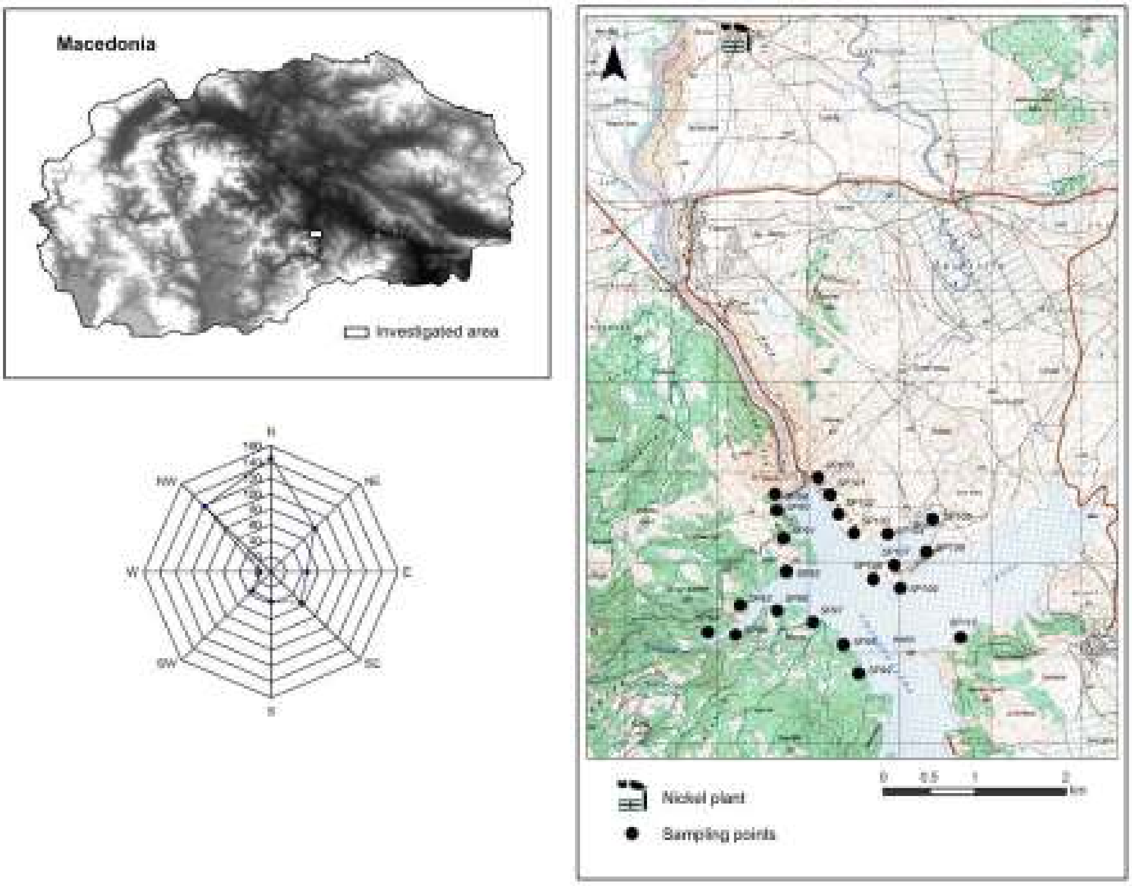

Fig. 1. Geographic map of the research area

The work of this factory for nickel production affects the change of the mineral and geochemical structure of urban dust in the valley. The factory was built during 1976–80, and it comprises equipment for reprocessing laterite nickel ore with annual capacity of 2 million tons of ore. It annually produces about 16 000 tons of metal in the form of ferronickel, which contains Ni from 25 to 40 %. As a result a big amount of solid particles are generated, especially PM-10, which basically change the structure of urban dust (Boev et al., 2013; Stafilov et al., 2008, 2010; Bačeva, 2011; Stafilov et al., 2013).

Sampling

Twenty the moss samples of the sort *Campothecium lutescens* are collected (Fig. 2) near the brake of the Tikveš Lake (Fig. 1) in the period September–October 2014. The moss samples are collected according to strategy of the European moss survey (Ruhling, 1996). In the surrounding where the moss samples are collected there are no main roads. The collected samples are packed in a paper bags.

Fig. 2(a and b). Picture of moss of the sorte *Campothecium lutescens* (I. Boev, 2014)

Sample preparations

In the lab, the moss samples were cleaned from the dust rests and other plants, and then dried on a room temperature. A moss sample in a quantity of 0.5 g is dissolved in a teflon bowl with addition of concentrated nitric acid and 2 ml H_2O_2 in a micro-wave oven. The moss sample is dissolved on a temperature of 180°C.

Instrumentation

For determination of the examined elements, Li, Be, B, Na, Mg, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Sr, Mo, Cd, Cs, Ba, Tl, Pb, Bi, Th, U the ICP-MS is applied as analytical method.

Instrument and instrumental conditions

Conditions for ICP-MS, 7500, Agilent	
Sample introduction	
Atomizer	PEEK, Babington-type
Atomizer chamber	Glass, double pass, temperature of the automizer chamber 2⁰C
Injector of ICP torch	Quartz, 2.5 mm
Conditions of the program	
Power of the plasma	1500 W
Speed of the pump/rpm	0,1 rps
Aux flow of Ar for plasma	1,0 l/min
Carrier gas flow Ar	0,9 l/min
Sampler cone	nickel
Skimmer cone	nickel
Sample depth	7.4
Points/mass	3
Time for integration	0,3 s
Total time for acquisition/ replicates	8 s
Replicates	3
Total time for acquisition/ sample	24 s

Element/mass			
Element	m/z	Element	m/z
Li	7	As	75
Be	9	Sr	88
Al	27	Mo	95
Ti	48	Pd	106
V	51	Cd	111
Cr	53	Cs	133
Mn	55	Ba	137
Co	59	Tl	205
Ni	60	Pb	208
Cu	63	Bi	209
Zn	66	Th	232
Ga	69	U	238
Ge	72	Sn	120
Sb	121		

Data processing

The processing of the data is made by the program support ESRI ArcGIS 10.2.1. and Geostatistical Analyst. Maps for distribution of all the researched elements are generated.

RESULT AND DISCUSSION

The results which are obtained from the research of the presence of elements of traces in the mosses near the Tikveš Lake are presented in Table 1, whereas the spatial distribution of the elements Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, Li, Mg, Mн, Mo, Na, Ni, P, Pb, Sr, Th, Ti, Tl, U, V, Zn is presented in Figures 3 to 32. From the spatial distribution it could be clearly seen that the researched area is a hot spot in terms of the quality of air.

Within Table 2, the medium and the min./max values of the elements As, Cd, Co, Cr, Cu, Fe, Mg, Ni, Pb, Zn are presented from the research made during 2014, as well as the values referring to the research from 2011 (Bačeva et al., 2011), and the values from the research made in Republic of Macedonia in 2006 (Barandovski et al., 2006) and the compared values for concertation of the mentioned elements in the mosses in Europe (Harmens et al., 2008). From the presented results in Table 2 it could be seen that there is an emphasized moment of increase of the medium values of the elements like As, Cd, Co, Cr, Cu, Fe, Mg, Ni, Pb, Zn in the moss samples collected in the surrounding of the Tikveš Lake in relation to the samples collected in the surrounding of Tikveš Lake in 2011. It is particularly obvious the increase in the concertation of elements like Ni, Cr, Co, Fe which are present in the research area as a result of the activities in the metallurgic factory for production of ferronickel. It should be mentioned that in the papers of (Boev, I. et al., 2014, 2013) the geochemical compound of articles PM-10 is determined in detail and their connection with the activities of the metallurgic factory for production of ferronickel. From the presented data, it is clear that the increase in the concertation of elements Ni, Cr, Fe, Co is a direct consequence from the increase of the quality of the processed mine in the metallurgic factory and the increased emission of particles PM-10 in this area which is located directly in direction of the wind in this area (Fig. 1) Also, it should be mentioned that the increased concertation of Pb, Zn, As is a direct consequence from the burning of a bigger quantity of liquid and hard flues during the metallurgic process.

Table 1

Trace elements in moss from the area around Tikveš Lake (ICP-MS, in mg/kg)

Elwment	SP89	SP90	SP91	SP92	SP93	SP94	Sp95	SP96	SP97	SP98	SP99
Li	2,7	1,8	2,3	2,1	1,95	2,2	2,2	2,5	1,9	1,8	1,7
Be	0,183	0,19	0,2	0,178	0,25	0,3	0,4	0,2	0,3	0,23	0,32
B	9	8	7	9	8	10	11	12	11	13	12
Na	86	95	98	100	110	95	97	110	105	97	85
Mg	4328	4500	4600	4400	4560	4400	4500	4250	4365	5000	4725
Al	4914	5100	5120	4890	4960	5180	5200	5240	5320	5410	5500
P	4633	4580	4630	4750	4560	4800	4870	4650	4320	4410	4760
Ca	9038	9540	9320	9150	9320	9100	9320	9870	9900	9650	9850
Ti	62	58	55	45	71	51	52	50	54	48	65
V	20	25	22	26	25	21	20	21	20	23	28
Cr	116	120	140	150	130	120	128	130	142	152	132
Mn	23	22	18	17	19	25	23	21	19	18	15
Fe	9218	9540	9650	9340	9820	9520	9630	9450	9900	9780	9320
Co	13	12	10	17	16	15	14	13	12	11	10
Ni	228	210	190	180	160	260	250	240	235	221	190
Cu	8,1	7,5	7,6	6,8	5,5	5,4	6,5	6,8	6,7	7,8	8,2
Zn	521	560	540	521	583	650	632	610	595	568	578
Ga	2,9	2,5	2,3	1,9	1,8	2,3	2,4	2,5	2,8	2,7	2,9
Ge	0,21	0,15	0,21	0,23	0,25	0,23	0,25	0,21	0,18	0,32	0,31
As	3,3	3,4	3,6	3,8	4,5	4,1	4,5	3,2	3,3	3,6	4,5
Sr	18	21	20	18	20	25	24	26	22	21	28
Mo	0,64	0,54	0,38	0,46	0,57	0,56	0,65	0,64	0,66	0,58	0,57
Cd	0,29	0,31	0,41	0,63	0,47	0,53	0,54	0,63	0,34	0,45	0,43
Cs	0,393	0,256	0,347	0,421	0,364	0,351	0,54	0,45	0,452	0,421	0,43
Ba	33	25	26	34	38	41	42	46	45	38	32
Tl	0,052	0,045	0,032	0,039	0,056	0,032	0,054	0,052	0,041	0,039	0,036
Pb	9,7	10,1	11,2	15,6	13,2	12,5	13,2	14,2	16,2	16,5	16,8
Bi	0,140	0,21	0,154	0,168	0,174	0,21	0,25	0,32	0,15	0,14	0,158
Th	1,73	1,21	1,63	1,45	1,51	1,52	1,42	1,87	1,65	1,87	1,95
U	0,31	0,28	0,32	0,34	0,36	0,34	0,45	0,42	0,31	0,29	0,3

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Comparison of median values and min/max range of elements content in moss between data of the present work and data of the whole territory of Macedonia and European moss survey programme and date of the work of Bačeva et al., 2011 (in mg/kg)

	European moss survey 2005/2006 (Harmenset all) (*n* = 6049)		Macedonian moss survey 2006 (Barandovski et al.) (*n* = 72)		Kavadarci moss survey 2011 (Bačeva et al.) (*n* = 31)		Tikveš Lake moss survey 2014 (this study) (*n* = 22)	
Element	median	min–max	median	min–max	median	min–max	median	min–max
As	0.31	0.11–4.04	0.68	0.18–4.32	0.92	0.10–6.20	4.2	3.2–5.6
Cd	0.20	0.07–1.26	0.29	0.056–3.01	0.19	0.040–0.51	0.44	0.21–0.63
Co	–	–	1.13	0.42–5.29	2.1	1.1–14	16	10–22
Cr	2.32	0.72–29.33	6.79	2.09–82	15	5.8–110	139	116–164
Cu	6.80	3.07–91.20	6.65	0.68–21.4	7.7	4.9–15	7.7	5.4–9.8
Fe	799	233–6147	2239	999–8130	2300	1300–8700	9296	8650–9900
Mg	–	–	1307	656–3994	3300	1300–7000	4582	4250–5100
Ni	2.26	0.71–63.39	5.82	1.80–43.1	40	14–300	216	160–280
Pb	4.91	1.76–46.94	7.62	0.1–46.6	8.4	5.4–19	14.7	9.7–17.2
Zn	33.6	15.2–176.8	35.6	16,4–91.3	55	30–190	575	521–650

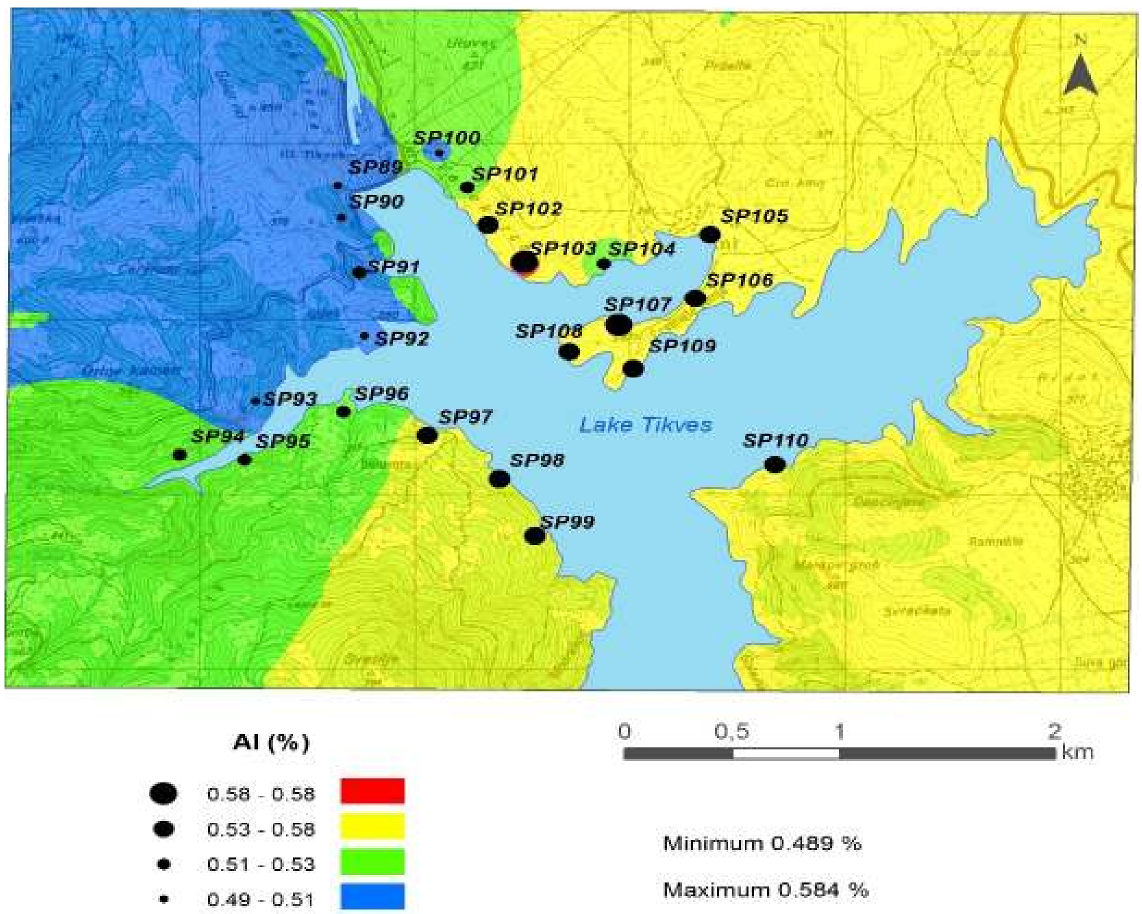

Fig. 3. Spatial distribution of Al in the moss from the area of Tikveš Lake

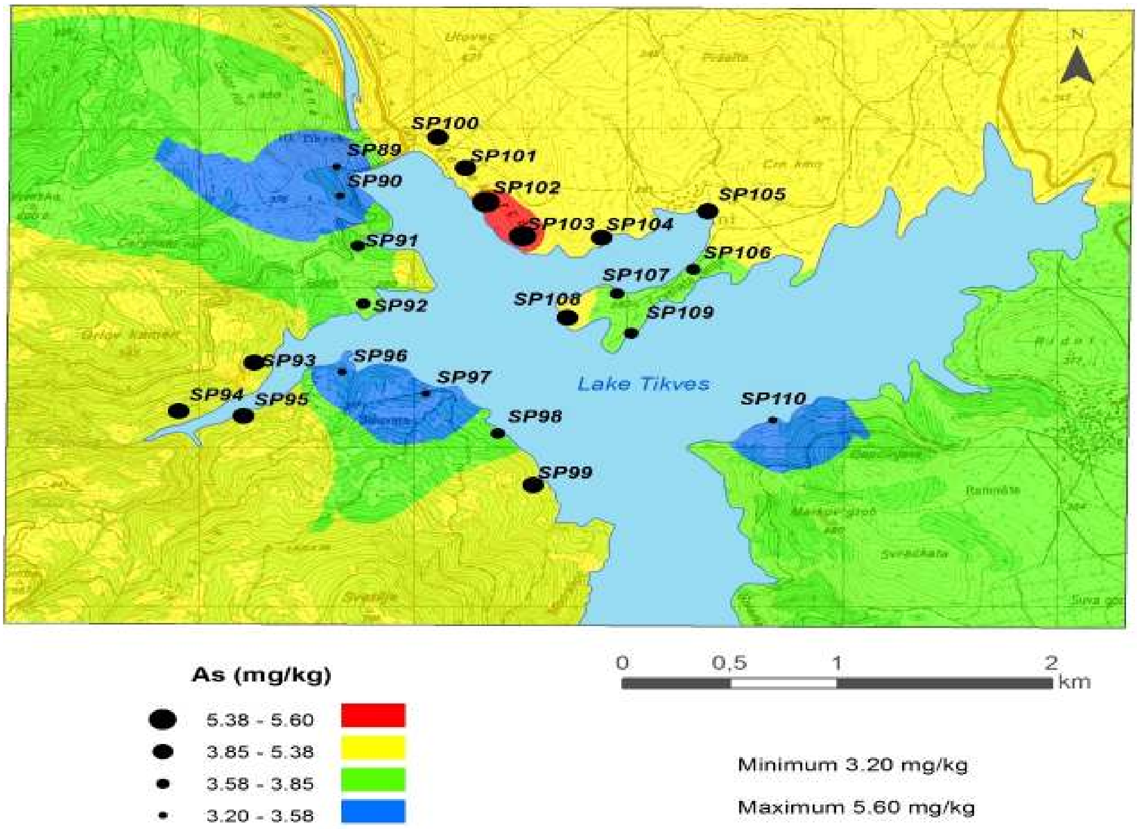

Fig. 4. Spatial distribution of As in the moss from the area of Tikveš Lake

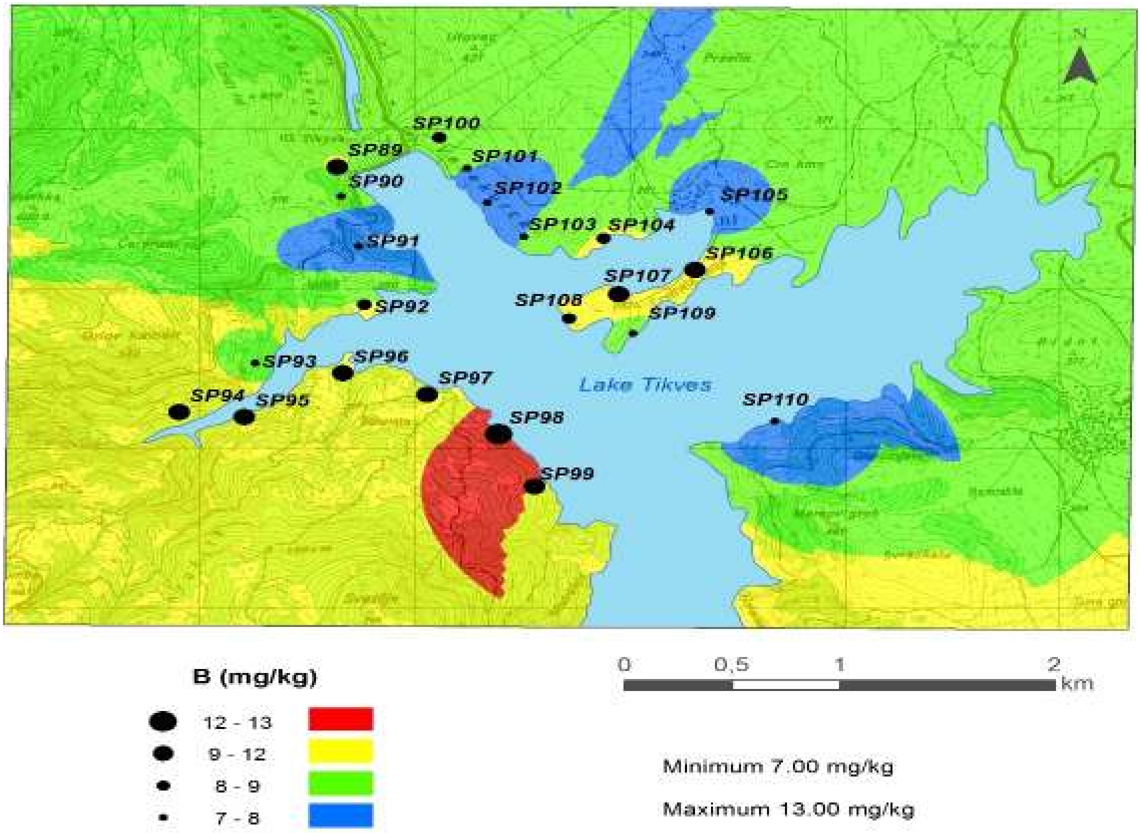

Fig. 5. Spatial distribution of B in the moss from the area of Tikveš Lake

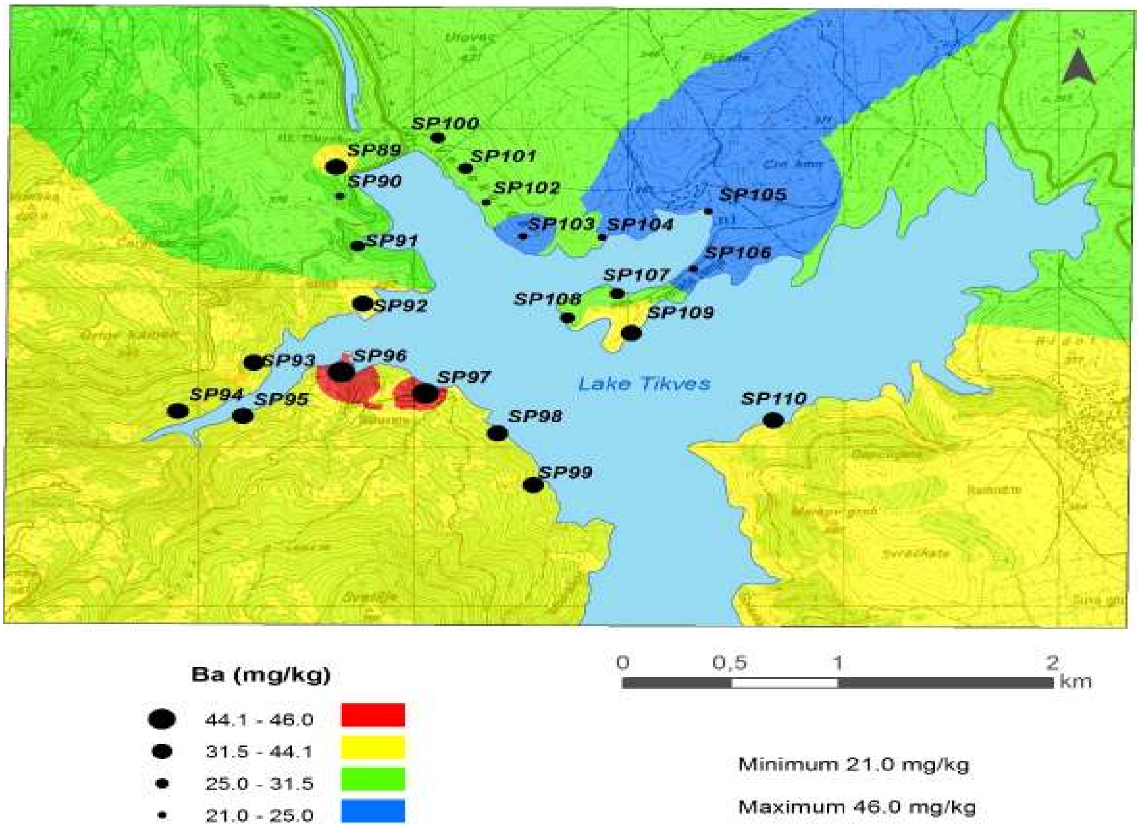

Fig. 6. Spatial distribution of Ba in the moss from the area of Tikveš Lake

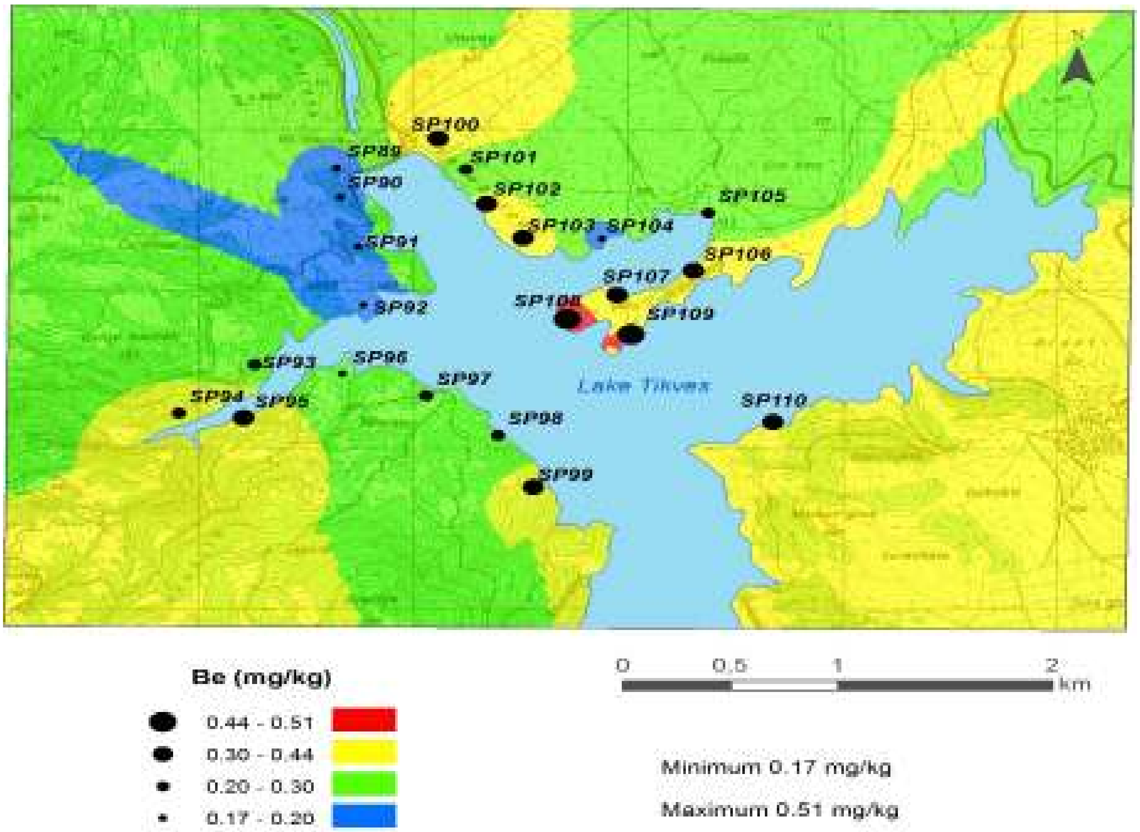

Fig. 7. Spatial distribution of Be in the moss from the area of Tikveš Lake

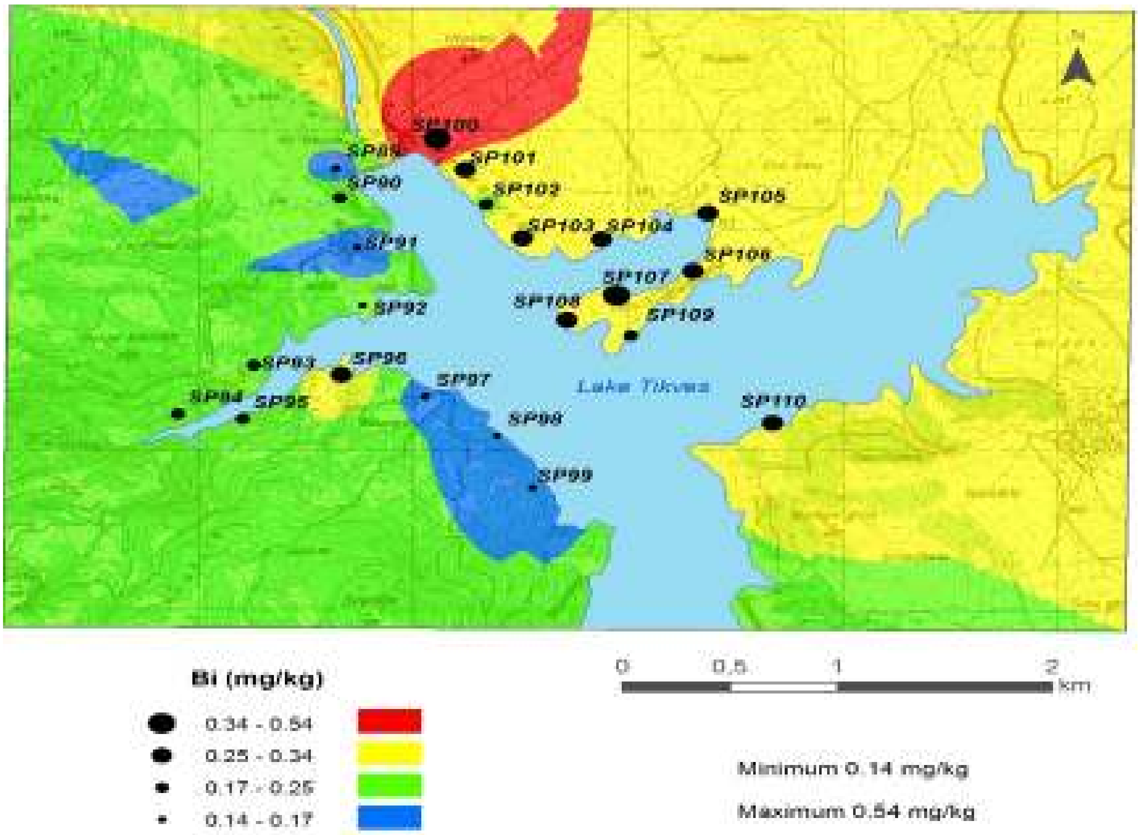

Fig. 8. Spatial distribution of Bi in the moss from the area of Tikveš Lake

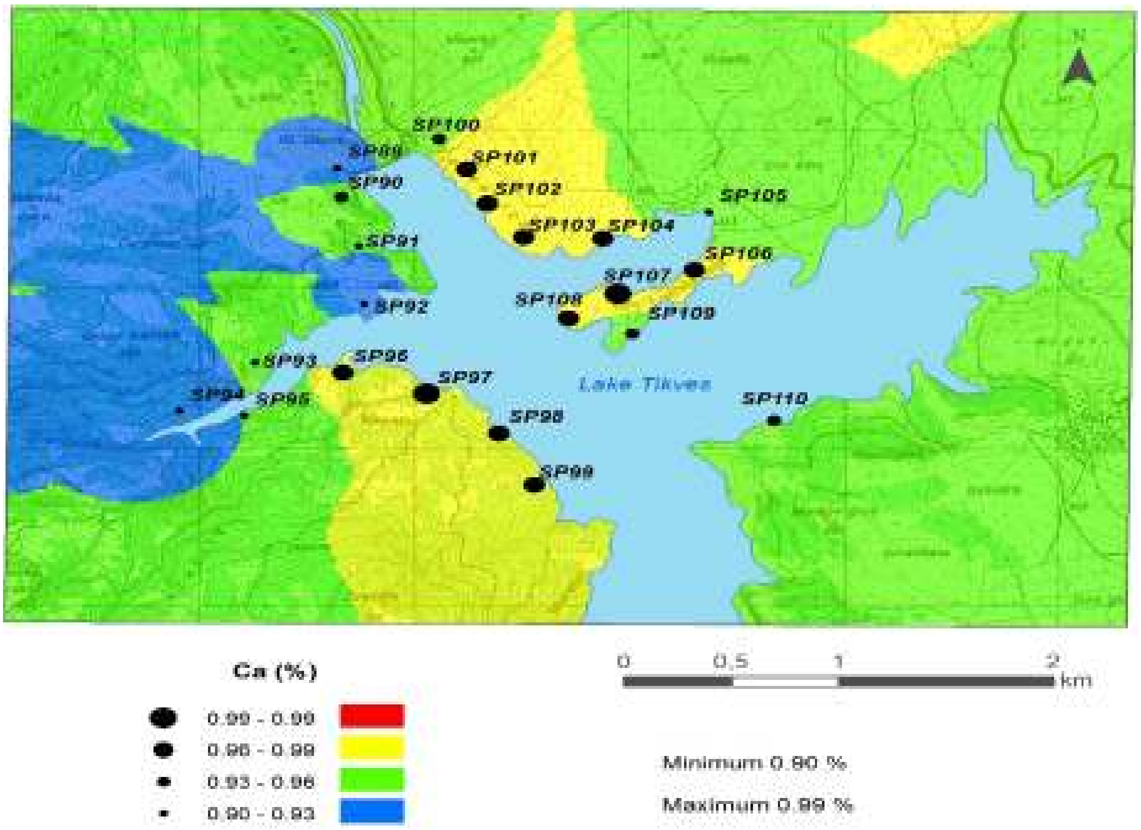

Fig. 9. Spatial distribution of Ca in the moss from the area of Tikveš Lake

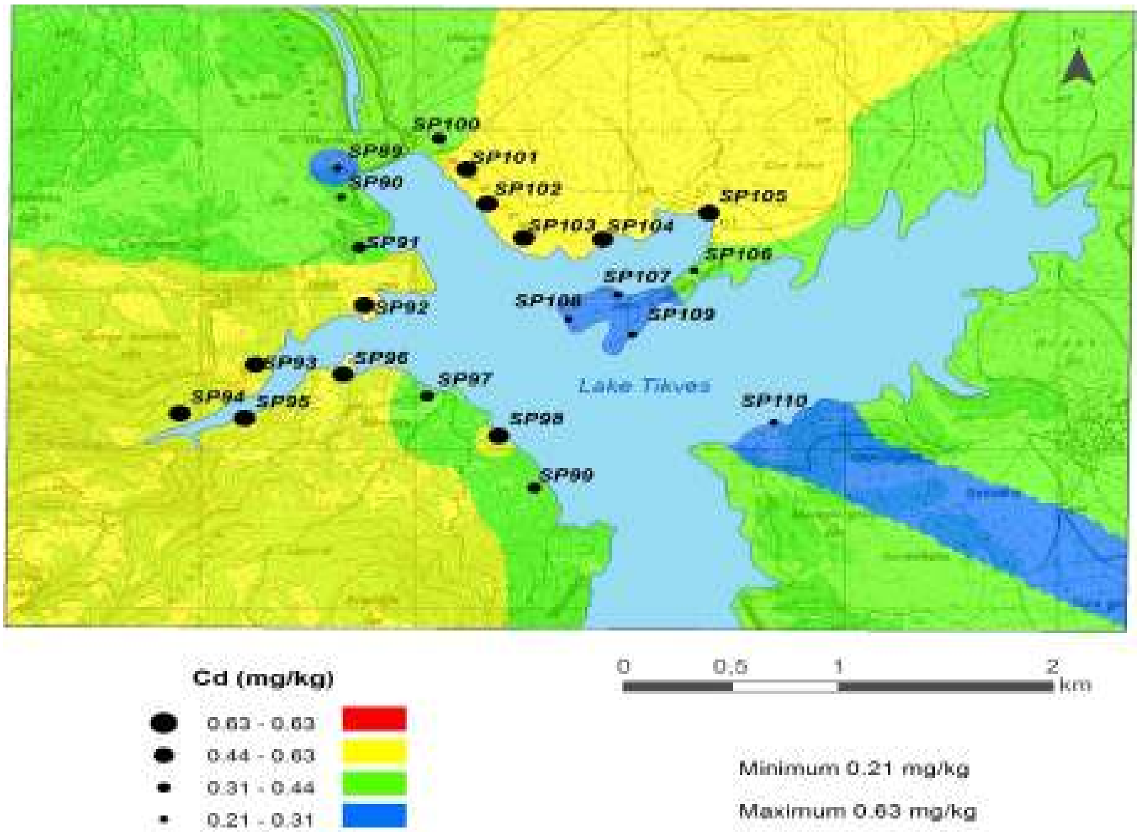

Fig.10. Spatial distribution of Cd in the moss from the area of Tikveš Lake

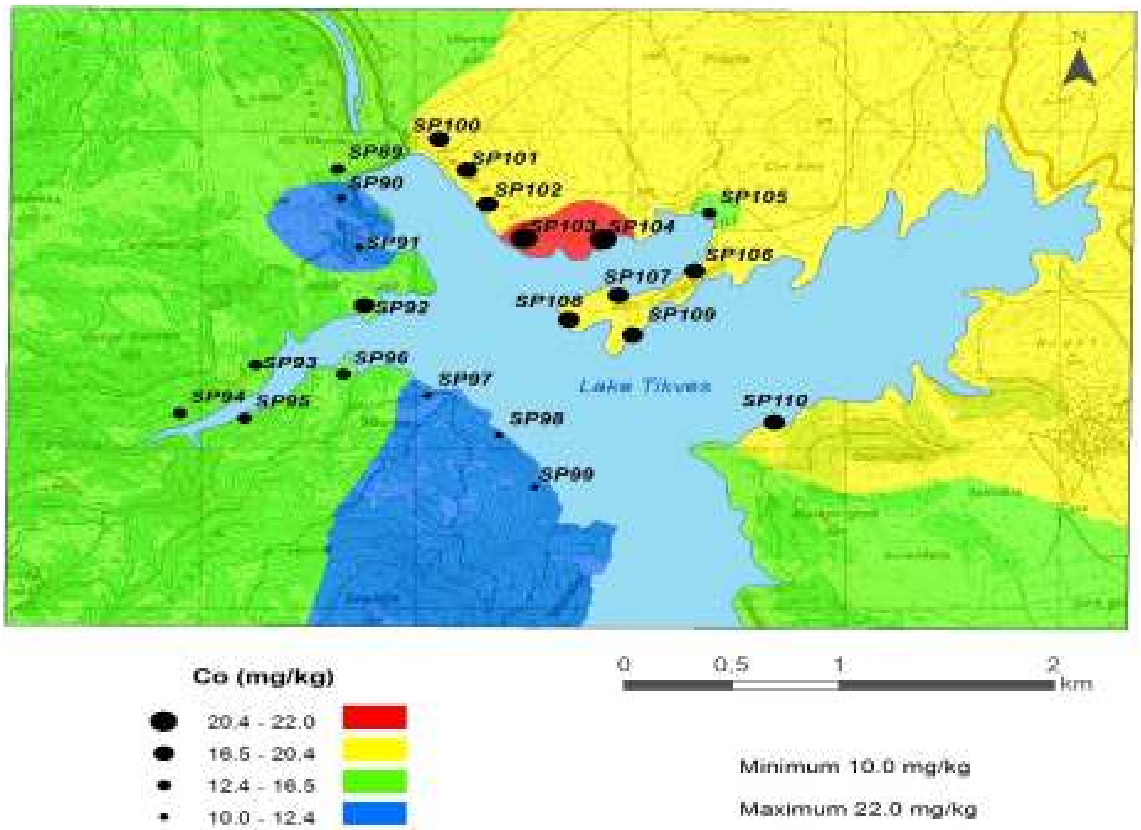

Fig.11. Spatial distribution of Co in the moss from the area of Tikveš Lake

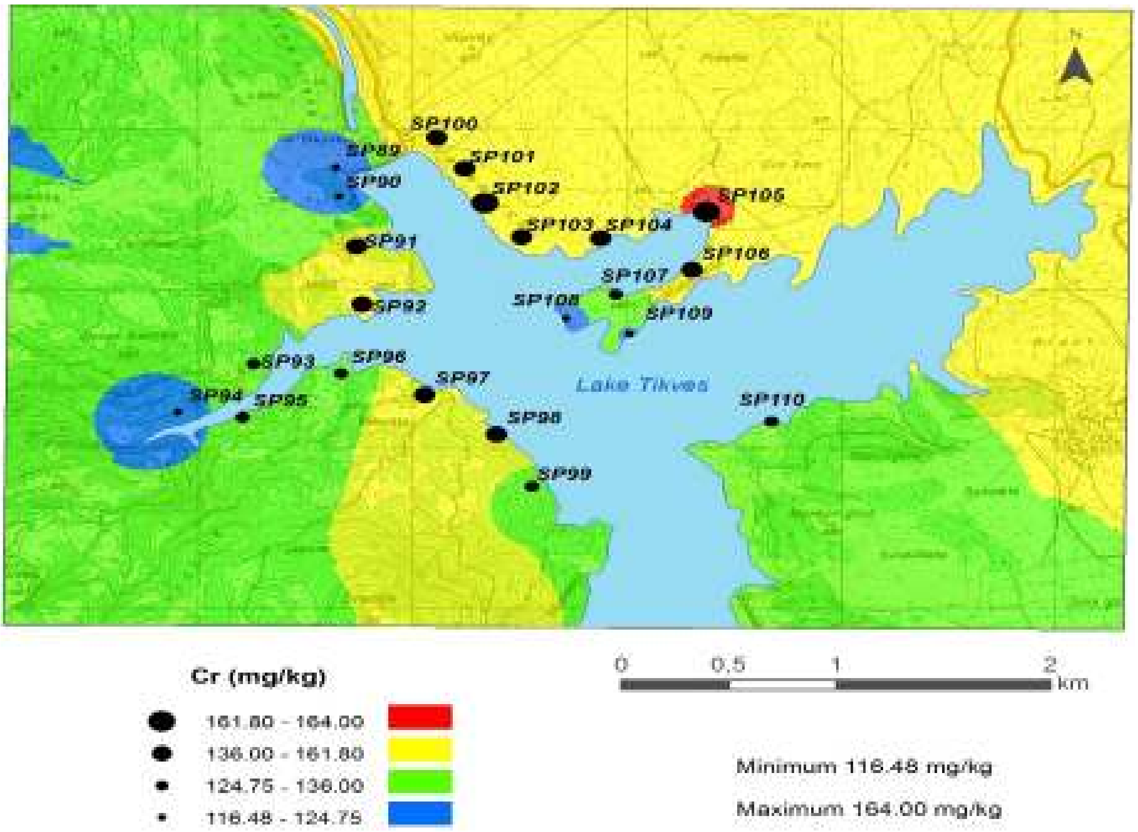

Fig. 12. Spatial distribution of Cr in the moss from the area of Tikveš Lake

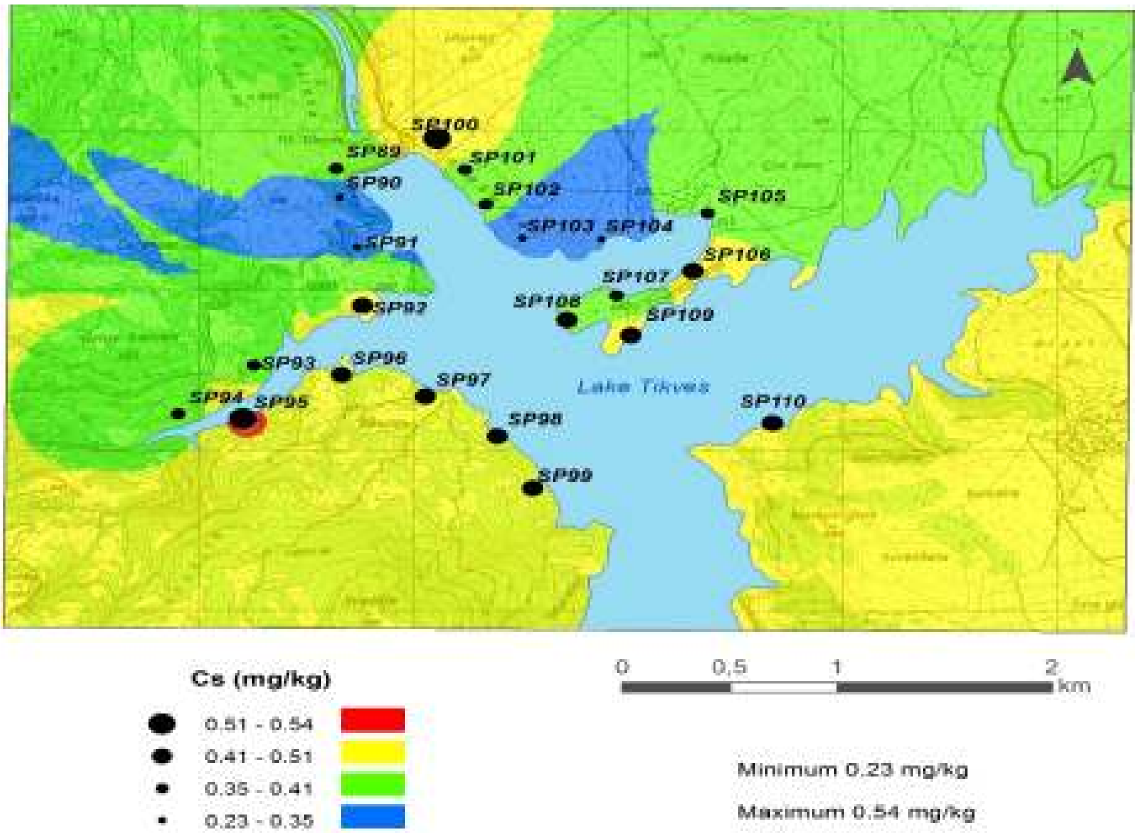

Fig. 13. Spatial distribution of Cs in the moss from the area of Tikveš Lake

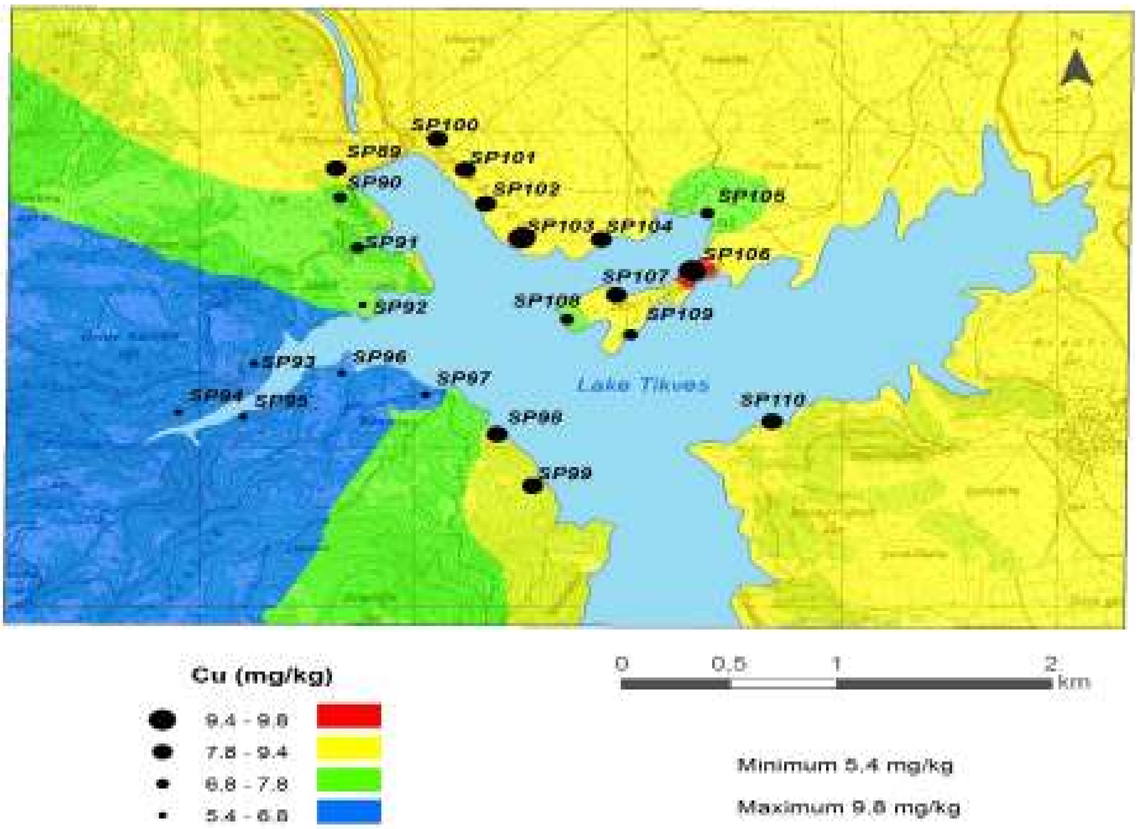

Fig. 14. Spatial distribution of Cu in the moss from the area of Tikveš Lake

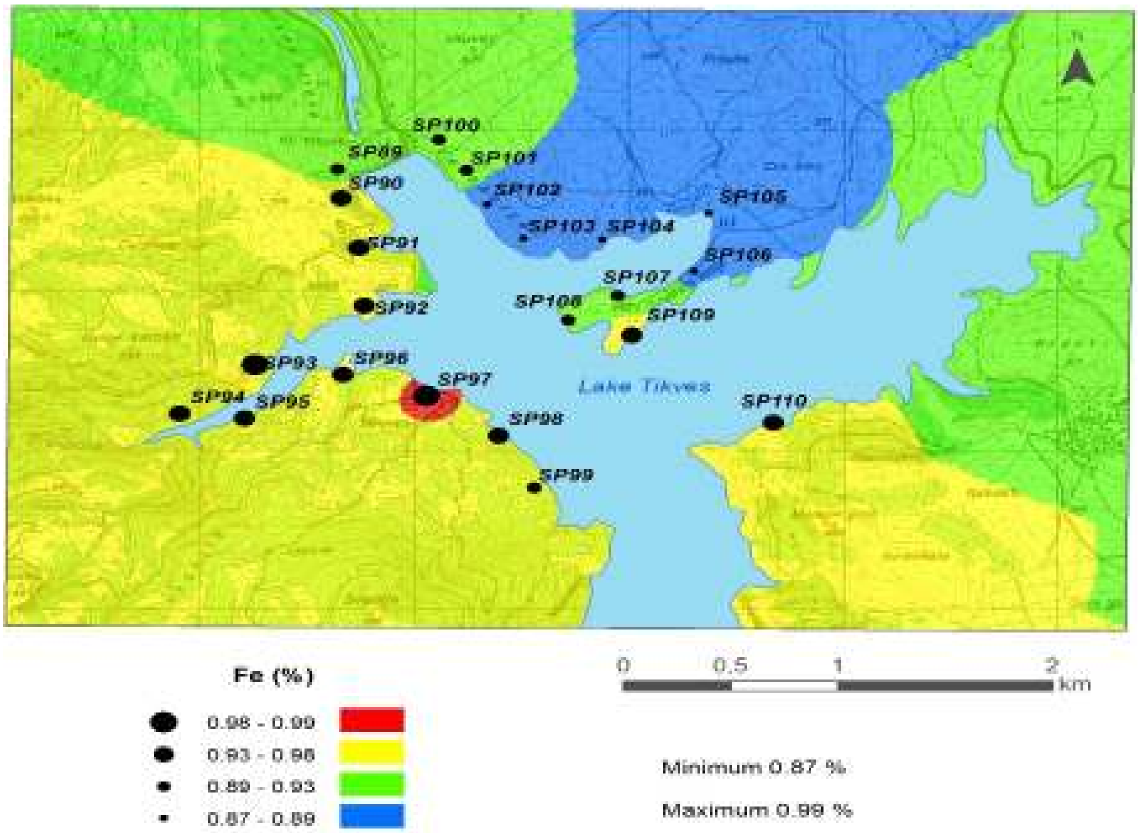

Fig. 15. Spatial distribution of Fe in the moss from the area of Tikveš Lake

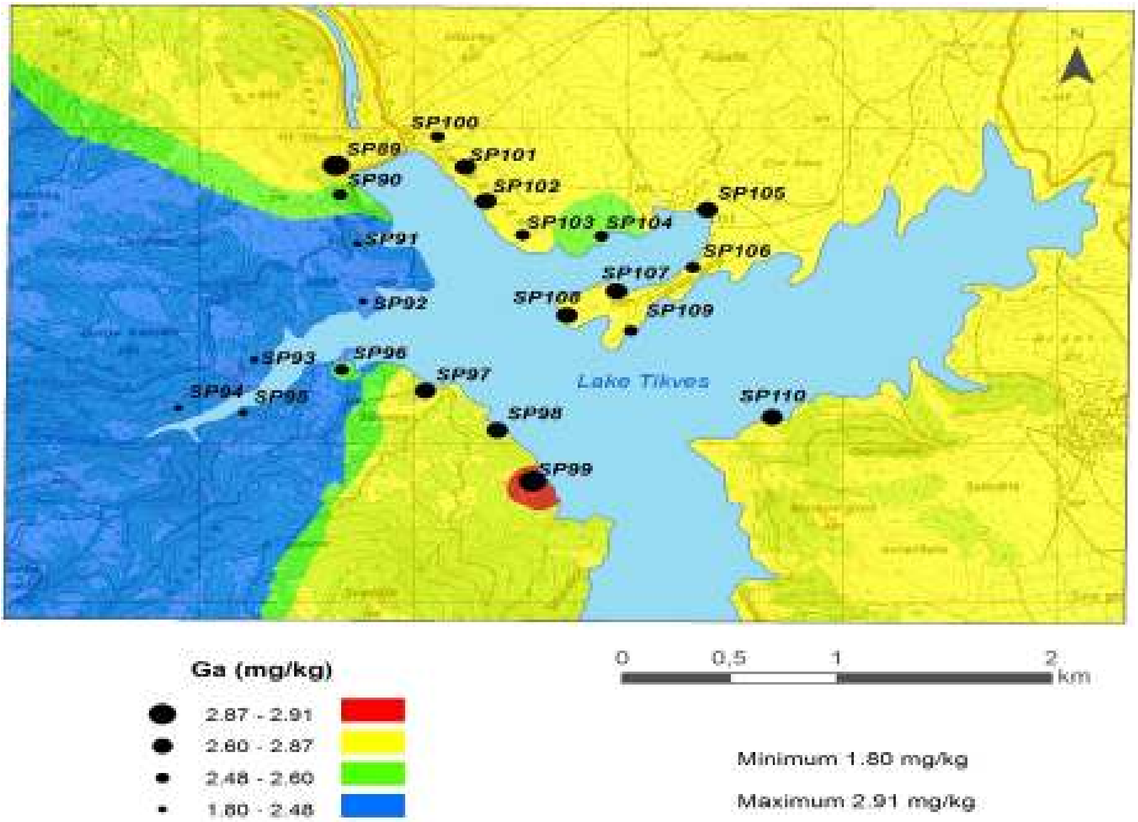

Fig. 16. Spatial distribution of Ga in the moss from the area of Tikveš Lake

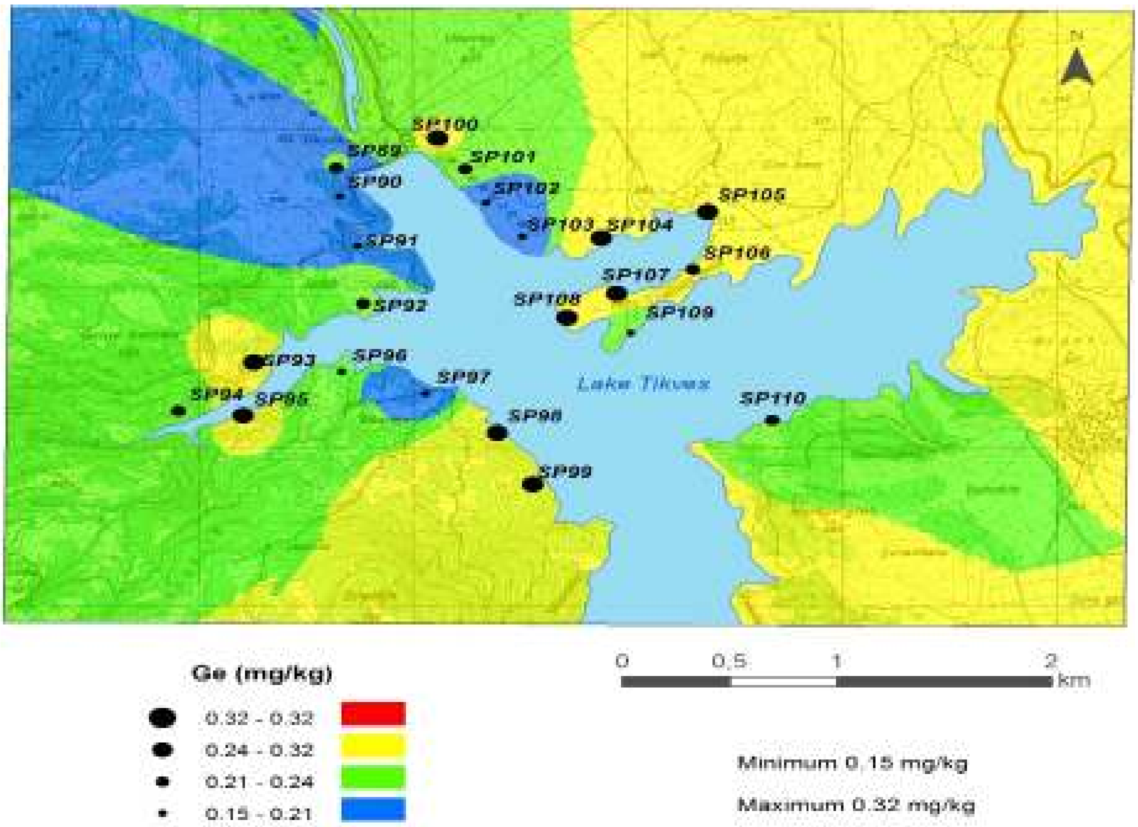

Fig. 17. Spatial distribution of Ge in the moss from the area of Tikveš Lake

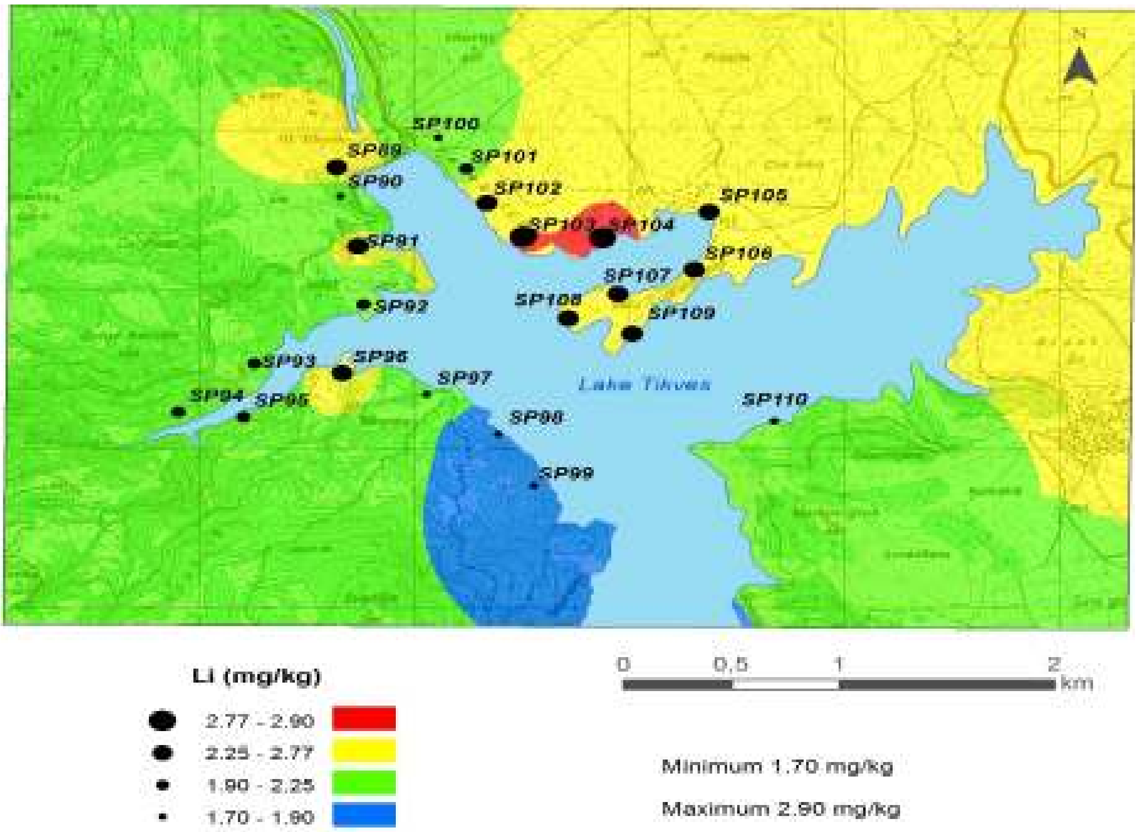

Fig. 18. Spatial distribution of Li in the moss from the area of Tikveš Lake

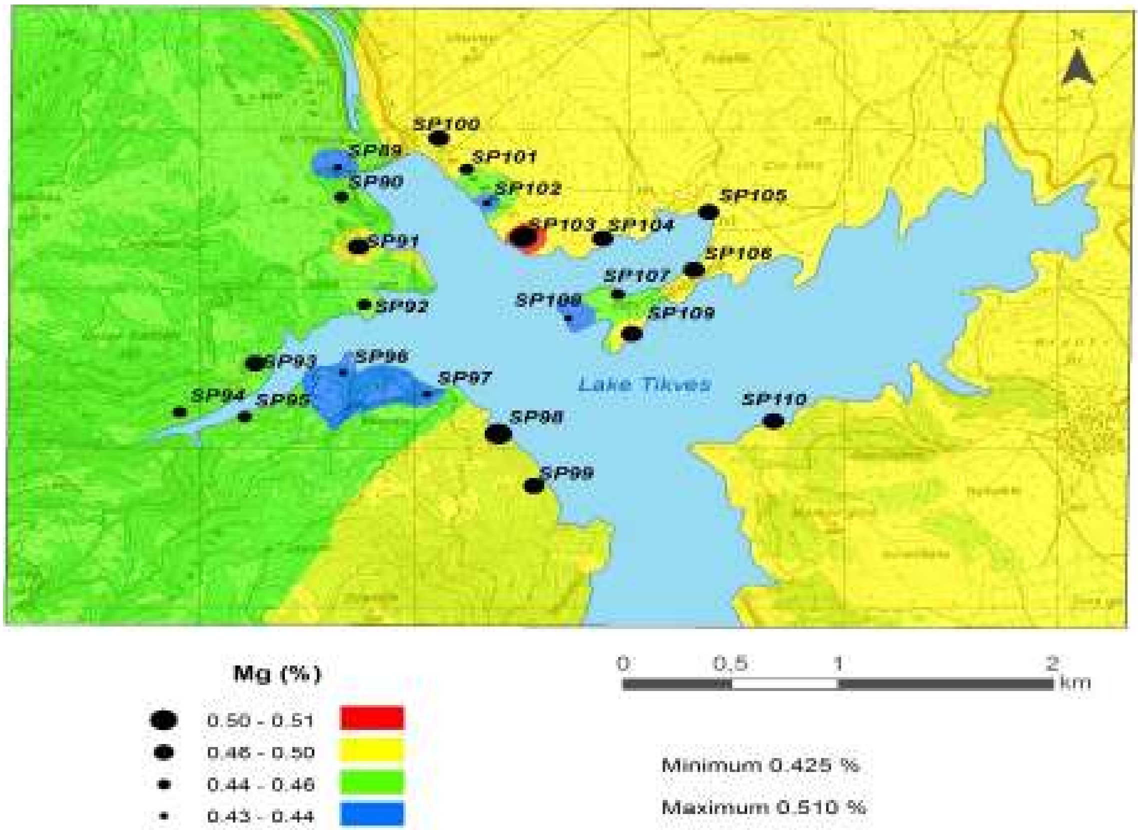

Fig. 19. Spatial distribution of Mg in the moss from the area of Tikveš Lake

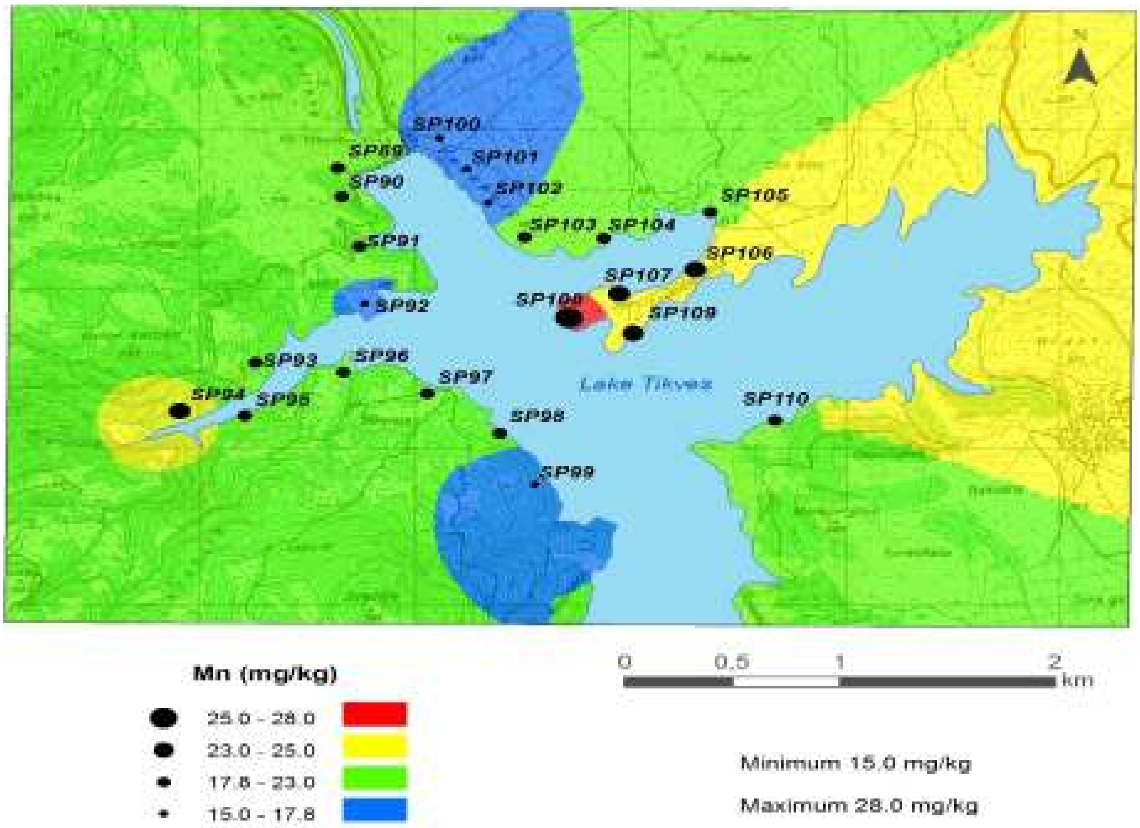

Fig. 20. Spatial distribution of Mn in the moss from the area of Tikveš Lake

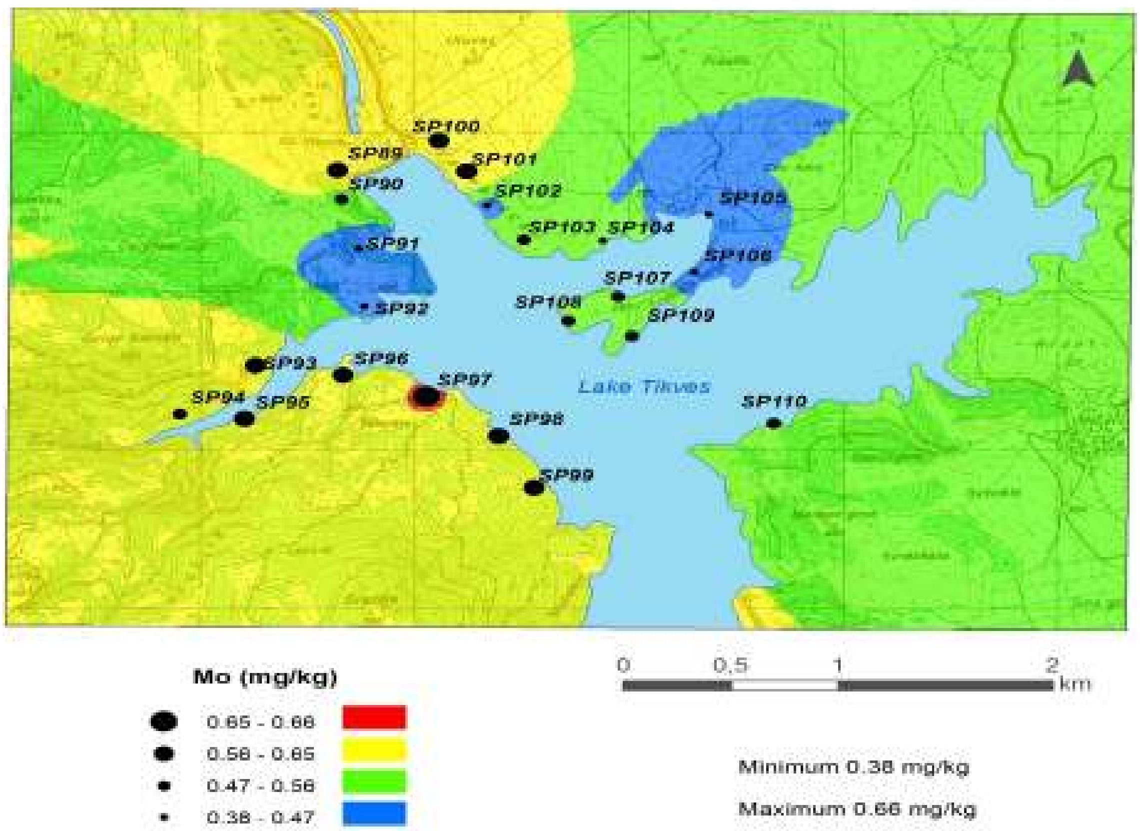

Fig. 21. Spatial distribution of Mo in the moss from the area of Tikveš Lake

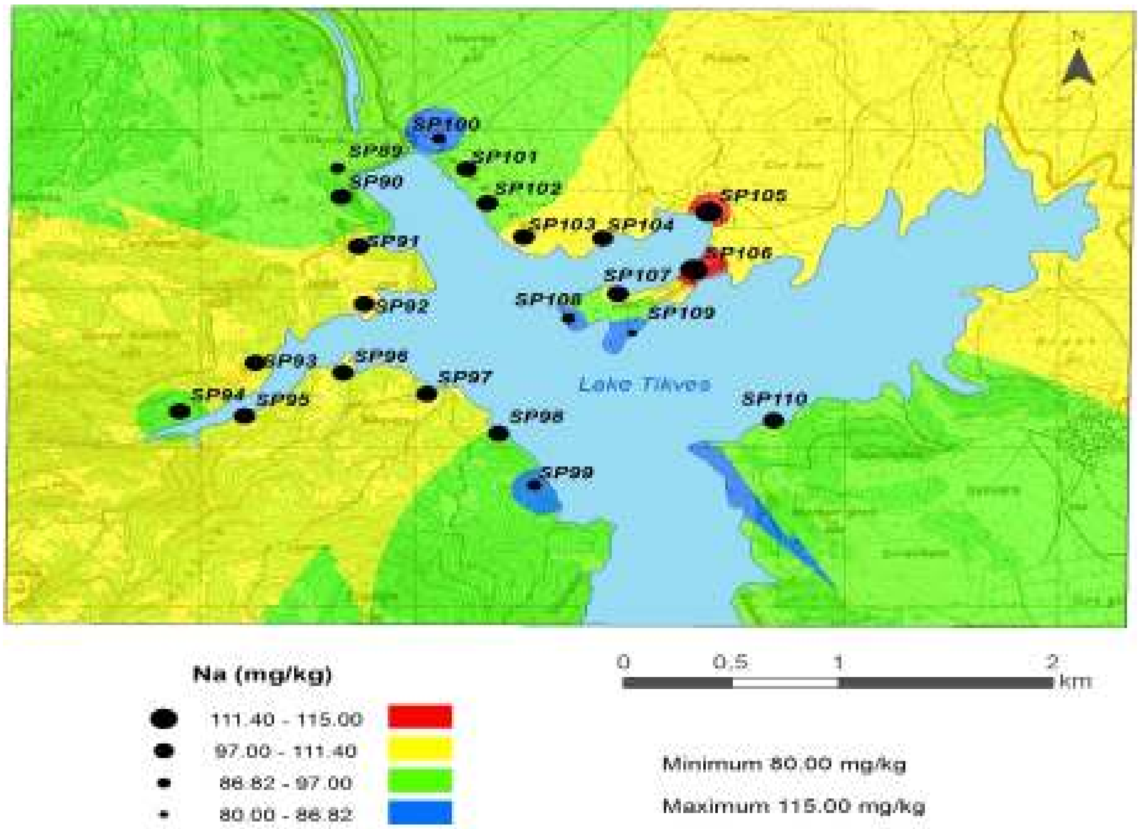

Fig. 22. Spatial distribution of Na in the moss from the area of Tikveš Lake

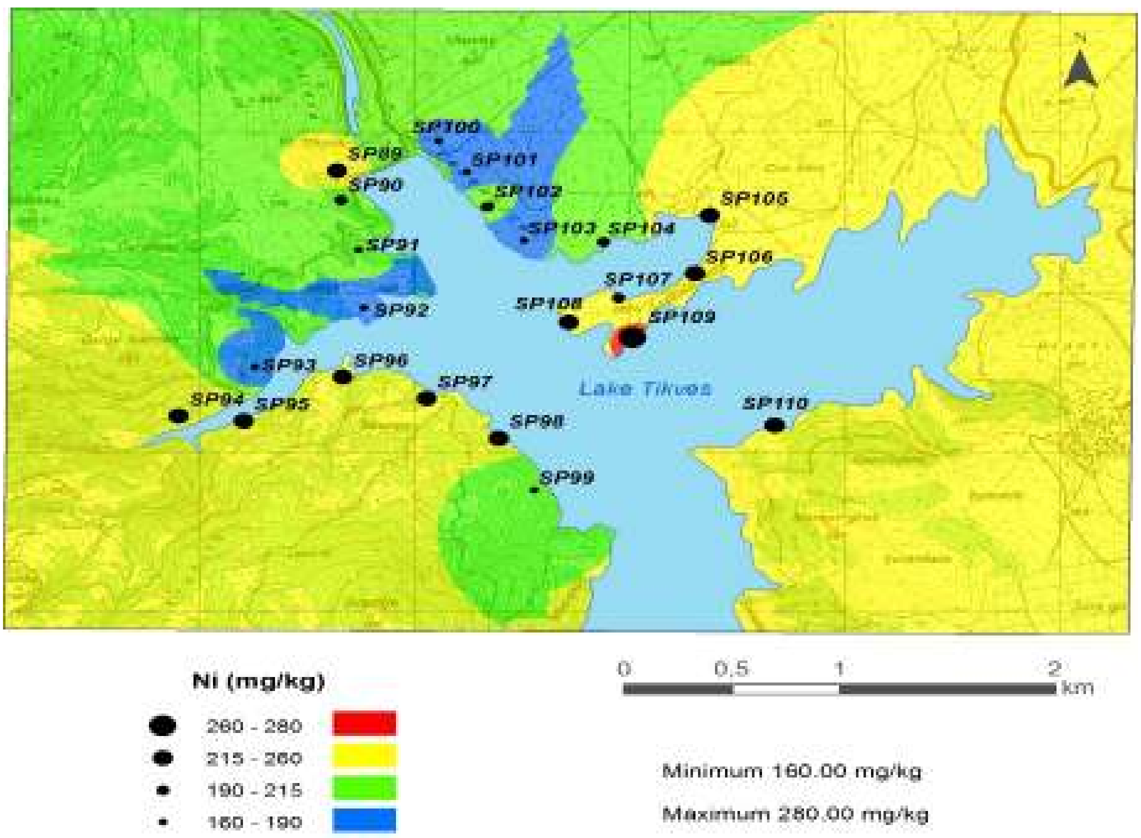

Fig. 23. Spatial distribution of Ni in the moss from the area of Tikveš Lake

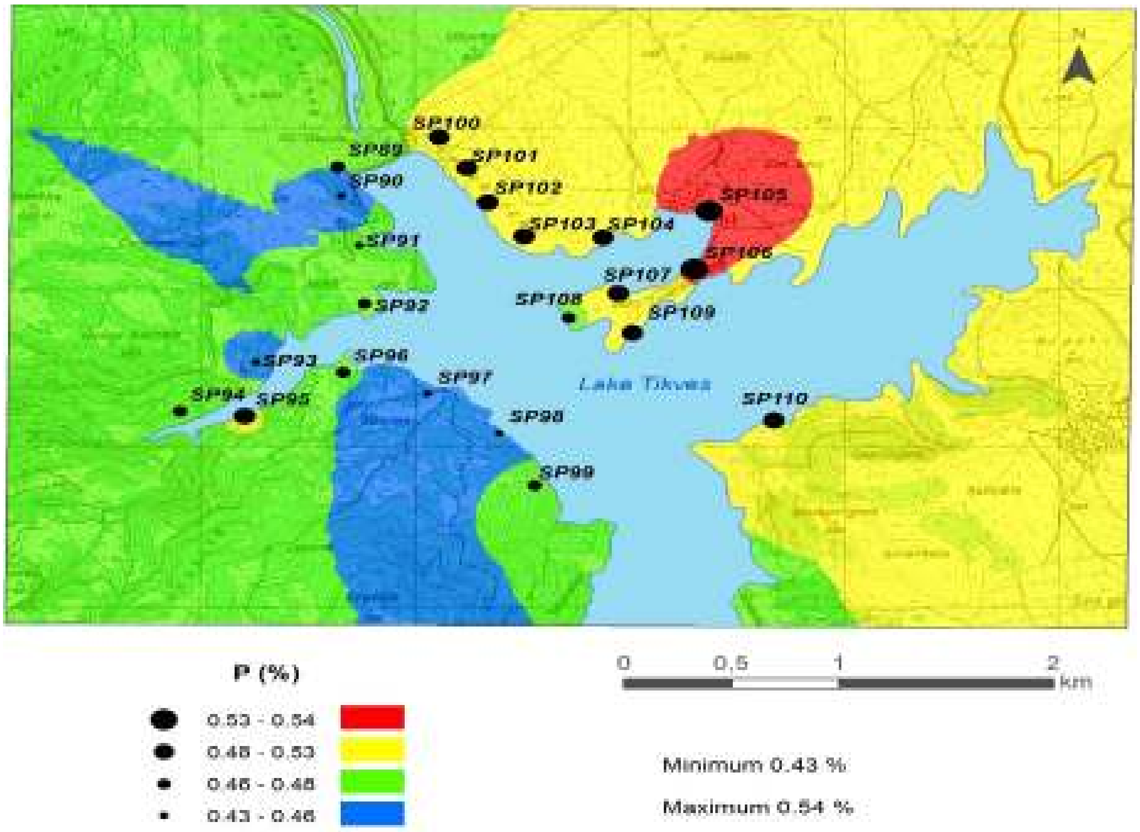

Fig. 24. Spatial distribution of P in the moss from the area of Tikveš Lake

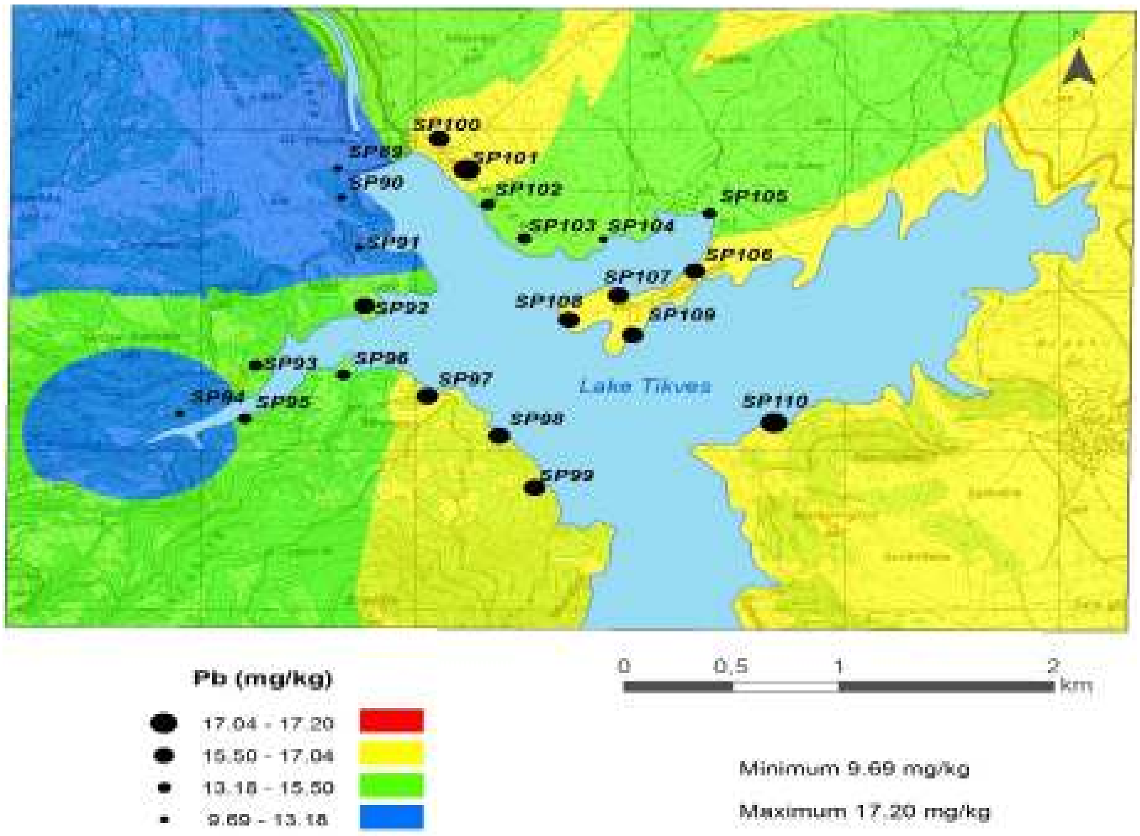

Fig. 25. Spatial distribution of Pb in the moss from the area of Tikveš Lake

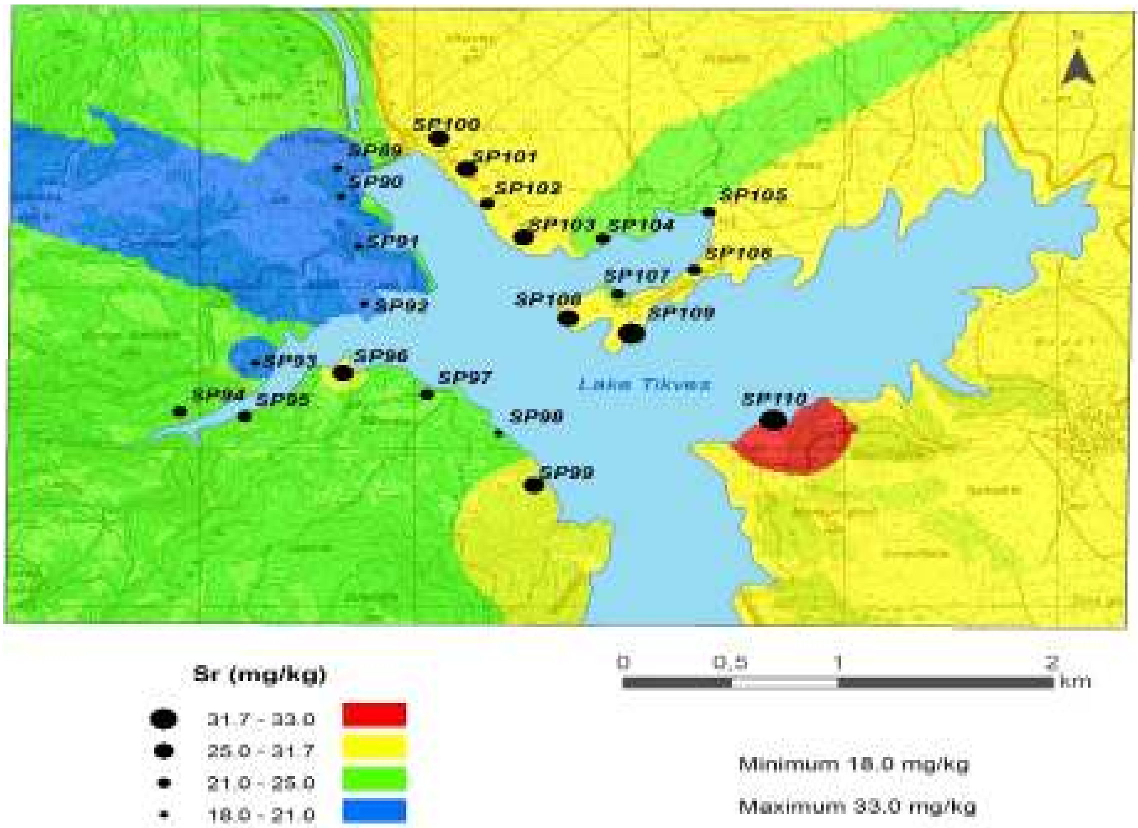

Fig. 26. Spatial distribution of Sr in the moss from the area of Tikveš Lake

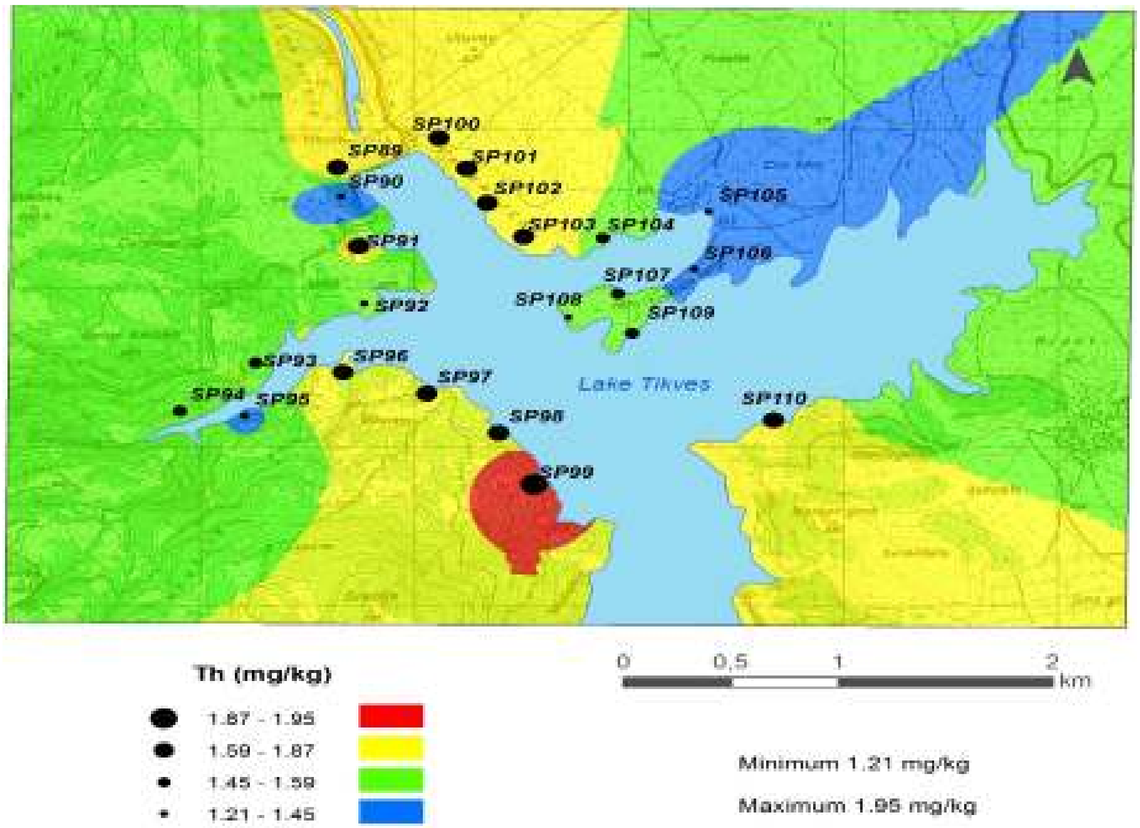

Fig. 27. Spatial distribution of Th in the moss from the area of Tikveš Lake

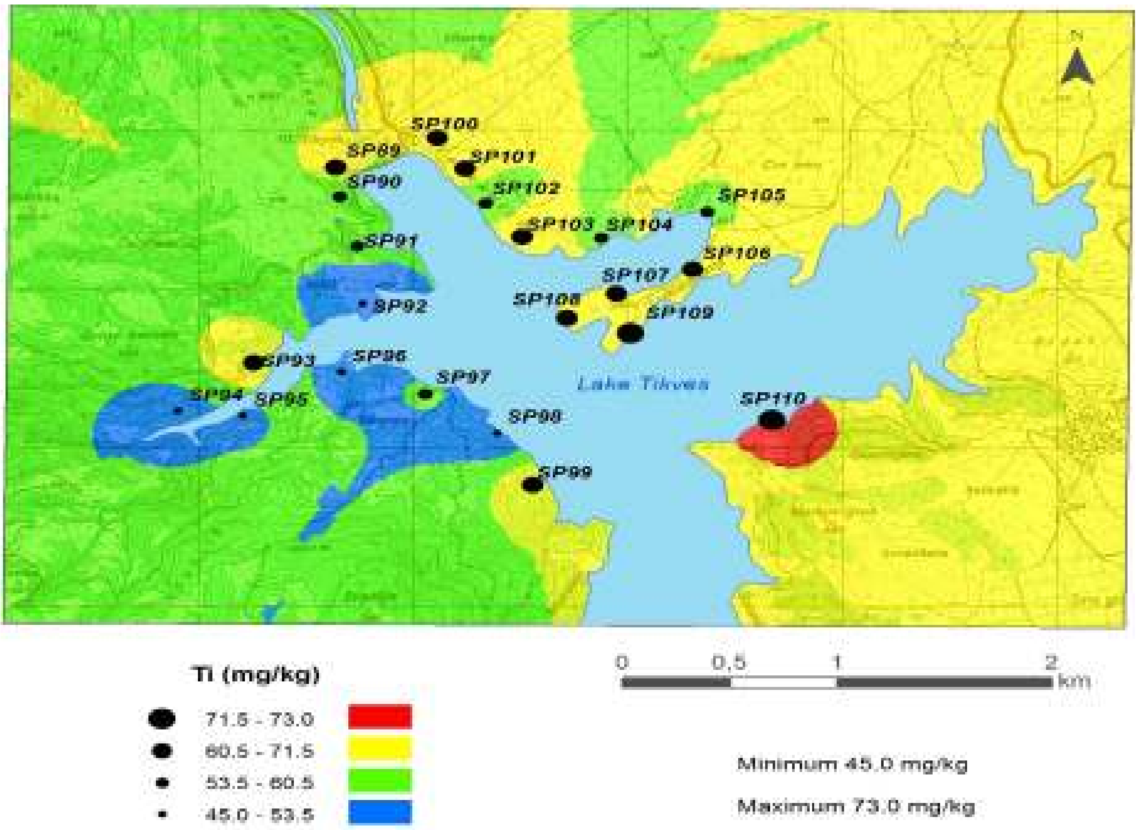

Fig. 28. Spatial distribution of Ti in the moss from the area of Tikveš Lake

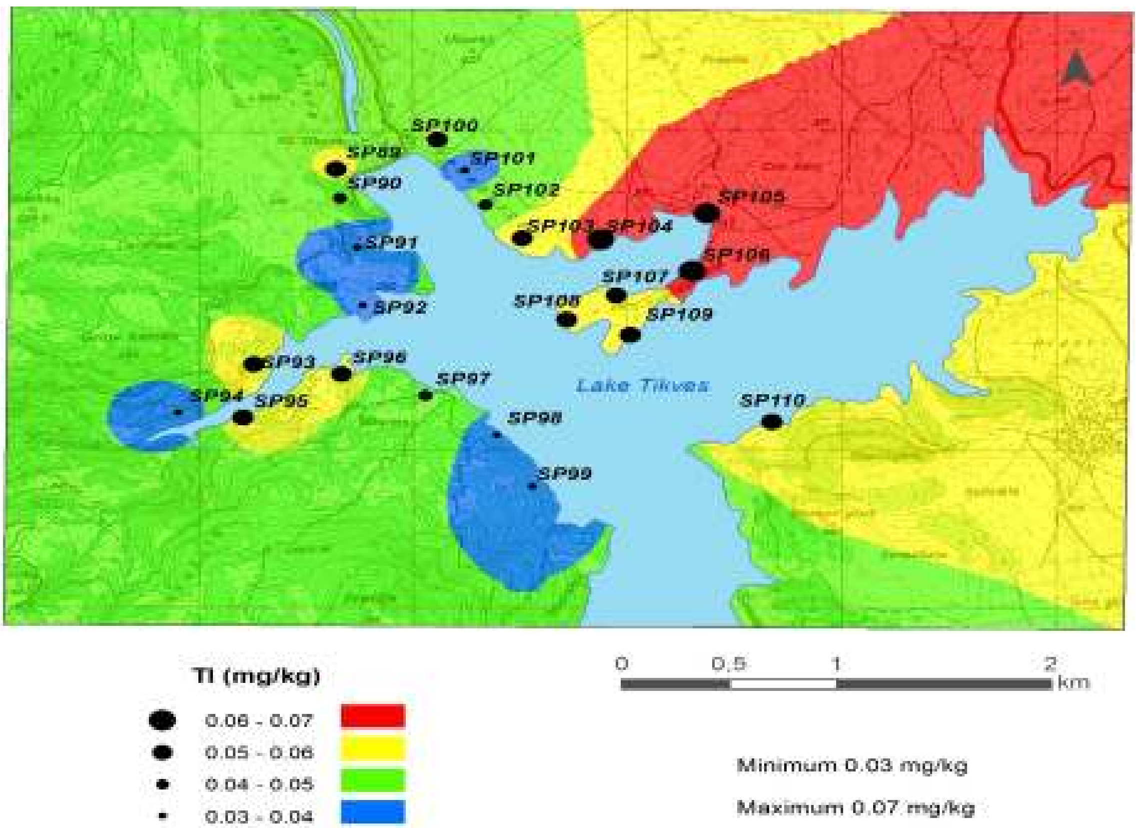

Fig. 29. Spatial distribution of Tl in the moss from the area of Tikveš Lake

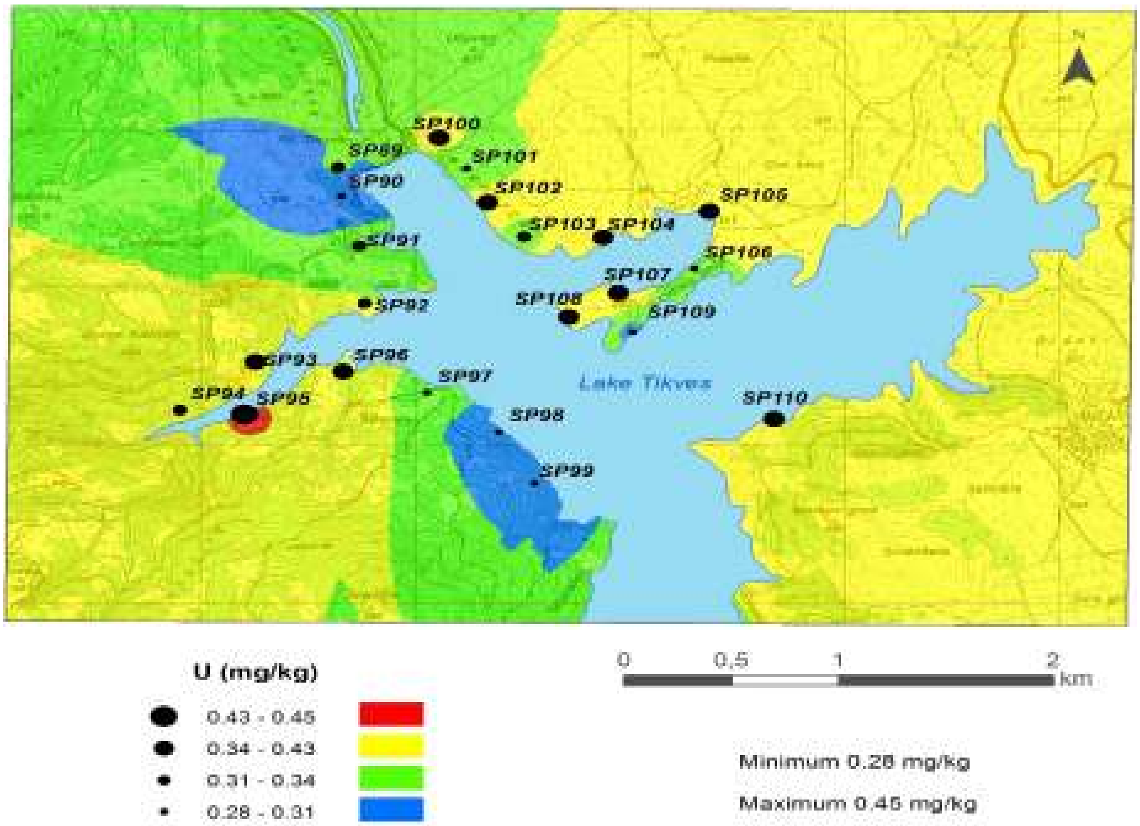

Fig. 30. Spatial distribution of U in the moss from the area of Tikveš Lake

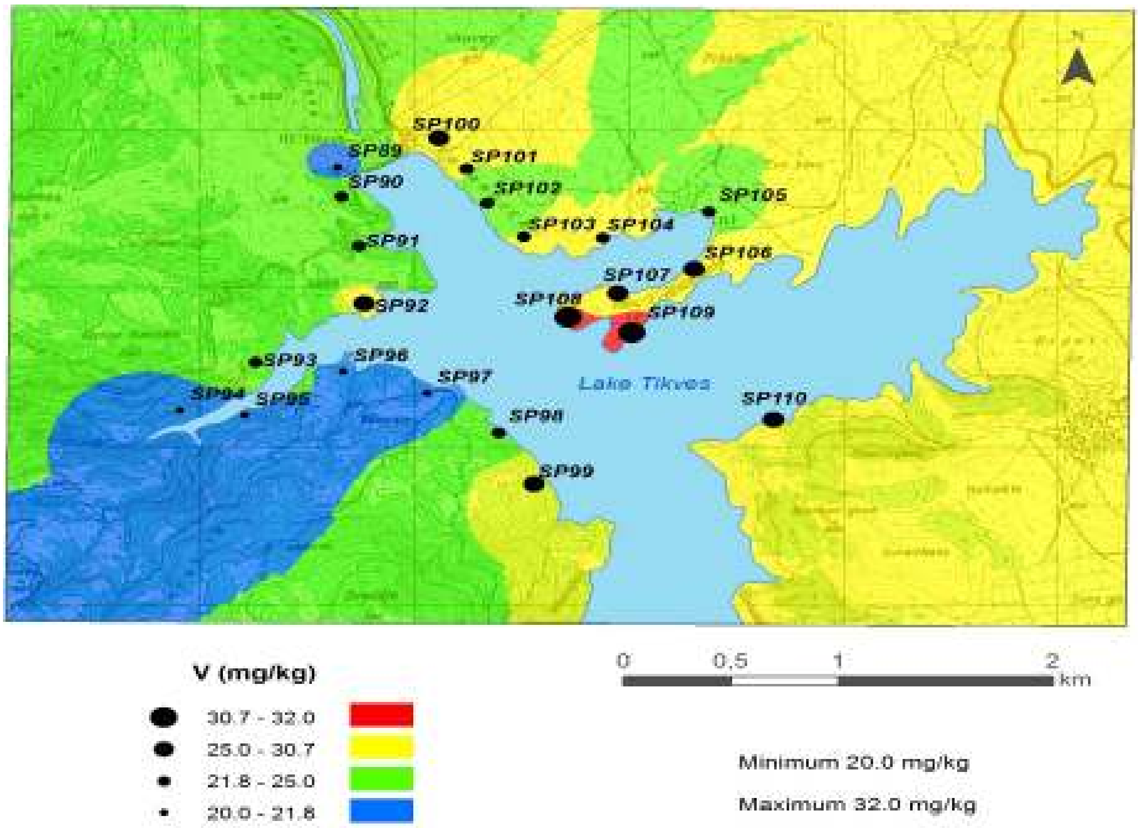

Fig. 31. Spatial distribution of V in the moss from the area of Tikveš Lake

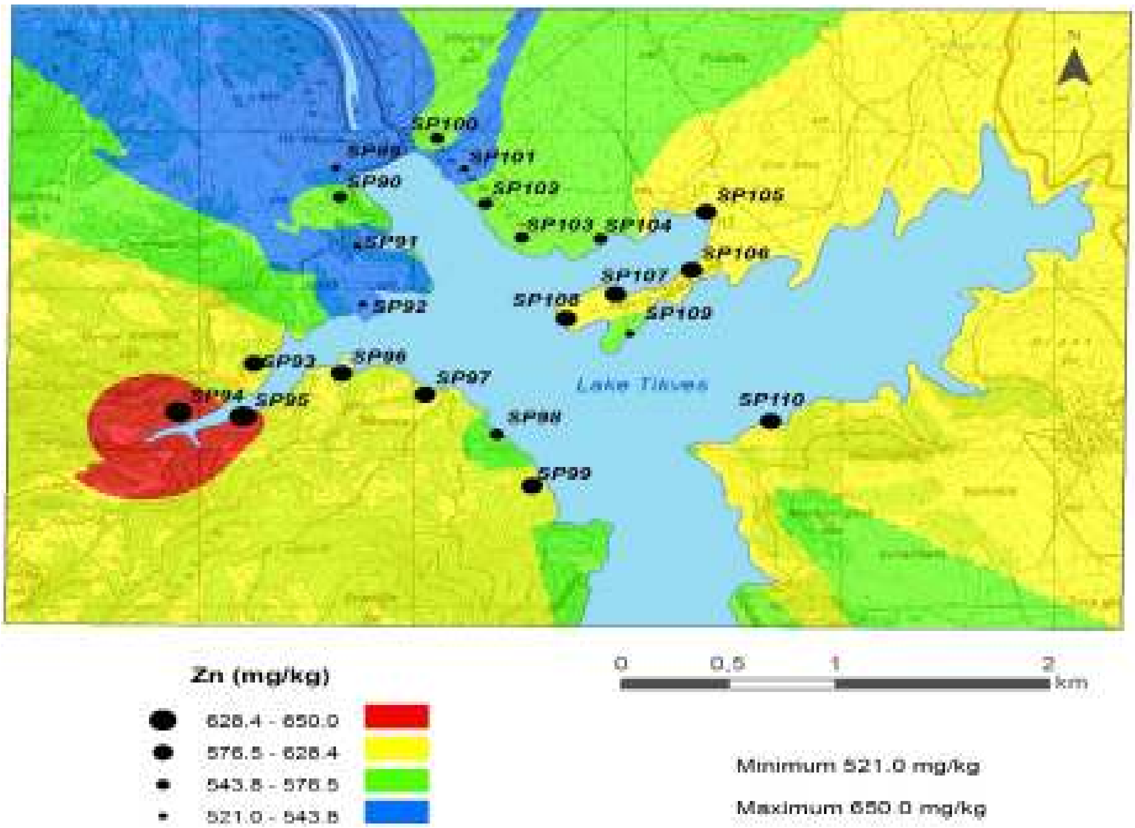

Fig. 32. Spatial distribution of Zn in the moss from the area of Tikveš Lake

CONCLUSION

The presence of the elements of traces Fe, Ni, Co, Cr, As. Pb, Zn in the researched samples of moss in the surrounding of the Tikveš Lake as well as the elaborated maps for spatial distribution of the elements of traces point to the fact that the researched area is a hot spot in relation to the air quality. The main source for pollution of the air in this area is the metallurgic factory for production of ferronickel which is located near the research area.

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Р е з и м е

ГЕОХЕМИСКИ КАРТИ НА ЕЛЕМЕНТИ ВО ТРАГИ ВО МОВ ОД ОКОЛИНАТА НА ТИКВЕШКОТО ЕЗЕРО ВО БЛИЗИНА НА КАВАДАРЦИ, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: мов; геохемиска карта; никел

Во трудот се прикажани геохемиски карти на дистрибуцијата на елементите Li, Be, B, Na, Mg, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Sr, Mo, Cd, Cs, Ba, Tl, Pb, Bi, Th, U во мов од видот *Campothecium lutescens* во околината на браната на Тиквешкото Езеро. Близината на комбинатот за производсво на фероникел до испитуваното подрачје, како и правецот на движењето на воздушните маси, придонесуваат во околината на браната на Тиквешкото Езеро да има зголемени концентрации првенствено на елементите NI, Fe, Co, Cr, Pb, Zn, As, со што оваа област може да се дефинира како жешка точка во однос на квалитетот на воздухот.