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MICROELEMENT DETERMINATION IN THE UNDERGROUND WATER OF THE ROMANIAN SHORE

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This study is a part of a comprehensive research programme on the Black Sea Romanian shore pollution.

The experimental results for the trace element contents in the underground water and some surface water courses, located in South Dobrogea are given. The Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP—AES) methods have been used. Twenty elements have been determined, whose concentrations are below the maximum permissible values for drinking water. Mn, Ag and Rb have not been evidenced. For two of the investigated surface water (Tatlageac and Albesti) the concentration of some microelements, exceeding the medium values in the underground water, impose a special attention in the future. The underground water from the Mesozoic rocks has a smaller contact with the pollutant agents, compared to the Sarmatian one.

INTRODUCTION

The water resources in the half East Dobrogea, including the Danube Delta and the Black Sea Romanian shore are non-uniformly distributed and with distinct drinkable characteristics, their areal extension depending on the geological profile of the region. The important aquifer accumulations in this region are exclusively located in carboniferous rocks and for this reason they are very vulnerable to the pollutant agents. There are several potential pollutant agents, the most significant being the Danube-Black Sea channel, the irrigation net Carasu and different human activities.

A comprehensive research programme has been developed, in view to determine a possible contamination of the littoral aquifer, its intensity and evolution in time. This paper is devoted to the microelement determination in the underground water and some surface courses located in South Dobrogea [1], as the first part of the mentioned programme, which is still in progress.

EXPERIMENTAL

Representative sampling points (wells, catchments, springs and surface courses) located in two kinds of carboniferous rocks — Mesozoic and Sarmatian, have been selected. Twelve sampling points are indicated in Fig. 1.

Amounts of 21 water have been systematically collected from each investigated site. Water samples have been evaporated, the resulted residuum of 300–500 mg weight being introduced into polyethylene bags. Samples and standards (SL 1 and SOIL 7) have been irradiated for 4 hours in a vertical channel of the reactor VVR–S in a flux of $1.4 \cdot 10^{13}$

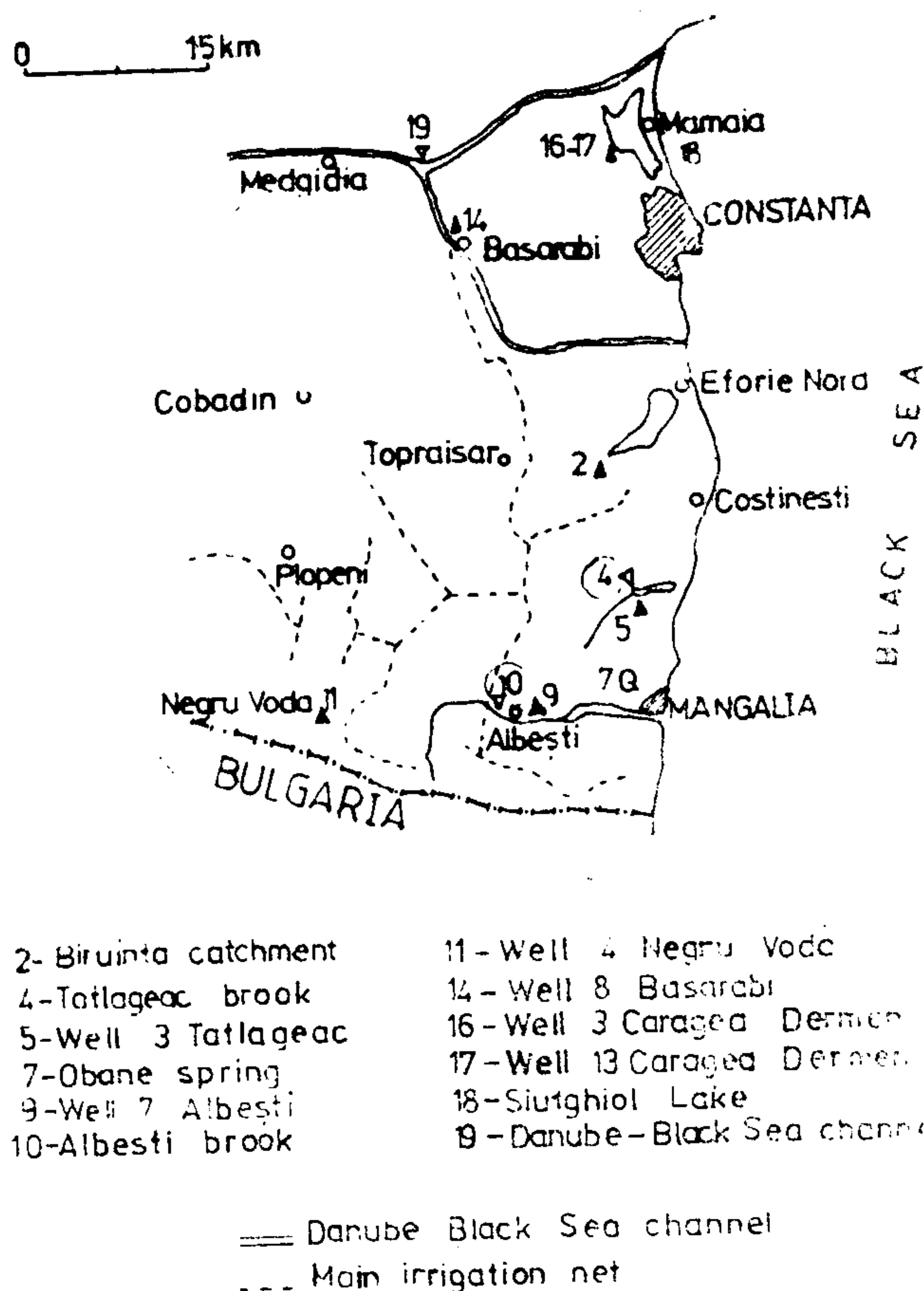


Fig. 1. - The map of South Dobrogea with location of sampling points — ▽ surface water; ▲ — underground water.

n/cm²s. Taking into account the radionuclide half life [2], the measurements have been performed after 4 d, 20 d and 60 d cooling time, for 1000–5000 s. The Instrumental Neutron Activation Analysis (INAA) has been used for the microelements determination in the water samples [3]. A Ge–Li detector of 80 cm³ volume, having a resolution of 1.9 keV and 18% efficiency at 1332 keV (Co -60), connected to a CANBERRA multichannel analyzer (4096) has been used.

Some microelements (V, Ni, Cu, Pb) have been determined by means of Inductive Coupled Plasma Emission Spectroscopy (ICP–AES).

RESULTS AND DISCUSSIONS

Experimental results are given in Tables 1, 2 and 3.

Table 1

The element concentrations in underground water, $\mu\text{g/l}$

Element	Mesozoic aquifer			
	P11	P14	P16	P17
Sc	0.04 ± 0.002	0.04 ± 0.002	0.04 ± 0.002	0.05 ± 0.002
V	18.7 ± 2.2	14.0 ± 1.7	15.8 ± 1.9	16.9 ± 2.0
Cr	3.50 ± 0.35	5.77 ± 0.57	5.65 ± 0.56	5.75 ± 0.57
Fe	130.0 ± 3.9	240.0 ± 7.2	180.0 ± 5.4	250.0 ± 7.5
Co	0.06 ± 0.003	0.10 ± 0.005	0.08 ± 0.004	0.10 ± 0.004
Ni	43.0 ± 4.3	49.1 ± 4.9	47.2 ± 4.7	47.5 ± 4.8
Cu	37.2 ± 3.7	40.0 ± 4.0	36.2 ± 3.6	36.3 ± 3.6
Zn	14.5 ± 2.2	12.3 ± 1.8	33.0 ± 5.0	31.5 ± 4.7
As	15.0 ± 0.9	16.1 ± 1.0	16.5 ± 1.0	16.4 ± 1.0
Se	1.79 ± 0.18	1.07 ± 0.11	1.60 ± 0.16	1.57 ± 0.15
Br	16.3 ± 0.8	13.6 ± 0.7	14.5 ± 0.7	27.4 ± 1.4
Sr	26.3 ± 2.9	59.4 ± 6.5	72.3 ± 7.8	79.0 ± 8.7
Zr	7.72 ± 1.08	8.80 ± 1.23	6.60 ± 0.92	6.72 ± 0.94
Sb	0.68 ± 0.10	0.24 ± 0.04	0.25 ± 0.04	0.42 ± 0.06
Cs	0.25 ± 0.02	0.30 ± 0.02	0.32 ± 0.02	0.18 ± 0.01
Ba	287.0 ± 28.7	168.0 ± 16.8	129.0 ± 12.9	98.4 ± 9.8
Hg	0.04 ± 0.006	0.08 ± 0.012	0.07 ± 0.01	0.07 ± 0.01
Pb	26.0 ± 3.9	33.1 ± 5.0	27.3 ± 4.1	25.4 ± 3.8
Ce	0.59 ± 0.04	2.27 ± 0.14	2.48 ± 0.15	2.78 ± 0.17
La	1.97 ± 0.13	2.05 ± 0.14	1.47 ± 0.10	1.95 ± 0.13

Table 2

The element concentrations in underground water, $\mu\text{g/l}$

Element	Sarmatian aquifer			
	P2	P5	P7	P9
Sc	0.16 ± 0.008	0.10 ± 0.005	0.16 ± 0.008	0.12 ± 0.006
V	22.0 ± 2.6	18.0 ± 2.2	17.1 ± 2.1	19.3 ± 2.3
Cr	49.0 ± 4.9	25.0 ± 2.5	11.3 ± 1.1	35.7 ± 3.6
Fe	350.0 ± 10.5	170.0 ± 5.1	590.0 ± 17.7	290.0 ± 8.7
Co	0.57 ± 0.03	0.10 ± 0.01	0.36 ± 0.02	0.11 ± 0.01
Ni	47.0 ± 4.7	47.1 ± 4.7	44.3 ± 4.4	61.8 ± 6.2
Cu	40.1 ± 4.0	33.2 ± 3.3	33.3 ± 3.3	42.3 ± 4.2
Zn	33.0 ± 5.0	9.5 ± 1.4	16.1 ± 2.4	42.2 ± 6.3
As	15.1 ± 0.9	15.3 ± 0.9	14.2 ± 0.9	13.5 ± 0.8
Se	1.84 ± 0.18	0.78 ± 0.08	0.75 ± 0.08	0.87 ± 0.09
Br	28.3 ± 1.4	33.0 ± 1.7	56.9 ± 2.8	20.9 ± 1.0
Sr	53.0 ± 5.8	49.2 ± 5.4	85.3 ± 9.4	35.2 ± 3.9
Zr	16.8 ± 2.4	24.6 ± 3.4	12.0 ± 1.7	27.8 ± 3.9
Sb	0.30 ± 0.04	0.30 ± 0.04	0.37 ± 0.05	0.47 ± 0.07
Cs	0.05 ± 0.003	0.06 ± 0.003	0.07 ± 0.004	0.03 ± 0.001
Ba	$103. \pm 10.3$	$120. \pm 12.0$	$412. \pm 41.2$	$100. \pm 10.$
Hg	0.10 ± 0.015	0.32 ± 0.048	0.42 ± 0.063	0.27 ± 0.04
Pb	28.0 ± 4.2	26.1 ± 3.9	17.3 ± 2.6	30.1 ± 4.5
Ce	1.94 ± 0.11	0.86 ± 0.05	1.65 ± 0.09	4.25 ± 0.25
La	3.28 ± 0.22	2.16 ± 0.15	1.10 ± 0.07	2.77 ± 0.19

Table 3

The element concentrations in surface water sources, $\mu\text{g/l}$ P18 — Lake Siutghiol, P19 — Danube—Black Sea Channel P4 — Tatlageac brook, P10 — Albesti brook

Element	P18	P19	P4	P10
Sc	0.16 ± 0.008	0.02 ± 0.01	0.07 ± 0.035	0.50 ± 0.025
V	15.1 ± 1.81	18.1 ± 2.17	18.3 ± 2.19	16.8 ± 2.02
Cr	4.77 ± 0.48	2.6 ± 0.26	87.2 ± 8.72	49.0 ± 4.90
Fe	$590. \pm 17.7$	$360. \pm 10.8$	$470. \pm 14.1$	$240. \pm 7.2$
Co	0.55 ± 0.027	0.09 ± 0.005	0.19 ± 0.009	0.01 ± 0.05
Ni	32.7 ± 3.27	50.3 ± 5.03	47.8 ± 4.78	49.2 ± 4.92
Cu	23.7 ± 2.37	40.0 ± 4.00	31.8 ± 3.18	33.8 ± 3.38
Zn	10.7 ± 1.61	11.6 ± 1.74	12.0 ± 1.80	20.3 ± 3.05
As	18.3 ± 1.10	16.7 ± 1.00	37.8 ± 2.27	22.3 ± 1.34
Se	0.15 ± 0.015	0.10 ± 0.01	1.23 ± 0.12	1.85 ± 0.19
Br	59.2 ± 2.96	3.39 ± 0.16	7.21 ± 0.36	8.47 ± 0.42
Sr	40.3 ± 4.43	63.7 ± 7.08	44.1 ± 4.85	33.2 ± 3.65
Zr	8.01 ± 1.12	6.87 ± 0.96	12.2 ± 1.71	27.1 ± 3.79
Sb	0.91 ± 0.13	0.13 ± 0.02	0.20 ± 0.03	0.24 ± 0.03
Cs	0.09 ± 0.005	0.03 ± 0.002	0.09 ± 0.005	0.18 ± 0.011
Ba	49.8 ± 4.98	16.7 ± 1.67	66.0 ± 6.60	81.0 ± 8.1
Hg	0.03 ± 0.005	0.03 ± 0.005	0.10 ± 0.015	0.22 ± 0.033
Pb	18.5 ± 2.77	22.3 ± 3.34	27.2 ± 4.08	30.7 ± 4.61
Ce	1.36 ± 0.08	0.50 ± 0.03	0.47 ± 0.03	4.98 ± 0.29
La	0.16 ± 0.01	0.32 ± 0.02	1.82 ± 0.13	2.07 ± 0.14

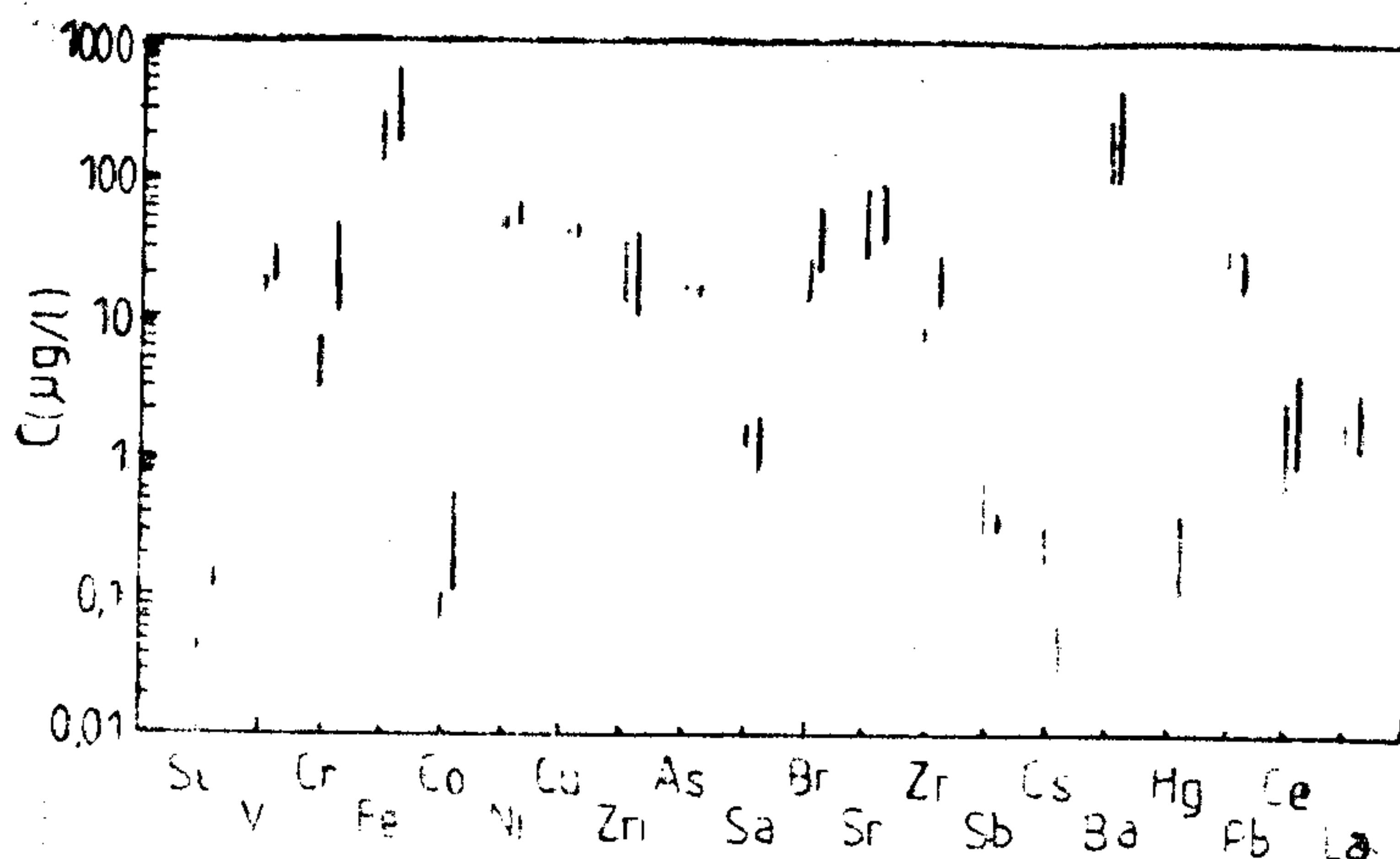


Fig. 2. — The dispersion of the element concentration values for the two groups of sampling points: Mesozoic and Sarmatian (shifted a little to the right side).

Twenty microelements (Sc, V, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Sb, Ba, Hg, Pb, Ce, La) have been determined. Their concentrations do not exceed the maximum admitted values for drinking water, excepting Cr in Tatlageac brook (P4). All water sources show an increased content of Fe, the explanation being related with the nature of

the traversed rocks. The elements Mn, Ag and Rb have not been detected in the investigated water samples.

For two of the surface courses P4 and P10 the concentration of some microelements exceeds the medium values, imposing systematic measurements in time.

The concentration of Sb in the lake Siutghiol exceeds the mean value too.

Comparing the results obtained for the underground water sources P 9 and P 5 with the surface water sources P 10 and P 4, located respectively in their vicinity, one may observe that the content of Cr, Co, As, Se and Cs is bigger in the surface water, because of the pollutant agents. The dispersion of the element concentration, values for the two groups of sampling points, Mesozoic and Sarmatian, is given in Fig. 2. From the spread of the concentration values of a given element one may conclude that the Mesozoic water group has a smaller contact with the pollutant agents, compared to the Sarmatian one.

CONCLUSIONS

The microelement determination in some water resources from South Dobrogea evidenced the presence of 20 elements, whose concentration do not exceed the admitted values for the drinking water (excepting Cr in P 4).

For two of surface courses, Tatlageac brook (P 4) and Albesti brook (P 10) the concentration of some elements exceed the medium values of underground waters, imposing systematic measurements in the future.

The Mesozoic water group has a smaller contact with the pollutant agents compared to the Sarmatian one.

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