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The seasonal geochemical variations in the active stream sediment of the tributaries of Lubatówka and Jasiołka by Rogi, near Krosno (Carpathians)

A small, but statistically significant, decrease in the geochemical background of Pb, Cu and Co in the active stream sediment of some Carpathian creeks was observed between April and October 1985. In the same time, a local peak of Mn was washed some hundred metres down along a stream channel. The geochemical background of Fe, Ni, Mo and probably also V, P and Hg remained stable in this period.

INTRODUCTION

Geochemical mapping, commonly used in geological exploration, now is applied more and more frequently to environmental monitoring. Geochemical samples are taken from outcropping rocks, surface and groundwaters, and soils, but the active stream sediment is probably the most commonly sampled object in geochemical mapping. The geochemical maps, the images of the distribution of elements in geological measures, are always blurred and biased by some errors, related to the imperfection of the geochemical technique. There are two principal kinds of errors: the precision error and the accuracy error. The precision error results in random dispersion of measurements around a true (and in general unknown) measured value. An average (or median) approaches the measured value as the number of the measurements grows. This is not the case of the accuracy error, where the approximation can not be improved by multiplying the measurements, but the mean approaches a value different from true measured value. Total error of a geochemical map is a combination of a set of errors committed at the location of sampling points, sampling itself, preparation of samples for the chemical analysis and errors of the chemical determinations. All these errors could be controlled and reduced by the correction of the applied methods. However, the

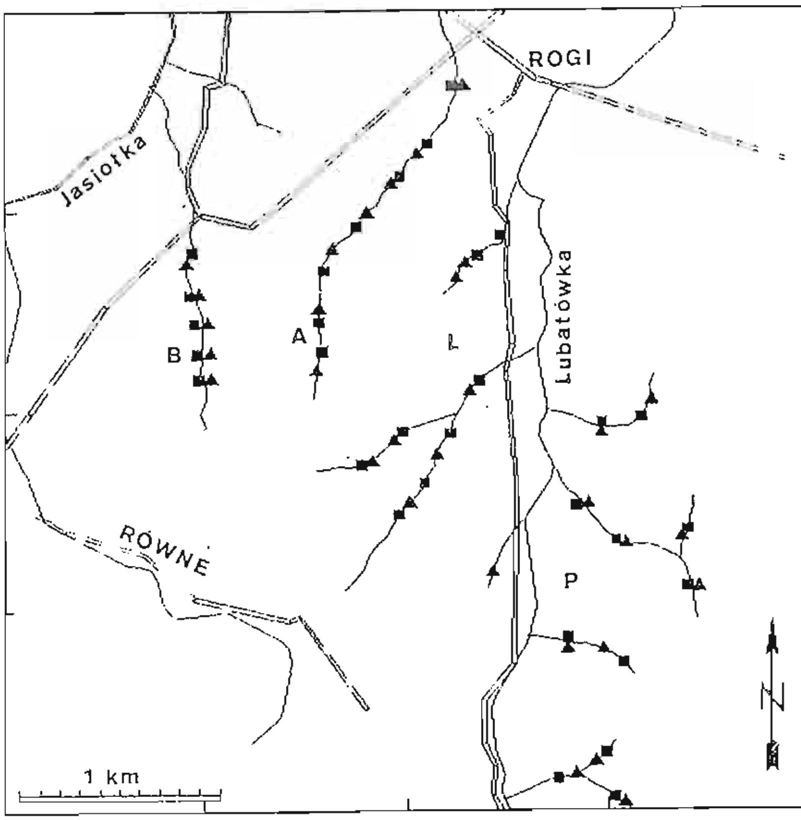

Fig. 1. The distribution of the sampling points in the zone of Rogi

A, B — eastern tributaries of the Jasiolka river, L — western tributaries of the Lubatówka river, P — eastern tributaries of the Lubatówka river; squares — sampling in April/May 1985; triangles — sampling in October 1985

Rozmieszczenie punktów opróbowania w rejonie Rogów

A, B — wschodnie dopływy Jasiółki, L — zachodnie dopływy Lubatówki, P — wschodnie dopływy Lubatówki; kwadraty — opróbowanie z kwietnia/maja 1985; trójkąty — opróbowanie z października 1985

total blurring and/or the total bias of a geochemical map also depends on the variability and heterogeneity of the sampled geochemical medium. The purpose of the present paper is an appreciation of the influence of possible natural variability and heterogeneity of the active stream sediment used in geochemically mapping in the Carpathians.

In 1984 to 1987, the joint teams of the Polish Geological Institute, the Enterprise of Geophysical Researches and the analytical laboratory of the Institute of Nuclear Chemistry and Technology have produced a set of geochemical maps covering about 5000 km^2 of selected zones in the Carpathians. In 1985 we had an opportunity to make a double sampling of a minor fragment in the mapped zone. The meteorological conditions seemed favourable

Table 1

Double analysis of the baches no. 4101/4200 and 7001/7100

Sample	Cu	Zn	Ni	Co	Pb	Fe	Mn	Mo	V	P	As
4101	20	160	33	15	25	2.47	363	0.8	31	717	1.8
4101	22	122	32	14	26	2.08	194	1.6	23	668	1.9
4110	8	42	21	11	9	1.66	613	0.5	20	222	2.6
4110	9	28	24	10	15	1.39	667	1.3	17	204	3.1
4116	17	85	36	21	24	3.94	2065	1.3	31	1300	6.4
4116	19	91	41	19	36	3.35	2281	1.5	25	1198	5.1
4120	4	32	13	7	5	0.96	200	0.3	10	193	1.3
4120	5	30	17	7	10	0.86	278	0.2	9	192	1.4
4134	33	103	58	27	30	4.20	1143	1.1	10	422	5.0
4134	34	106	58	25	32	4.10	1140	0.9	9	446	6.1
4137	20	48	17	10	12	0.98	389	1.2	38	272	3.0
4137	18	35	18	9	12	1.20	376	1.4	42	260	2.2
4139	18	34	20	11	13	1.15	464	1.0	12	201	3.8
4139	15	56	21	11	20	1.21	458	0.8	13	311	2.4
4142	11	50	26	14	20	1.10	804	0.7	14	414	2.5
4142	12	43	25	13	16	1.64	750	0.5	15	382	3.1
4148	10	47	24	12	15	1.05	446	0.8	15	209	2.7
4148	12	37	25	12	13	1.34	472	0.6	16	213	3.1
4158	7	21	13	7	10	0.79	100	0.6	7	140	1.1
4158	7	19	15	5	7	0.72	165	0.8	6	141	1.2
4163	22	61	40	24	17	2.90	2816	3.0	16	493	5.9
4163	29	59	40	21	22	2.84	3061	3.3	19	476	5.2
4185	27	178	46	18	36	2.97	727	0.6	27	735	4.3
4185	32	178	47	22	29	3.07	713	0.8	31	753	4.1
7018	22	183	52	18	20	3.56	6055	1.2	37	939	2.6
7018	22	194	50	19	18	3.46	6034	1.6	28	874	3.1
7027	5	38	17	6	7	1.08	309	0.8	6	194	0.8
7027	5	35	17	6	7	1.15	291	0.6	6	165	1.2
7032	45	114	96	20	21	3.68	757	0.9	47	662	3.2
7032	44	110	99	20	22	3.84	802	1.2	45	638	4.3
7050	7	37	18	6	7	0.93	617	0.8	8	155	0.5
7050	6	34	18	6	8	1.03	669	0.8	7	157	0.5
7068	5	43	38	6	9	0.90	230	0.4	6	162	0.7
7068	5	39	40	5	8	0.92	220	0.4	8	148	0.8
7081	8	48	22	7	8	1.07	647	1.1	7	220	1.5
7081	8	44	22	7	8	1.22	649	1.5	7	200	1.2

Fe in per cent, other elements in $\mu g/g$

to study the influence of the seasonal changes of the active stream sediment geochemistry on the accuracy of geochemical mapping in Carpathians.

DESCRIPTION OF THE ACTIVE STREAM SEDIMENT

The active stream sediment is a particular kind of alluvial sediment, found in local hollows or other places in the streams channels, where the water current slows down. In the

Table 2

Analytical control — sampling: April/May 1985

Sample	Cu	Zn	Ni	Co	Pb	Fe	Mn	Mo	V	P	As	Hg
4154	10	33	23	12	12	1.94	611	1.0	16	335	4.0	89
4154	10	51	26	11	13	1.94	660	1.3	20	nd	8.0	nd
4155	12	30	25	14	14	1.94	792	0.9	23	248	3.0	76
4155	11	31	29	13	12	1.96	833	1.4	24	nd	8.6	nd
4156	14	43	28	15	17	1.81	805	0.8	18	264	3.9	87
4156	13	60	32	16	17	1.87	836	1.5	24	nd	8.5	nd
4157	11	30	24	13	13	1.56	403	0.6	19	240	2.7	74
4157	10	62	28	12	14	1.55	458	0.9	22	nd	4.2	nd
4158	7	21	13	7	10	0.79	100	0.6	7	140	1.1	28
4158	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4159	27	47	39	19	19	2.48	638	3.3	15	375	4.4	144
4159	24	62	38	19	17	2.25	625	4.2	16	nd	9.8	nd
4160	12	25	26	12	14	1.36	638	2.7	16	203	3.1	51
4160	11	36	24	12	13	1.27	640	2.6	16	nd	6.2	nd
4161	19	47	26	23	25	2.10	714	4.0	34	297	4.8	81
4161	18	55	28	23	22	2.00	725	4.8	35	nd	6.6	nd
4162	25	47	38	20	21	2.66	2321	3.2	23	516	5.6	89
4162	18	62	40	17	17	2.56	2300	5.2	26	nd	9.6	nd
4163	22	61	40	24	17	2.90	2816	3.0	16	493	5.9	132
4163	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4164	16	25	21	12	15	1.54	319	1.7	16	266	2.5	45
4164	12	58	24	12	12	1.45	340	1.8	19	nd	5.0	nd
4165	15	53	29	13	17	1.95	663	1.2	17	368	2.8	71
4165	14	62	34	14	12	1.83	645	1.6	26	nd	6.5	nd
4166	19	47	26	14	16	1.95	765	2.2	17	319	3.2	58
4166	15	53	30	14	13	1.75	760	1.8	26	nd	6.4	nd
4167	18	53	30	13	18	2.18	561	1.3	26	289	2.9	134
4167	17	60	34	14	16	2.02	650	1.5	27	nd	7.0	nd
4168	12	50	28	12	9	1.82	242	0.8	15	297	2.6	43
4168	11	60	32	12	8	1.66	240	1.3	29	nd	5.4	nd
4169	12	34	25	11	13	1.54	612	0.8	17	297	2.3	67
4169	11	48	29	12	12	1.48	600	1.6	22	nd	5.8	nd
4171	11	44	21	9	14	1.54	510	0.4	9	211	2.3	58
4171	9	54	23	10	10	1.45	560	0.9	20	nd	4.0	nd
4172	8	31	15	7	8	0.90	319	0.5	10	180	1.4	34
4172	7	30	18	8	8	0.90	340	0.7	15	nd	4.0	nd
4173	6	22	14	7	10	1.00	472	0.4	17	172	1.8	28
4173	6	37	17	7	9	0.99	495	0.7	16	nd	4.6	nd
4174	15	38	29	13	16	1.69	778	2.1	15	211	3.7	75
4174	16	47	35	13	11	1.64	790	3.0	14	nd	6.6	nd
4175	20	28	19	9	13	1.41	434	0.8	15	219	2.4	47
4175	9	37	22	9	11	1.30	430	2.0	19	nd	6.3	nd
4176	21	44	37	15	18	2.04	612	4.4	17	258	3.7	96
4176	19	54	42	15	16	1.92	610	6.0	18	nd	5.7	nd
4177	13	38	28	11	14	1.31	497	1.2	18	252	2.2	78
4177	13	68	30	11	12	1.27	520	3.0	18	nd	4.2	nd
4178	13	28	28	11	12	1.23	383	2.3	21	240	2.0	60
4178	12	54	30	11	13	1.32	410	3.0	22	nd	5.7	nd
4179	26	66	50	17	23	2.37	1071	1.7	30	327	2.5	159
4179	23	90	52	17	19	2.05	1045	3.7	32	nd	7.6	nd
4180	18	50	37	14	20	2.02	357	1.1	24	331	3.0	101
4180	17	76	40	14	14	1.86	350	1.7	25	nd	5.0	nd
4181	17	56	30	12	16	1.86	434	0.5	22	284	2.5	95
4181	12	61	32	12	15	1.68	420	1.0	24	nd	4.5	nd
4182	16	50	31	14	16	1.97	408	0.5	18	327	2.8	95
4182	13	59	33	13	15	1.77	400	0.6	22	nd	3.1	nd
4183	9	38	19	10	13	1.39	344	0.3	14	197	1.9	79
4183	8	50	21	10	13	1.26	350	0.5	17	nd	2.6	nd
4184	25	72	40	16	23	2.65	638	0.5	29	351	3.2	36
4184	18	79	42	16	19	2.37	625	0.7	23	nd	4.3	nd

nd: no data, Fe in per cent, Hg in ng/g, other elements in µg/g zone of moderate climate, it is developed as a combination of the fine-grained sands, muds and clays. The mineral composition of the sediment corresponds mostly to that of the local bedrock (A. Steenfeld, H. Kunzendorf, 1979). Among the detrital components the most common is quartz, followed by feldspars and micas (A. Tessier *et al.*, 1982). The mixed-layer clay minerals, as well as clay minerals of the kaolinite and illite group, are frequent and important components of the sediment. Heavy minerals, amphiboles, garnets, sphene and zircon are present in lesser quantities (M. A. Olade, W. D. Goodfellow, 1979). An important part of the oxides and hydroxides of manganese and iron, mostly goethite and hematite, belong to the group of detrital components (G. N. Nowlan, 1982; R. E. Learned *et al.*, 1981, 1985). But the bulk of the cryptocrystalline oxides and hydroxides of manganese and iron is precipitated as the result of the changing pH/Eh conditions (R. F. Horsnail *et al.*, 1968). It was found (V. Austria, C. Y. Chork, 1976; G. N. Nowlan, 1976; C. D. Kaback, D. D. Runnels, 1980) that the precipitated oxides and hydroxides are important scavengers of heavy metals. Some minor quantities of carbonates (mostly calcium carbonate) could be precipitated in similar pH/Eh conditions as oxides/hydroxides.

Organic matter is present in the active stream sediment in various quantities, from a few percentage to practically negligible content (S. J. Hoffman, W. K. Fletcher, 1979). Stream sediment with more than 1% of organic matter is rather rare. Among the components of the active stream sediment, organic matter is always one of the most important scavengers of heavy metals. Organic matter of the stream sediment consists of disintegrated and partly decomposed plant detritus. Humic and fulvic acids are common (K. S. Jackson, G. B. Skippen, 1978). The precipitation of the oxides/hydroxides of Mn/Fe is reduced or excluded in the zones of the non-aerated sedimentation of organic matter as the effect of reducing conditions of such sedimentation (H. Sandström, 1984). Such conditions are favourable, however, to the precipitation of the iron sulphides connected with the coprecipitation of the other heavy metal sulphides (S. J. Hoffman, W. K. Fletcher, 1979).

The detrital quartz and feldspars, present mostly as coarser grains in active stream sediment, represent the inactive components. Quantity of the inactive grain can be reduced by screening and rejecting of the coarser fraction of the sediment. Then, the fine fraction is destined for the chemical analysis. The most frequently used screens are those of 0.2, 0.1 or 0.06 mm mesh diameter. Screening is considered as a good method of normalization of the analytical samples (Y. T. Maurice, 1979; E. Wilhelm *et al.*, 1979). The fine fraction is enriched in active components: clay minerals, organic matter, oxides/hydroxides of Mn/Fe, sulphides and freshly precipitated carbonates. All these components, when still present in the loose sediment in the stream, take part in the mutual chemical reactions between the stream water and sediment. The chemical elements present in water are fixed in the sediment as the result of the different chemical reactions such as adsorption, chelate formation, precipitation and coprecipitation. In that manner, the geochemical composition of the active stream sediment became a function of the hydrogeochemistry of the stream water and indirectly of the geochemical composition of the local bedrock (G. F. Bonham-Carter, W. D. Goodfellow, 1986). Local environmental pollutants also appears as anomalies of the stream sediment geochemistry. Desorption, extraction, digestion or re-dissolution can release the chemical elements back from the sediment to stream water. In that way the equlibrium between the sediment and water is probably controlled by seasonal changes of

Table 3

Analytical control — sampling : October 1985

Sample	Cu	Zn	Ni	Co	Pb	Fe	Mn	Mo	V	P	As	Hg
7018	22	183	52	18	20	3.56	6055	1.2	37	939	2.6	182
7018	21	171	46	19	19	3.28	5285	1.6	35	836	9.3	nd
7019	10	53	28	10	9	1.52	652	1.2	18	284	1.1	91
7019	11	49	27	11	9	1.53	598	1.1	18	264	4.5	nd
7020	14	68	41	15	13	2.32	1573	2.4	17	329	1.9	70
7020	16	62	41	17	13	6.94	1486	2.3	25	315	7.4	nd
7021	29	93	57	33	21	3.44	1136	3.9	34	630	3.1	193
7021	31	84	56	36	21	3.33	1027	4.1	34	592	11.0	nd
7022	31	87	52	25	23	3.08	734	4.6	20	500	2.6	163
7022	29	72	46	24	22	2.62	618	5.2	30	408	9.4	nd
7023	10	41	24	12	13	1.40	1107	2.2	20	225	1.4	65
7023	10	45	23	14	13	1.32	1027	2.1	21	201	5.9	nd
7024	7	43	21	11	10	1.96	1864	2.9	13	284	1.5	47
7024	8	35	20	12	11	1.97	1634	1.2	18	280	6.5	nd
7025	9	47	26	9	10	2.00	1124	0.4	17	743	1.7	62
7025	10	46	26	11	11	2.15	1044	0.7	17	275	7.1	nd
7026	15	76	41	13	16	2.32	611	1.2	28	392	2.0	102
7026	15	76	41	13	16	2.27	611	1.2	28	392	7.6	nd
7027	5	38	17	6	7	1.08	309	0.8	6	194	0.8	53
7027	30	72	46	24	22	2.65	618	5.2	30	408	3.9	nd
7028	7	41	21	8	9	1.16	425	0.4	14	180	0.6	36
7028	9	43	23	9	9	1.11	388	0.5	13	162	2.9	nd
7029	7	45	22	8	8	1.18	361	0.3	15	180	0.6	44
7029	7	39	21	8	9	1.16	314	0.3	14	164	2.6	nd
7037	9	48	27	9	9	1.40	396	0.2	13	365	0.8	63
7030	9	44	27	10	10	1.41	357	0.3	18	300	3.0	nd
7038	17	85	41	13	16	2.36	641	0.4	26	405	1.5	89
7038	17	70	40	15	16	2.34	611	0.5	27	327	6.0	nd
7039	10	57	26	9	9	1.58	727	0.7	14	309	0.6	70
7039	10	47	27	10	10	1.48	661	0.4	7	274	4.0	nd
7041	9	43	24	8	8	1.25	382	1.0	14	252	0.6	85
7041	9	39	25	9	9	1.21	370	1.0	15	215	3.9	nd
7042	12	65	31	10	14	1.66	586	0.9	21	296	1.0	83
7042	13	55	33	11	15	1.71	549	1.1	21	274	5.3	nd
7043	13	48	33	10	9	1.49	567	2.9	21	270	1.0	85
7043	13	46	35	11	11	1.46	558	2.8	17	254	6.4	nd
7044	8	38	23	8	8	1.12	610	2.2	17	243	0.8	50
7044	9	34	25	9	11	1.05	580	1.8	12	223	4.4	nd
7045	20	79	50	14	14	1.99	2034	3.5	19	245	1.4	153
7045	20	60	49	16	14	1.90	1763	3.0	30	314	7.0	nd
7046	14	59	35	11	14	1.70	647	2.9	17	292	1.1	75
7046	15	56	38	12	15	1.64	600	2.1	24	282	5.8	nd
7047	10	42	28	10	8	1.25	690	2.5	18	256	0.9	56
7047	10	37	29	11	8	1.26	643	1.6	18	251	4.7	nd
7048	10	50	33	10	9	1.43	771	2.5	21	318	1.0	69
7048	14	48	33	12	10	1.44	692	1.5	20	278	4.8	nd
7049	8	64	21	8	7	1.10	542	1.2	15	212	0.7	46
7049	8	44	22	9	8	1.17	500	0.8	14	199	3.5	nd
7050	7	37	18	6	7	0.93	617	0.8	8	155	0.5	33
7050	6	33	17	7	8	1.06	582	0.3	13	165	4.2	nd
7051	7	42	19	7	7	1.16	690	0.7	13	168	0.6	41
7051	7	40	20	8	8	1.16	643	0.4	14	158	2.8	nd
7052	7	35	19	8	7	1.10	665	0.8	14	225	0.7	40
7052	7	34	21	8	8	1.11	629	0.5	12	205	3.8	nd
7053	9	51	24	10	9	1.41	1097	1.1	14	265	0.8	67
7053	10	45	26	11	11	1.34	960	0.6	16	249	3.9	nd
7054	10	65	26	10	11	1.59	1338	1.2	14	270	0.8	58
7054	10	54	28	12	12	1.53	1340	1.0	18	239	4.8	nd
7055	13	65	33	11	13	1.62	727	1.9	21	301	1.0	69
7055	13	68	35	12	13	1.55	665	1.8	22	270	5.9	nd

nd: no data. Fe in per cent. Hg in ng/g, other elements in µg/g

Table 4

Double sampling: April/May (no. 4154–4184) and September 1985 (no. 7025–7055)

Sample	Cu	Zn	Ni	Co	Pb	Fe	Mn	Mo	V	P	As	Hg
4154	10	42	24	11	12	1.94	636	1.1	18	335	6.0	89
7025	9	47	26	10	11	2.08	1084	0.5	17	509	4.4	62
4155	11	31	27	13	13	1.95	813	1.1	23	248	5.8	76
7026	15	76	41	13	16	2.30	611	1.2	28	392	4.8	102
4156	13	52	30	15	17	1.84	821	1.2	21	264	6.2	87
7027	18	55	32	15	15	1.86	464	3.0	18	301	2.3	53
4157	11	46	26	12	14	1.56	431	0.7	21	240	3.5	74
7028	8	42	22	8	9	1.14	407	0.4	13	171	1.8	36
4158	7	21	13	7	10	0.79	100	0.6	7	140	1.1	28
7029	7	42	21	8	9	1.17	338	0.3	14	172	1.6	44
4159	25	54	38	19	18	2.36	632	3.8	15	375	7.1	144
7022	30	79	49	24	22	2.85	676	4.9	25	454	6.0	163
4160	12	31	25	12	14	1.32	639	2.6	16	203	4.7	51
7023	10	43	23	13	13	1.36	1067	2.2	20	213	3.7	65
4161	18	51	27	23	23	2.05	720	4.4	35	297	5.7	81
7024	8	39	20	11	11	1.96	1749	2.1	15	282	4.0	47
4162	22	54	39	19	19	2.61	2311	4.2	25	516	7.6	89
7021	30	89	57	35	21	3.39	1082	4.0	34	611	7.1	193
4163	22	61	40	24	17	2.90	2816	3.0	16	493	5.9	132
7020	15	65	41	16	13	4.63	1530	2.4	21	322	4.6	70
4164	14	42	23	12	13	1.49	330	1.8	17	266	3.8	45
7019	11	51	27	10	9	1.53	625	1.2	18	274	2.8	91
4165	15	58	32	14	14	1.89	654	1.4	21	368	4.7	71
7018	22	177	49	18	19	3.42	5670	1.4	36	888	5.9	182
4166	17	50	28	14	14	1.85	763	2.0	22	319	4.8	58
7054	10	59	27	11	12	1.56	1339	1.1	16	255	2.8	58
4167	18	57	32	14	17	2.10	606	1.4	27	289	5.0	134
7055	13	67	34	12	13	1.59	696	1.8	21	286	3.5	69
4168	11	55	30	12	9	1.74	241	1.1	22	297	4.0	43
7049	8	54	22	8	8	1.14	521	1.0	14	206	2.1	46
4169	11	41	27	12	13	1.51	606	1.2	20	297	4.1	67
7050	6	35	17	7	8	0.99	600	0.6	10	160	2.4	33
4171	10	49	22	9	12	1.49	535	0.7	15	211	3.2	58
7051	7	41	19	8	8	1.16	667	0.5	13	163	1.7	41
4172	8	31	16	7	8	0.90	330	0.6	12	180	2.7	34
7053	10	48	25	10	10	1.38	1029	0.9	15	257	2.4	67
4173	6	29	16	7	9	0.99	484	0.6	17	172	3.2	28
7052	7	34	20	8	8	1.11	647	0.6	13	215	2.2	40
4174	16	42	32	13	14	1.66	784	2.5	14	211	5.2	75
7047	10	39	28	10	8	1.26	667	2.0	18	254	2.8	56
4175	15	33	21	9	12	1.36	432	1.4	17	219	4.3	47
7048	12	49	33	11	10	1.44	732	2.0	20	298	2.9	69
4176	20	49	39	15	17	1.98	611	5.2	17	258	4.7	96
7043	13	47	34	11	10	1.48	563	2.9	19	262	3.7	85
4177	13	53	29	11	13	1.29	509	2.1	18	252	3.2	78
7044	9	36	24	8	9	1.09	595	2.0	14	233	2.6	50
4178	12	41	29	11	13	1.28	397	2.7	22	240	3.9	60
7046	15	57	37	11	14	1.67	624	2.5	20	287	3.5	75
4179	24	78	51	17	21	2.21	1058	2.7	31	327	5.1	159
7045	20	70	50	15	14	1.94	1899	3.3	25	280	4.2	153
4180	18	63	39	14	17	1.94	354	1.4	25	331	4.0	101
7041	9	41	24	9	8	1.23	376	1.0	14	234	2.3	85
4181	14	59	31	12	16	1.77	427	0.8	23	284	3.5	95
7042	13	60	32	11	14	1.69	568	1.0	21	285	3.1	83
4182	14	55	32	14	15	1.87	404	0.5	20	327	3.0	95
7037	9	46	27	10	10	1.41	377	0.3	15	333	1.9	63
4183	8	44	20	10	13	1.33	347	0.4	15	197	2.2	79
7039	10	52	26	9	9	1.53	694	0.6	10	292	2.3	70
4184	21	75	41	16	21	2.51	632	0.6	26	351	3.7	36
7038	17	77	40	14	16	2.35	626	0.4	27	366	3.7	89

Fe in per cent, Hg in ng/g, other elements in µg/g the local hydrogeochemistry of streams (C. Y. Chork, 1977; A. K. Ishak, A. C. Dunlop, 1985).

FIELD WORKS

The geochemical sampling of Carpathian streams in Beskid Niski, Bieszczady and Pieniny was done during the four seasons of field work between 1984 and 1987 (I. Bojakowska *et al.*, 1989). In 1985, the sampling was doubled at thirty points near the town of Rogi, some 11 km south of Krosno, the local administrative center of the region of Beskid Niski (Fig. 1). The purpose of the double sampling was control the precision and accuracy of the geochemical mapping, but above all, the observation of seasonal variations in the stream sediment geochemistry. The studied zone is placed in the drainage area of two small rivers, Jasiołka and Lubatówka. The bedrock of the zone is mostly composed of the Krosno sandstones, a narrow band of menilite schists, extending from WWN to EES, is traversing the central part of the zone. The geochemical map of the zone (I. Bojakowska *et al.*, 1989) shows the mean geochemical background with a local peak of manganese, but without any geochemical anomaly.

The first sampling was done during the two cloudy days of April 27 and May 2, 1985. The heavy winter of 1984/1985 in the Carpathians resulted in important surface retention and stream water deficit in the period preceding the first sampling. The mean temperatures of air in January and February 1985, measured at the meteorological observatory at Zakopane, were –9.2 and –9.3°C, compared with the means –5.0 and –3.8°C calculated for the same months during the 30-year period 1951–1980. The amount of precipitation, 24 and 48 mm in January and March respectively, were significantly smaller than means in the 30-year period 1951–1980 for the same months (47 and 52 mm respectively). In contradiction to January and March, the precipitation in February 1985 (53 mm) was higher than the mean (45 mm) for this month in the 30-year period 1951–1980.

The second sampling was done on the sunny day of October 17, 1985. The summer of 1985 was rather rainy; the precipitation amounted to 863 mm in the period from May to September, that is higher than mean sum of 714 mm of precipitation in the mentioned 30-year period (meteorological data according *The Statistical Yearbook*, 1986). The important difference of the water flow in spring and autumn 1985, compared with the important retention during the preceding winter, was expected to bring a change in the sedimentation conditions at the contact of the stream water and stream sediment, as well as in the sediment itself. The change should affect also the concentration of the chemical elements in the active stream sediment.

The positions of the sampling points were chosen in advance and plotted on the topographic map at 1:25,000 scale. The emplacement of sampling points in the field and the collection of samples was done by two independent teams. Fifteen of thirty doubled sampling points were placed almost identically in the creeks by both teams. The distances between the first and the second emplacement were smaller than 50 m. Ten distances between the first and the second emplacement were greater than 50 m but still less than 100 m, four distances were greater than 100 m and only one was greater than 300 m. Such results should be evaluated as quite good at the 1:25,000 scale. It was supposed then, that the relatively unimportant displacement of the sampling points has probably a minor influence on the final difference in geochemical composition of the doubled sampling.

EXPERIMENTAL STUDIES

METHODS

The air-dried samples were disaggregated in a porcelain mortar, without grinding, then sieved through a 0.1 mm nylon screen. The fine fraction was destined for chemical analysis. One gram analytical weights were digested at a temperature of 90°C, in a mixture of concentrated bydrochloric, nitric and perchloric acids. In that way, the chemical elements previously fixed in clay minerals, organic matter, oxides/hydroxides of Mn/Fe, sulphides and carbonates pass into the analytical solution. The analytical solutions were diluted finally to 50 ml in volumetric flasks. The determinations of Cu, Zn, Ni, Co, Pb, Fe, and Mn were made by Atomic Absorption Spectrophotometry (AAS) and atomization in an acetylene-air flame. Vanadium and molybdenum were atomized by electrothermic heating in a graphite furnace. Arsenic was analysed by the method of hydride generation. Phosphorus was determined by a spectropbotometric method, using the molybdenum phosphate complex.

The determinations of mercury were made by Atomic Absorption Spectrophotometry and the "cold vapor" technique. Fifty milligram portions of the samples were weighed into quartz test tubes, that were placed in an aluminum block and heated to 500–600°C to release mercury vapor and other gases. The gases and the mercury vapor were pumped to the absorption cell of the *Scintrex HGG-3* mercurometer to measure the specific atomic absorption. The determinations were repeated and the arithmetic means of two determinations were calculated.

A detailed description of the analytical procedures, with other data on the geochemical mapping of the Carpathians can be found in a report of the Polish Geological Institute (PGI) in Warsaw (I. Bojakowska *et al.*, 1989). The determinatons of Cu, Zn, Ni, Co, Pb, Fe, Mn, Mo, V, P and As were done in the analytical laboratory of the Department of Analytical Chemistry — Institute of Nuclear Chemistry and Technology (INCT). The determinations of mercury were made in the laboratory of the Enterprise of Geophysical Researches (EGR).

About 10% of the samples analysed in the laboratory of INCT were chosen at random for analytical control. The control samples were analysed in pairs, together with all the other samples of the controlled batch, that were analysed individually. The samples from the area of Rogi belong to two batches (no. 4101/4200 and 7001/7100), where eighteen samples were chosen and analysed twice for analytical control (Tab. 1). Five of these control samples were analysed again in the geochemical control. The samples collected in April/May (no. 4101/4200) and in September 1985 (no. 7001/7100) were analysed for the first time in winter 1985, and reanalysed almost five years later, in summer 1990. In both cases, the same powdered samples and the same analytical methods were used (Tab. 2 and 3). Unfortunately, the quantities of powders were not abundant enougb for the complete repetition of the analysis, so we were forced to drop the second set of phosphorus determinations. Two samples (no. 4158 and 4163) were lost, and they were analysed only one time.

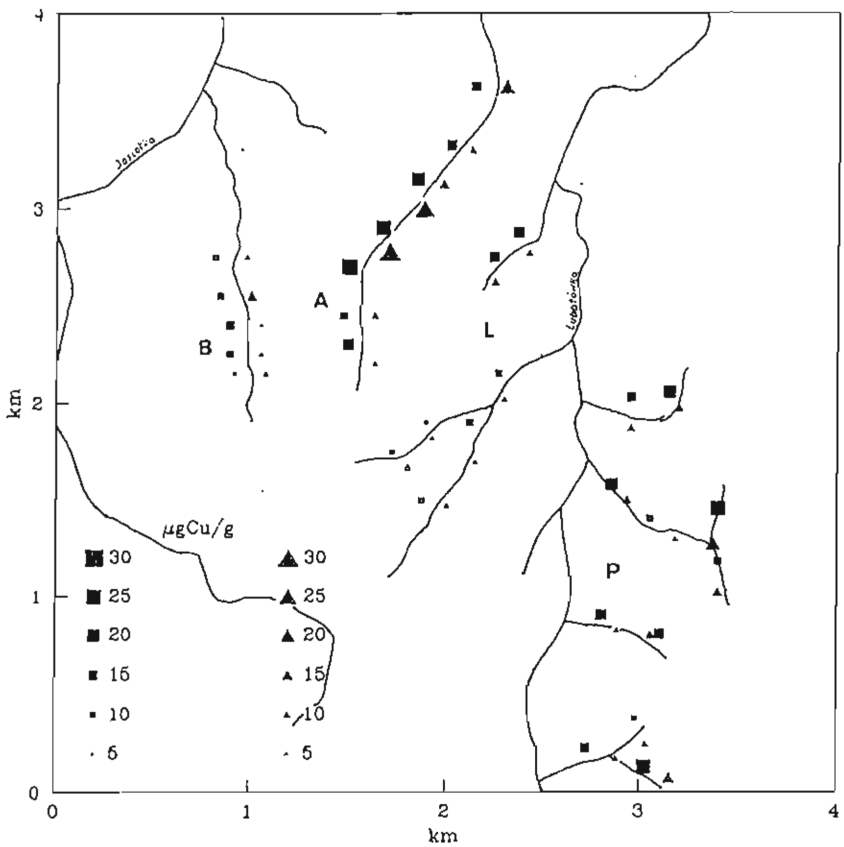

Fig. 2. The distribution of copper in the active stream sediment in the zone of Rogi
Explanations as in Fig. 1
Rozmieszczenie miedzi w czynnym osadzie strumieniowym z potoków w rejonie Rogów
Objaśnienia jak na fig. 1

The means of the first and the second determination for each sample of both batches (with the exclusion of missing determinations) were taken as the base for the geochemical comparison (Tab. 4).

DISCUSSION OF RESULTS

THE DIFFERENCES BETWEEN MEDIANS

Since the statistical distributions of the elements in the examined populations are not known, and probably not normal, the use of a nonparametric test is reasonable. In consequence, the estimation of the significance of differences between a pair of medians was

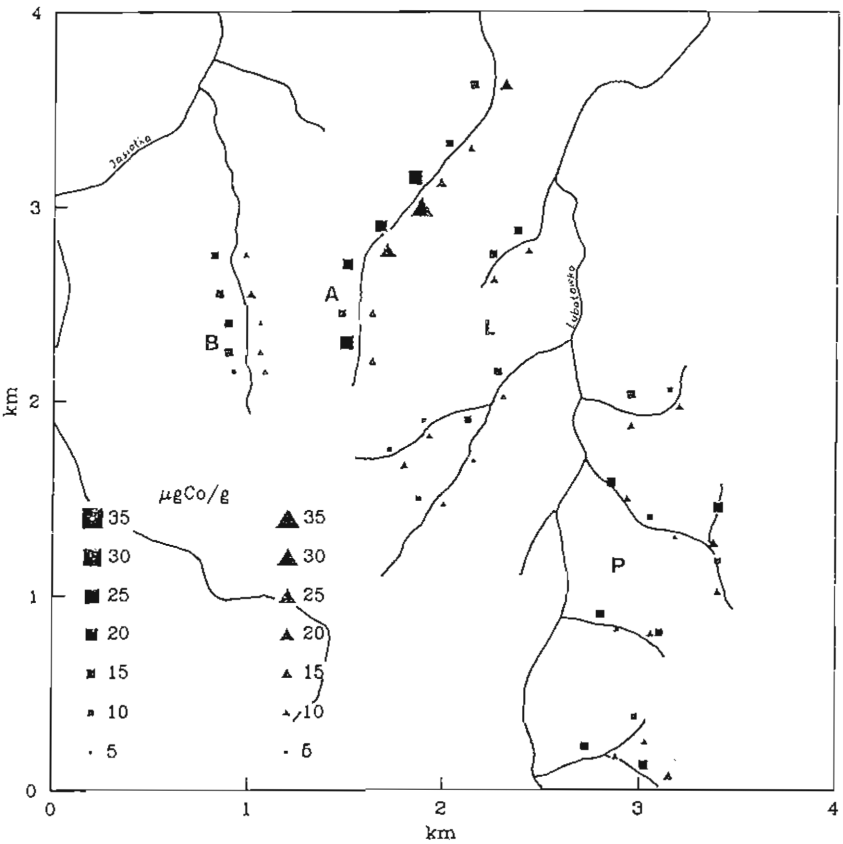

Fig. 3. The distribution of cobalt in the active stream sediment in the zone of Rogi
Explanations as in Fig. 1
Rozmieszczenie kobaltu w czynnym osadzie strumieniowym z potoków w rejonie Rogów
Objaśnienia jak na fig. 1

done by the nonparametric F. Wilcoxon rank test (1945). The hypothesis of the equality of the medians was verified at the probability level $P = 0.05$. The values of two-tailed probability equaling or exceeding Z are presented in the Table 5. The small values of probability ($P < 0.05$) indicate that the hypothesis of the equality of medians should be rejected. The probabilities $P > 0.05$ show the cases where there is no reason to reject the hypothesis of equality of medians.

The analysed elements are classified in view of the rejection or confirmation of the equality of medians as the effects of changing analytical accuracy and/or the seasonal variations of the stream sediment geochemical composition. In the case of Ni, Fe and Mo, all the probabilities of equaling or exceeding Z are higher than 0.05, that is a proof of a lasting analytical accuracy and of the seasonal geochemical stability of these elements in the stream sediment. Phosphorus and Hg possibly fit the same pattern, but the control data are defective. Vanadium could be included into the same group of elements on a lower level

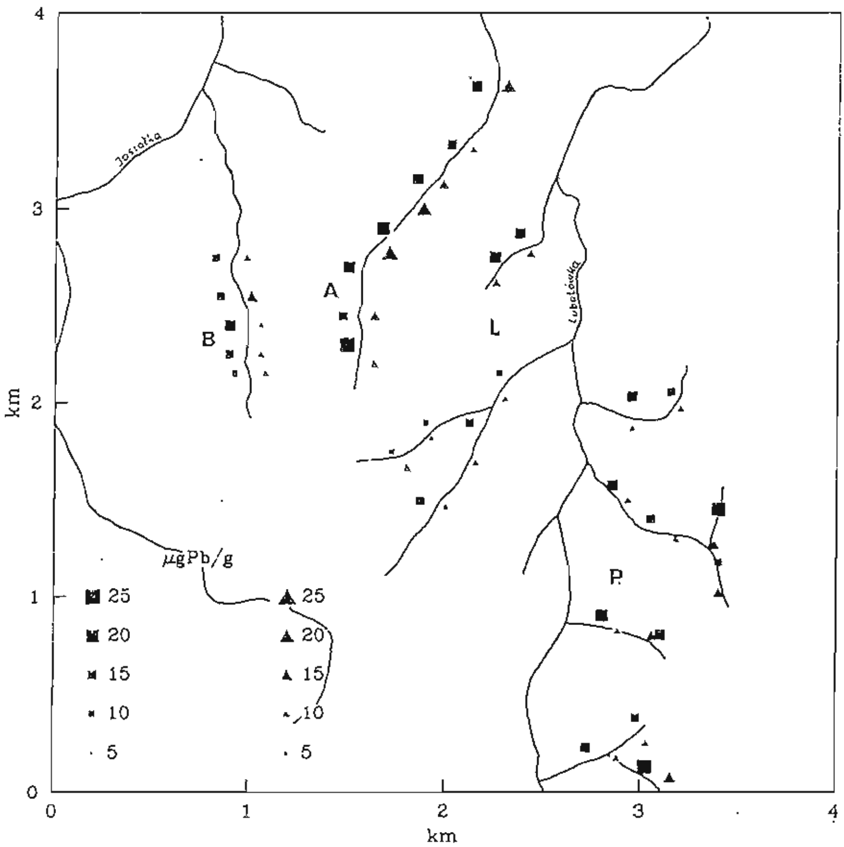

Fig. 4. The distribution of lead in the active stream sediment in the zone of Rogi
Explanations as in Fig. 1
Rozmieszczenie ołowiu w czynnym osadzie strumieniowym z potoków w rejonie Rogów
Objaśnienia jak na fig. 1

of probability (one of two analytical control probabilities exceeds Z at the level $P = 0.05$, the other fits this criterion at the level $P = 0.03$). Summing up, the accuracy of the determination of Ni, Fe, Mo, V, P, and Hg is stable and the seasonal variations are absent.

In the group contaning Mn, Co, Cu and Pb the high probabilities of equaling or exceeding Z in the analytical control prove the stability of the analytical accuracy. The low values of the probability in the repeated sampling confirm the presence of the seasonal, geochemical variations.

Important differences between all the medians of As, particularly in the analytical control, should be related to the significant changes in the analytical accuracy. Zinc follows, in principle, a pattern similar to As. However, one of two control probabilities of exceeding Z ($P = 0.3710$) confirms the concordance of the medians. Probably the accuracy of Zn determinations in the batch no. 7001/7100 (September 1985) is good, whereas the accuracy of the determination in the batch no. 4101/4200 (April/May 1985) is defective.

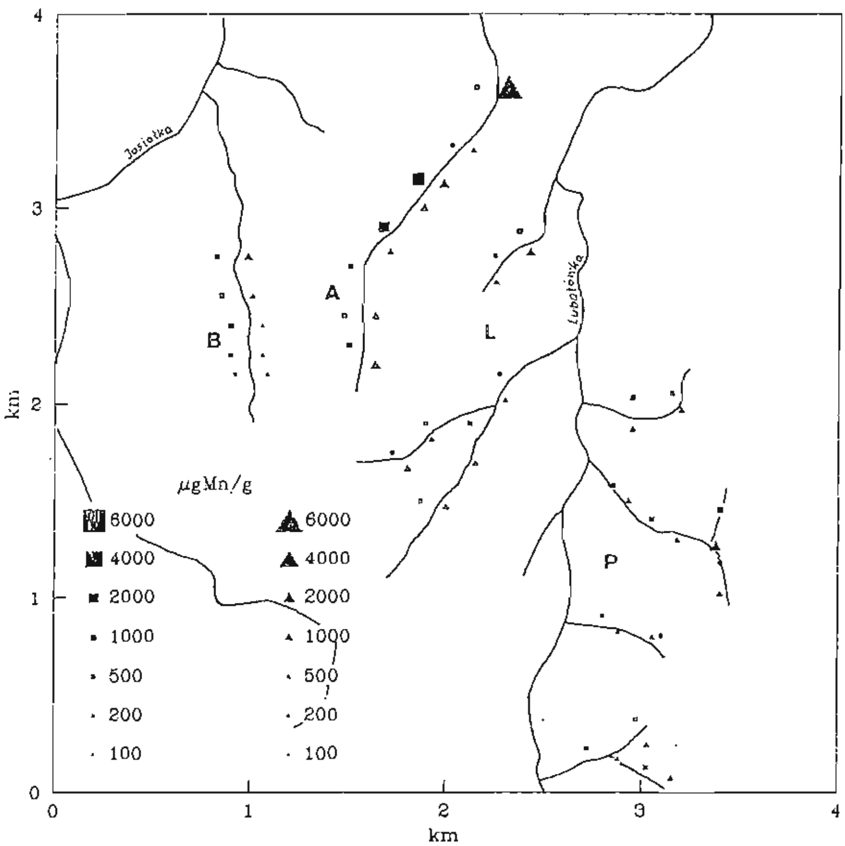

Fig. 5. The distribution of manganese in the active stream sediment in the zone of Rogi
Explanations as in Fig. 1
Rozmieszczenie manganu w czynnym osadzie strumieniowym z potoków w rejonie Rogów
Objaśnienia jak na fig. 1

TEST OF RANDOM DISTRIBUTION

The statistically proven, seasonal variations of Mn, Co, Cu and Pb in the active stream sediment could have a random or a systematic arrangement. The test of randomness was based on the emplacement of the differences between the corresponding contents in April/May and September 1985. The data were arranged in order, according to their position in the stream channels (Fig. 1), starting from the east tributary of Jasiołka (B), to stream A, then to the west tributaries of Lubatówka (L), ending with its east tributaries (P). Inside every stream, the data were arranged in order from the source to the stream outlet. The medians of differences were calculated for every four examined elements. Each sequence of the differences higher or lower than the median was defined as a run. The quantities of 17, 20, 16 and 16 runs were found for Cu, Co, Pb and Mn respectively. They fall into the two-tailed confidence interval of the runs distribution (10, 21), for $\alpha = 0.05$ and the sizes

Table 5

Probabilities of equaling or exceeding Z

Elements	Between the double determinations analysis 1985	DIFFERENCES: Between the analysis 1985 and control analysis 1890 sampling 1985 April/May	September	Between the double sampling April/May–September
Ni	0.7517	0.1331	0.5492	0.7731
Fe	0.6808	0.4118	0.8130	0.2088
Mo	0.3665	0.0500	0.6203	0.5691
Mn	0.9804	0.8418	0.4161	0.0286*
Co	0.8370	0.8473	0.0581	0.0103*
Cu	0.8494	0.1904	0.3867	0.0072*
Pb	0.8124	0.0744	0.1167	0.0001*
V	0.8370	0.0285*	0.1492	0.4244
Zn	0.6016	0.0005*	0.3710	0.0017*
As	0.9118	0.0000*	0.0000*	0.0000*
P	0.8868		0.4773	0.7787
Hg				0.6099
	Number of pairs			
	18	28	30	30

*) The hypothesis on the equality of medians should be rejected

$n_1 = n_2 = 15$ (J. Greń, 1984). In consequence, there is no reason to reject the hypothesis of random distribution of the Mn, Co, Cu and Pb variations in the stream sediment between April/May and September 1985.

THE GEOCHEMICAL MAPS

The graphical symbols, proportional to the concentrations of the elements in the stream sediment, show the two-dimensional distribution of Cu, Co, Pb and Mn on a set of geochemical maps (Figs. 2–5). The squares indicate the distribution in April/May 1985, while the triangles show the distribution in September 1985. Superposition of symbols was prevented by a slight shift of the symbols in relation to the true emplacement of the sampling points (Fig. 1). In streams A, B and L the rectangles were shifted to the west, the triangles

Table 6

Comparison of medians

Elements and units	Sampling 1985	Medians	Confidence limits=0.95	Differences between medians April/May – – September
As µg/g	April/May September	2.83 0.96	2.5–3.2 0.8–1.4	1.87 µg/g *) 66.1 % **)
Pb µg/g	April/May September	15.3 9.2	13–17 9–13	6.1 µg/g *) 39.9 % **)
Cu µg/g	April/May September	15.3 10.	12–18 9–13	5.3 µg/g *) 34.6 % **)
Co µg/g	April/May September	12.8 10.	12–14 9–11	2.8 µg/g *) 21.9 % **)
Fe %	April/May September	1.84 1.51	1.5–2.0 1.3–1.7	0.33 % *) 17.9 % **)
Hg ng/g	April/May September	76. 68.	58–89 56–83	8. ng/g *) 10.5 % **)
Ni µg/g	April/May September	27.9 26.5	25–30 24–33	1.4 µg/g *) 5.0 % **)
V µg/g	April/May September	17.2 16.7	16–19 14–20	0.5 µg/g *) 2.9 % **)
P µg/g	April/May September	275. 277.	240–319 245–309	–2. µg/g *) –0.7 % **)
Mn µg/g	April/May September	586. 677.	434–638 611–711	–91. µg/g *) –15.5 % **)
Zn µg/g	April/May September	43.6 50.4	33–47 43–65	–6.8 µg/g *) –15.6 % **)
Mo µg/g	April/May September	1.00 1.22	0.8–1.7 0.8–2.2	–0.22 µg/g *) –22. % **)

*) Absolute difference, **) Relative difference

to the east, whereas in streams P the shift was done in the north and south directions respectively. The two-dimensional distribution, presented on the geochemical maps, confirm in general the random pattern of the seasonal variations. However, a local maximum of manganese concentration is apparently washed down stream A at a distance of about 750 m.

THE CHANGES OF THE GEOCHEMICAL BACKGROUND

The medians for each kind of control and its confidence limits at the significance level $\alpha = 0.05$ (K. R. Nair, 1940; P. J. Ellis, 1980) are listed in Table 6. The data for the sampling of April/May 1985 are placed in the first row of every element record, whereas those of September 1985, in the second row. The absolute differences between the medians ($ME_{(Apr./May)} - ME_{(Sept.)}$) as well as the relative differences in percent (in relation to $ME_{(Apr./May)}$) are placed in the last column. The elements are arranged in descending order of relative differences.

An extreme relative difference (over 66%) between medians was found in As determinations, where we have stated important fluctuation of the analytical accuracy. In effect, the determination of As was considered erroneous. Zinc, the other element, where we have found much less important fluctuations of accuracy, is placed in the next to last place in Table 6, with much smaller (absolute) relative difference between medians (–15.6%). An incomprehensible contradiction is noticed in the case of Mo, that occupies the last place in the Table 6. The difference between medians is not significant (Tab. 5), in spite of its importance (–22%). The remaining elements, excluding As, Zn and Mo, are divided into two distinct groups.

Pb, Cu and Co, the elements joined in the first group, show a significant drop in the geochemical background (relative 22–40%) with a random distribution of seasonal variations in the creek channels. They can be qualified as the variable components of the active stream sediment. The group is non-homogeneous from the geochemical point of view. Pb and Cu are considered as chalcophile, but Co is relatively siderophile with a tendency for chalcophile behaviour. Cu is one of elements scavenged by organic matter (e.g., H. Sandström, 1984). Pb, Cu and Co in certain conditions can be associated with the Fe/Mn hydroxide (E. Wilhelm *et al.*, 1979), that is not, however, the case of the studied sediment. We suppose, rather, that the elements of the first group could be associated with the organic matter of the sediment, and that they can be fixed or released in changing pH/Eh conditions (K. S. Jackson, G. B. Skippen, 1978).

The geochemical background of the elements belonging to the second group (Fe, Hg, Ni, V, P, and Mn) is quasi constant or only slightly variable. We have included here Mn in spite of a small growth of its geochemical background. The elements of the group could be qualified as stable components of the active stream sediment. The second group seems more homogeneous than of the first one. All the elements except Hg are considered as oxyphile (lithophile or siderophile). On the contrary, Hg is classified as chalcophile. It has been shown, however, that in some lake sediments, Hg is adsorbed mostly on the Fe hydroxides (J. P. Vernet, R. L. Thomas, 1972). Similar binding of Hg could exist in the studied sediment too. We suppose that the second group encloses the hydroxides of Fe and Mn as well as the elements fixed by them. The elements of the group are probably strongly bound in the stream sediment and they are not released during the pH/Eh variations.

CONCLUSIONS

Chemical analysis of the active stream sediment samples, collected in April/May 1985 and then in September 1985, in some Carpathian creeks near Rogi-by-Krosno, have proved the presence of the significant variations of the sediment composition.

The observed random variations of Pb, Cu, and Co content are connected with the distinct decrease of the geochemical background from 15.3 μgPb/g, 15.3 μgCu/g and 12.8 μgCo/g to 9.2 μgPb/g, 10.0 μgCu/g and 10.0 μgCo/g respectively.

An important shift of a local Mn maximum at the distance of about 750 m is connected with its enhancement from 0.28 to 0.57% Mn. In the same time the geochemical background of Mn has grown slightly from almost 0.06 to almost 0.07% Mn.

The contents of Ni, Fe, Mo, V, P and Hg were stabilized at the levels: 26.5–27.9 μgNi/g, 1.51–1.84% Fe, 1.00–1.22 μgMo/g, 16.7–17.2 μgV/g, 275–277 μgP/g and 68–76 μgHg/g between April/May and September 1985 respectively.

The significant, seasonal variations of the geochemical background found in the active stream sediment of a few Carpathian creeks by Rogi could be present in other regions. The seasonal variations should be controlled by a periodic re-sampling of the streams. Otherwise the seasonal variations could cause important distortion of the regional geochemical maps.

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STABILNOŚĆ I ZMIENNOŚĆ SEZONOWA GEOCHEMII CZYNNEGO OSADU DOPŁYWÓW LUBATÓWKI I JASIOŁKI W REJONIE ROGÓW K. KROSNA (KARPATY)

Streszczenie

Zbadano stabilność i zmienność geochemiczną czynnego osadu strumieniowego niektórych dopływów Jasiołki i Lubatówki w rejonie Rogów (ok. 11 km na południe od Krosna — Karpaty). Próbki pobrano dwukrotnie: po raz pierwszy — wiosną 1985 r., po ostrej zimie 1984/1985, połączonej z intensywną retencją zimową, po raz drugi — jesienią 1985 r., po lecie obfitującym w opady. Duża różnica między przepływami wiosennymi i jesiennymi potoków karpackich mogła wywołać istotne zmiany warunków fizykochemicznych na granicy osadu

czynnego i wody, a także w obrębie osadu. Zmiana taka powinna zaznaczyć się zmianami zawartości pierwiastków chemicznych w czynnym osadzie strumieniowym.

W pobranych próbkach oznaczono metodami atomowej spektrometrii absorpcyjnej zawartości Cu, Zn, Ni, Co, Pb, Fe, Mn, Mo, V, As i Hg oraz metodą spektrofotometryczną — fosforu. Przeprowadzono kontrolę błędów analitycznych na podstawie oznaczeń podwójnych i odtworzenia oznaczeń po upływie pięciu lat. Stwierdzono duży błąd dokładności w oznaczeniach arsenu oraz mniejszy błąd dokładności w oznaczeniach cynku. Błędy te uniemożliwiają wykrycie i ocenę zmian sezonowych. W oznaczeniach wanadu popełniono tylko niewielki błąd dokładności, co nie przeszkodziło jednak w stwierdzeniu niezmiennej zawartości tego pierwiastka w osadzie. Nie dysponowano pełnymi danymi kontrolnymi w zakresie oznaczeń fosforu i rtęci. Stałość zawartości tych pierwiastków w badanym osadzie, określona nawet na podstawie niekompletnych danych, jest jednak niewątpliwa.

Między kwietniem i październikiem 1985 r. niezmienne okazały się zawartości niklu, żelaza, molibdenu, wanadu, fosforu i rtęci. Zanotowano niewielkie, lecz znaczące statystycznie, zmiany tła geochemicznego miedzi, kobaltu i ołowiu. Mediana zawartości kobaltu w czynnym osadzie strumieniowym spadła z 12,8 μgCo/g w kwietniu do 10,0 μgCo/g w październiku 1985 r. Jeszcze bardziej obniżyło się wyrażone medianą tło geochemiczne ołowiu, które w kwietniu 1985 r. wynosiło 15,3 μPb/g, zaś w październiku tegoż roku spadło do 9,2 μgPb/g. Tło geochemiczne miedzi obniżyło się w tym samym okresie z 15,3 do 10 μgCu/g. Lokalne maksimum zawartości manganu (0,28%) przemieściło się w dół potoku na odległość ok. 750 m i wzrosło do 0,57%.