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GEOCHEMICAL INVESTIGATIONS OF THE SOILS IN THE REPUBLIC OF MACEDONIA

Blažo Boev and Sonja Lepitkova

Faculty of Mining and Geology, Štip, Republic of Macedonia

The paper presents data from studies aiming at determination of individual elements in the soils in some valleys in Macedonia, with particular reference to the concentration of Mg, which is one of the most important biogene elements in the process of photosynthesis in plants.

The authors determined concentrations of individual microelements and toxic elements in some soils in the territory of the Republic of Macedonia. The aim of the studies was to determine the amounts of those elements that exceed the values allowed and are toxic and harmful for the normal growth and development of plant strains.

Key words: soils; microelements; magnesium

INTRODUCTION

Soil is the top part of the lithosphere and basic factor of life. It is an important natural source that conditions the status, social and economic development of society.

Scientists dealing with the nature of soil consider that soil is "a natural body of minerals and organic components, divided into horizons differing from the matter lying in the basement in morphology, composition, chemistry and biology. A specific feature of soils is that they have different composition and characteristics in individual layers at depth. This must be taken in consideration when analysing the composition and the character of soils.

The characteristics of soils are different from those of the source material ensuing them. This is due to biological activity since the influence of certain organic components in the development and growth of plants is sometimes greater than that of the source rock.

Since soil, its nature, setting and influence are a component part of the biosphere and a product of joint action between biogene and abiogene environment, the soil – organism system becomes an important mechanism for the formation and productivity of biosphere. Therefore, determination of the character of soil is of particular importance to the development of some plant strains making possible the improvement of the composition of the soil through certain mechanisms.

METHODS OF WORK

Analytical method

Forty samples collected from the three largest valleys in Macedonia were studied. Samples were collected from six sections, from 0 to 70 cm in depth and analysed by ICP–AES method. This method was chosen following the large number of reports presenting good results in the determination of trace elements in some soils (Dahlquist and Knoll, 1978; Horwitz, 1980; David, 1978; Lyons and Lynch, 1985; Willet and Zarcinas, 1986).

The advantages of this method compared with other methods for trace elements analysis (i.e. AAS by flame atomization) are as follows:

– the possibility to obtain spectra for more elements or multi-element analyses after one exciting;

– low detection limits for several elements, even for elements such as V, P etc.;

– lower probability for chemical interference;

– greater range of concentrations for which there is linear dependence of instrumental signal from concentrations of elements or the possibility for simultaneous determination of major and trace elements;

– high precision.

The ICP-AES method can determine up to 75 elements. With samples collected from agricultural material several elements can be determined directly in extracted solutions, whereas some need preconditioning by ion exchangers.

Since soil samples can differ, it is necessary to provide a representative sample. This can be achieved by drying the sample with no 2 mm fraction at room temperature in well-aired premises for several days, taking smaller sample by quartering and screening with sieves of 200 meshes.

Soil samples can be treated in a variety of ways applying a number of reagents depending on whether the total concentration or the amount of elements available to plants are analysed.

The total amount of elements in soil samples is the concentration of elements obtained after their complete and thorough digestion.

Content of elements obtained by acid liquid extraction from soils investigated combined with inorganic acids can be regarded as approximate indicators of the concentration of elements available to plants. This is so because analysis of samples in such "rigorous" conditions is not consistent with the conditions in which biological processes take place.

The content of so called accessible elements is a logical estimate of the amount of elements in the soil available to plants and is obtained by extraction of weak acids from the soil such as acetic acid or complexon III.

The M CaCl solution and 0.1 M thriethanolamine puffered 0.005 M dyethilene-thriamine-pentaacetic acid (DTPA) adjusted to pH 7.3 is used to determine accessible forms of metals such as Fe, Cu and Mn. For the exchangeable cations such as Ca, Mg, Na and K extraction was made with neutral 1 M ammonium acetate (Dahlquist and Knoll, 1978). Extraction for Fe, Al and P was made using ammonium oxalate–oxalic acid solution (known as Tamm's reagent), (Novozamski, Van Esk, Houba, Van der Lee, 1986).

ANALYTICAL METHODS

Approach

Air-dried sample prepared in accordance with ISO 11464 (ground sample and sieved through the sieve the aperture the size 150 μm, is extracted with a HCl/HNO_3 acid mixture at room temperature for a period of 16 hours followed by distillation for a period of 2 hours. After this the extract is diluted with nitric acid.

After this step the contents of trace elements are determined by ISP-AES method.

Reagents

Reagents used are of sufficient purity required by ISP-AES determinations, confirmed by conducting a blank test. Water must comply with degree 2 purity ISO 3696.

Hydrochloric acid, c(HCl) – 12.0 mol/l,

p – 1.19 g/ml,

Nitric acid, $c(HNO_3)$ – 15.8 mol/l,

Nitric acid, $c(HNO_3)$ – 0.5 mol/l/.

Apparatus

Glass apparatuses are carefully cleaned with warm nitric acid for at least 6 hours and then rinsed with water.

Grinding mill dry samples, to a size less than 150 μm without contamination by the elements to be determined.

Test sieve the aperture the size 150 μm made of plastics materials.

Disiccator-Exicator, the volume of 2 l.

Reaction vessel, the volume 250 ml.

Reflux condenser with conical ground joints.

Absorption vessel, non-return type if mercury is determined.

Glass beads, the diameter of 2 mm.

Heating apparatus.

Volumetric flask, the volume of 110 ml.

Filter paper, the pore size of 8 μm and a diameter of 150 mm.

Preparation of sample

Representative portion of air dried sample according to ISO 11464 is ground and screened with sieve the meshes of 150 μm in order to obtain a sample approximately 20 g in size.

Procedure

Sample of 3 g is weighed by analytical scale and put in a distillation vessel. The sample is moistened with 0.5 – 1 ml water and mixed with 21 ml HCl and 7 ml HNO_3 drop by drop in order to reduce foaming. Fifteen ml HNO_3 is added to the absorption flask and distillation apparatus is assembled. The sample in the flask is extracted at room temperature for 16 hours and then distilled at boiling temperature for 2 hours. The distilled material is placed into a volumetric flask the size of 110 ml and filled with nitric acid c(HNO_3) – 0.5 mol/l.

RESULTS AND DISCUSSION

The samples under study were collected from several sites, e.g. Vardar – Gradsko, Rosoman; Tikveš – Kraište, Lozovo and ZK Pelagonia.

The results obtained are shown in Tables 1–3. The presence of some major elements (Mg, Fe, Ca, Al) and trace elements (B, Co, Ni, Mo, Pb, Zn, Cu, Cd etc) was studied in samples collected from 40 sampling sites. The influence of pH factor on the distribution of individual elements in some soils was taken into account in the study of concentration of some elements.

Results were compared with measurable concentrations allowed for such elements. Table 1 shows that Mg, as one of the most important biogene elements in most of the samples studied, is below the average value for individual types of soils (6300 ppm).

Only in measurement sites 13, 14, 21 and 22 increased concentrations of Mg were found, where as in all other measurement sites the concentration of Mg is below the average value in the soil. This indicates that the soils in the Republic of Macedonia are poorly magnesic, and magnesic fertilizers should be used in soils in order to improve the development and growth of plants.

Calcium concentration in most of the samples is higher than the allowed, the highest values were detected in the Tikveš – Kraište site, and the lowest in Pelagonia.

Iron is also an important biogene element, especially to many functions with plants and its concentration in soils is an important precondition to the determination of the kind and quality of soil. Only some probes in the measurement sites indicated values closer to the average Fe concentration in soils (of 38000 ppm), indicating that soils in the area under survey are poor in iron.

Table 1

Total amounts of B and Mg in the soil (mg/kg)

No	B	Mg	No	B	Mg
1	36.7	6066	21	32.2	10109
2	33.2	5597	22	42.5	12798
3	38.4	5925	23	33.1	3648
4	38.7	5833	24	41.2	2867
5	51.9	7665	25	41.5	4304
6	32.6	6328	26	49.8	3774
7	34.8	5484	27	43.1	4390
8	39.4	6340	28	41.5	5618
9	54.8	8323	29	64.0	7141
10	43.6	9927	30	73.2	7102
11	43.0	7428	31	69.0	7637
12	36.4	8115	32	72.9	5322
13	32.1	14608	33	59.0	6573
14	26.3	14896	34	70.2	6342
15	43.7	5977	35	50.7	5077
16	33.3	6246	36	78.6	5172
17	33.3	6791	37	60.1	4778
18	30.5	5620	38	69.3	3700
19	65.2	4114	39	61.3	4606
20	33.5	3778	40	80.9	5504

Sulphur is also a biogene element important to the development of plants and animal life. In soils under survey the concentration of sulphur ranges below average values, only in measurement sites 11, 12, 13, 16, 17, 21 and 22 being over the average (of 850 ppm). The concentration of Al is also below the average in all measurement sites (Table 2).

The contents of individual microelements are given in Tables 2 and 3. Data indicate that most of the microelements are below the average measurable concentrations allowed.

Table 2

The concentration of Pb, Cu, Zn, Cd, Fe, Mn and Al in the soil (mg/kg)

No	Pb	Cu	Zn	Cd	Fe	Mn	Al
1	34.5	31	43	0.61	12807	803	11910
2	20.8	24.5	43.3	0.90	11601	574	11914
3	22.4	17.7	37.6	0.70	15172	804	13807
4	22	25.6	40	0.77	13977	788	12860
5	21.1	15.7	46	1.03	17385	768	16075
6	14.5	15.7	34.1	0.56	10875	790	11140
7	19.6	20	33.1	0.75	10704	503	10931
8	20.6	24.6	42.4	0.79	12052	526	12276
9	15.4	10.2	33.4	0.61	11817	574	8075
10	15.9	16.2	55	1.06	15344	447	11903
11	12.2	22.2	37	0.73	12182	673	9824
12	25.2	13.8	36.9	0.85	14280	511	11257
13	11.1	18.8	33.9	0.79	11563	425	6790
14	5.1	16.4	31	0.63	7405	520	7669
15	14	10.5	42.2	0.77	1078	694	9776
16	12.7	10.5	33.3	0.71	10969	487	10619
17	6.2	10.3	35.4	0.95	11854	433	9715
18	5.5	7.6	32	0.66	10410	417	8127
19	9.7	6.3	44.5	0.58	8891	340	6965
20	4.3	4.7	27.7	0.63	7929	265	6119
21	9.3	9.7	27.7	0.73	8445	199	6257
22	15.7	16.4	43.8	1.11	14953	401	10161
23	19	10.6	30.6	0.53	11499	614	12313
24	17.6	16.4	44.4	0.58	10712	690	10401
25	24.3	10.6	52.4	0.98	16230	650	16680
26	21	17.1	38.3	0.69	12633	605	13577
27	13.9	13.0	38.9	0.95	12284	711	12839
28	13.9	15.2	45.4	0.99	13367	601	13771
29	22.1	28.9	69.1	1.69	26288	635	13423
30	26.1	33.3	74.3	1.81	29100	869	14294
31	26.5	31.3	74.7	1.84	29299	894	14603
32	19.6	21.8	58	1.46	21950	862	10701
33	17.8	20.4	52.3	1.57	20343	747	10260
34	20.1	24.1	57.7	1.30	22355	639	11901
35	9.9	23.2	41.5	1.24	21658	763	10692
36	13.5	23.8	45.9	1.47	25734	679	13564
37	13.9	24.7	44.3	1.52	21102	796	10694
38	8	24.2	41.2	1.18	18924	695	8973
39	18.1	24.2	44.7	1.57	27175	764	13535
40	12.4	20.5	45.5	1.20	18876	644	9194

Table 3

The concentration of Co, Ni, As, Ca, Mo and S in the soil (mg/kg)

No	Co	Ni	As	Ca	Mo	S
1	13.10	83.6	< 0.50	4182	< 0.20	145
2	10.15	63.3	< 0.50	29337	< 0.20	540
3	13.59	88.5	< 0.50	4186	< 0.20	153
4	13.16	85.5	< 0.50	4119	< 0.20	151
5	14.20	103.5	< 0.50	4390	< 0.20	147
6	9.80	60.7	< 0.50	47064	< 0.20	652
7	9.28	58.7	< 0.50	30374	< 0.20	560
8	10.50	63	< 0.50	29032	< 0.20	591
9	9.31	58.4	3.50	20151	< 0.20	441
10	13.23	86.8	1.65	25299	< 0.20	592
11	9.05	51.9	< 0.50	53795	< 0.20	992
12	9.41	56.7	< 0.50	62231	< 0.20	1091
13	8.05	47.5	< 0.50	108000	< 0.20	1072
14	6.82	42.6	< 0.50	109000	< 0.20	1895
15	7.72	45.6	< 0.50	29918	< 0.20	808
16	8.34	43.7	< 0.50	52263	< 0.20	920
17	8.93	44.9	< 0.50	69601	< 0.20	1219
18	7.49	42.8	< 0.50	56870	< 0.20	1000
19	6.86	43.2	< 0.50	22260	< 0.20	432
20	5.83	41.7	< 0.50	29404	< 0.20	514
21	6.96	37	< 0.50	62598	< 0.20	1050
22	10.29	36.2	< 0.50	78976	< 0.20	1329
23	10.61	44.1	< 0.50	4189	< 0.20	130
24	10.56	42.7	< 0.50	2829	< 0.20	127
25	11.02	53.3	< 0.50	3754	< 0.20	149
26	12.61	52	< 0.50	4302	< 0.20	166
27	10.91	59.7	< 0.50	18606	< 0.20	385
28	11.29	76.5	< 0.50	24227	< 0.20	496
29	19.22	39.5	< 0.50	2490	< 0.20	195
30	19.37	40.3	< 0.50	2363	< 0.20	234
31	19.43	41.4	< 0.50	2638	< 0.20	221
32	16.16	33.3	< 0.50	2222	< 0.20	133
33	13.40	30.6	< 0.50	3045	< 0.20	168
34	15.49	34.7	< 0.50	4574	< 0.20	171
35	19.53	31.2	< 0.50	1631	< 0.20	103
36	23.65	34.9	< 0.50	1896	< 0.20	102
37	22.11	31.8	< 0.50	1364	< 0.20	96
38	20.32	26.1	< 0.50	888	< 0.20	70
39	23.27	36.1	< 0.50	1778	< 0.20	104
40	19.13	29.5	< 0.50	1290	< 0.20	81

The average distribution of lead amounts to 70 ppm and in samples studied lead concentration ranges from 4 to 34.5 ppm. This indicates that the soils in the areas under survey are not contaminated by the metal. This is an important precondition for the quality of soils and plant growth because Pb is one of the most toxic heavy metals.

Zn contents are within the concentrations allowed (ranging from 30 to 370 ppm) depending on pH (Veselinović et al, 1996). This indicates that the soils in the Republic of Macedonia have normal Zn values. It is an important fact since Zn is one of the most important biogene elements.

Cd was found in limits allowed (ranging from 0.5 to 2 ppm) and is one of the important preconditions to the quality of soils since Cd is one of the most toxic heavy metals.

The concentrations of Co and Ni were found in increased values compared with the average concentration in the soils (Co ranging from 10 to 15 ppm, and Ni from 20 to 30 ppm) due to the proximity to the FENIMAK-Kavadarci flotation plant where these metals are processed.

Arsenic was found in lower amounts than the average. Taking in consideration the fact that arsenic is one of the very toxic heavy metals it is a good fact that the sampling sites in this study are not affected by human activities.

Copper contents were detected within the values allowed (from 20 to 120 ppm depending on pH) ranging from 6.3 to 33.3 ppm (Table 2).

Legend of samples:
1–8, samples from Rosoman;
9–10, samples from Ribarci;
11–22, samples from Tikveš – Kraište;
23–28, samples from Gumaja – Lozovo;
29–40, samples from Pelagonia

CONCLUSION

Considering the results of the studies carried out on the contents of the major elements affecting the soil it can be inferred that the soils in the territory of the Republic of Macedonia are poorly magnesic and all other concentrations of microelements are lower than the average.

The contents of some microelements were studied in order to determine their values, because besides their biophilic character the concentrations of some microelements over the values allowed are extremely harmful for the normal growth and development of plants. Increased concentrations over the allowed were found for Ni and Co in all measurement sites studied. Ni was detected in the soils in the Tikves – Kraište, and Rosoman sites, whereas Co was detected in the Pelagonia site.

REFERENCES

[1] Веселиновиќ, Д., Гржетиќ, И., Ќармати, Ш., Марковиќ, Д., 1996: *Сшање и процеси у живошној средини*. Књига 1, Београд.

[2] David, D. J., 1978: *Analysis of soil, plants, fertilizers and other agrocultural materials*, Prog. Analyt. Atom. Spectroscopy, I, 225–254.

[3] Dahlquist, R. L., Knoll, J. W., 1978: *Induktive coupled plasma-atomic emission spectrometry: analysis of biological materials and soils for major, trace elements*. Applied Spectroscopy, **32**, 1–29.

[4] Lyons, J. J., Lynch, P. J., 1985: *Determination of exchangeable cations (Ca, Mg, Na, K) in aqueous and alcoholic NCl extracts of solid using ICP-AES*. Commun in soil Sci. Plant. Anal., **16** (1), 15–26.

[5] Horwitz, W., 1980: *Methods of analysis of the association of official analytical chemists*. Washington: Association of oficial analytical chemists, 13th edition.

[6] Novozamsky, I., Van Esk, R., Houba, V. J. G., Van der Lee, J. J., 1986: *Use of ICP-AES for determination of iron, aluminium and phosphorus in Tamm's soil extracts*. Neth. Jour. Agri. Sci., **34**, 185–191,

[7] Willet, I. R., Zarcinas, B. A., 1986: *Natric acid dissolution multi-element analysis of soil*. Sci. Plant. Anal., **17** (2), 183–193.

Резиме

ГЕОХЕМИСКИ ИСПИТУВАЊА НА ПОЧВИТЕ ВО РЕПУБЛИКА МАКЕДОНИЈА

Блажо Боев и **Соња Лепиткова**

Рударско-геолошки факултет, Штип, Република Македонија

Клучни зборови: почви; микроелементи; магнезиум

Во трудот се презентираат податоци од изучувања насочени кон детерминирање на одделни елементи во почвите во некои котлини во Република Македонија. Посебно внимание е обрнато на Mg кој е еден од многу важните биогени елементи во процесот на фотосинтезата кај растенијата.

Целта беше да се утврди присуството на овие елементи во почвата во количества кои се штетни или токсични за развојот на растенијата.