

**HYDRODYNAMICS OF THE BICAZ LAKE. CONSIDERATIONS BASED ON
SELECTED MAJOR AND TRACE ELEMENTS**

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Abstract

The drainage area of the dammed Bicaz lake comprises the mining district of the Bistrița river and may act an important role in the transport of trace elements issued from polymetallic ore deposits. From July 2005 to June 2006, four surveys allow to describe and understand physical and (bio) chemical processes regulating the lake composition. In this paper, we present results on major compounds and alkali and alkaline earth trace elements in order to assess the hydrodynamics of the lake. Results evidence currents issue from the river inflow and current induced by the sluice drawing off. The lake composition originate mainly from a mixing between a lake end-member and the spring recharge. Na and Cl evidence an anthropogenic input which probably originate from the road salting. Trace elements allow to distinguish different sources (Bistrița/Bistricioara) and to estimate a transit time of waters.

Key words: Bicaz lake, alkali and alkaline earth elements, trace elements, mixing, transit time of waters

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Introduction

Among superficial aquatic systems, lakes are particularly interesting systems to identify and quantify processes occurring because of their high replacement time of water. Lakes can be considered as large scale reactors. Element cycle within lake depends on the conditions of the water column stratification and of the trophic level of the lake. The trophic level influences not only nutrients but elements whose behaviour depends on the redox state of the solution. Numerous studies dealt with trace elements behavior in natural lakes and evidenced a scavenging of trace elements from the water column to sediments (e.g. Nriagu and Wong, 1989; Bendell Young and Harvey, 1992; Balistrieri et al., 1992; Hamilton-Taylor et al., 1996; Viollier et al., 1995).

The dammed lake of Bicaz is located in a mountainous area, in East Carpathians, in Romania (fig. 1).

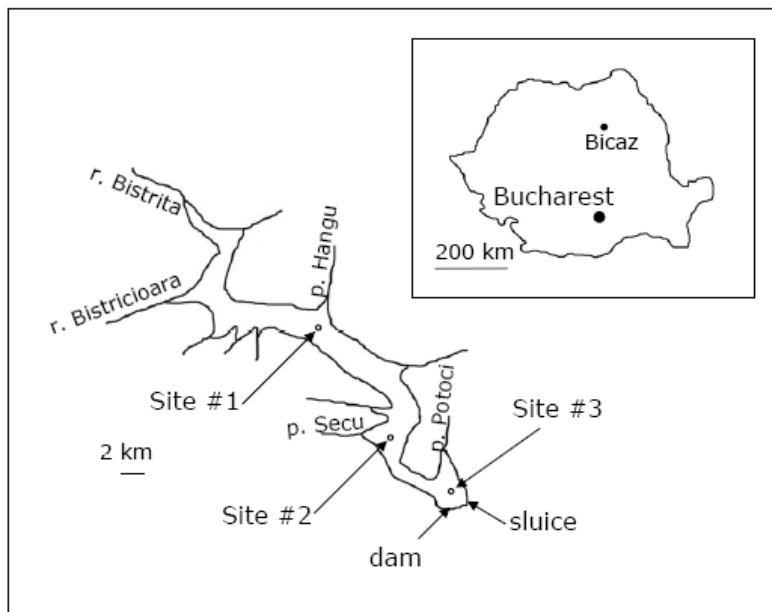


Fig. 1 Location of the lake of Bicaz and of the sampling sites

The Bistrița river is the main tributary of the lake. Its watershed is a mining district rich in manganese and polymetallic sulfide ore deposits. In this rural area, mining activities have ceased for several years. No ore treatment was undergone onsite,

unproductive rocks are still exposed to weathering on dumps. The natural high content in trace metals of the substratum together with the enhanced water circulation caused by mine levels and dumps may be involved in the rise of trace elements, such as Cu, Co, Pb and Zn in rivers. As all the waters from the Bistrița watershed are collected by the lake, the objective of this study is to determine the impact of the lake on the transfer of trace elements. This lake does not end the hydrologic system. The water of the Bicaz lake participate to the supply of three lakes downward, located between the city of Bicaz and Piatra Neamț. In addition, as a fish farm is settled up in the Potoci inlet, it is important to determine the bioavailability and quantity of trace elements in the water column.

For these reasons, a geochemical study on the Bistrița river and on the lake of Bicaz has been started. During one hydrological year a physico-chemical study of waters was started from July 2005 to June 2006, along four surveys distributed according to seasons. Prior to assess the behaviour of trace elements, as a first step, we need to determine the lake hydrodynamics. Because the Bicaz lake is very long (31 km) and its use for hydroelectricity production, important horizontal and vertical heterogeneities have to be considered. In this paper, we present results recorded on major components and some alkali and alkaline earth trace elements to assess hydrodynamics of the lake.

Environmental surroundings and physical characteristics of the lake

Large data sets on the lake can be found in Miron et al. (1983) and in Apetroaei (2003).

The Bicaz lake is located in the centre part of East Carpathians, and is boarded at the eastside by the Stanisoara block (1000 m maximum elevation) and at the westside by the Ceahlau block (1900 m maximum elevation). The hydrographical basin of Bicaz lake (3855 km² surface area) is situated between 2280 m to 425 m elevation (minimum elevation of the bottom of the lake). This middle mountain area exhibits a continental climate. An average annual temperature of 7 to 7.5°C is recorded in the screened area of the lake, with a mean minimal temperature about -4.2°C (January - February) and a mean maximal temperature about 16.6°C (July – August), while at the Ceahlau summit the recorded mean minimal temperature is about -8.5°C and the recorded mean maximal temperature is about 8.8°C (Erhan, 1988). The lake catches between 717 mm/year at the upstream Ceahlau station to 678 mm/year at the downstream station (Potoci). Apopei (1985) estimates that about 75% of precipitation received by the basin is lost by evapotranspiration.

Tab. 1 Physical characteristics of the lake of Bicaz measured at the maximum elevation (513 m)

Surface area	3105 ha	Water volume	1.150 km ³
Length	31.1 km	Maximum depth	88 m
Width	2 km	Bank length	94 km

The Bicaz lake has a long and narrow shape (fig. 1), with 31.1 km length and 2 km width (tab. 1). The main tributaries of the lake are the Bistrița river (2985 km² surface catchment area) with a mean water load of about 1.25 km³/year, and the Bistricioara river (770 km² surface area) with about 0.21 km³/year (fig. 2). Other tributaries can be neglected with a mean annual water load of about 0.016 km³/year (about 100 km² surface area).

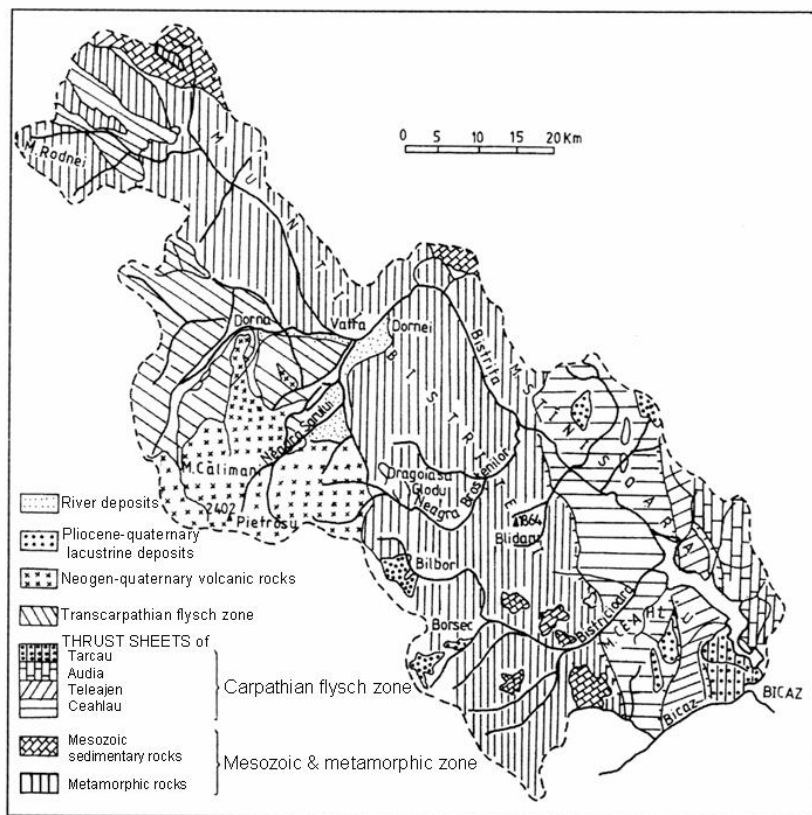


Fig. 2 Geological map of the hydrographical basin of the Bicaz lake (modified from the geological map at 1:200 000, I.G.G. Bucharest)

The water outflow occurs through an admission tunnel (sluice) located at about 45 m below the maximum level of the lake, between Potoci and the dam (fig. 1).

The hydrographic basin of Bicaz lake is characterized by a complex lithology. The Bistrița river (fig. 2) crosses three major geologic units: the Mesozoic crystalline zone

(schists, micaschists, gneisses, amphibolites), the Carpathian flysch zone of Cretaceous to Eocene - Oligocene age (conglomerates, sandstones, clays, marls and limestones), the Neogene – Quaternary pyroclastic rock zone (pyroclastites, dacites, andesites, microgabbros, diorites and microdiorites) (fig. 2). The lake itself lays within the flysch zone.

Hydrological context

The water level of the lake varies considerable along time as a function of water inflow from the rivers and as a function of the hydroelectric activity (Apopei, 1983). The daily variations are in the range of 0 to 10 cm in March (period of the relative stability of the minimum level) to 140 cm in April – June (period of level rise). Monthly variations lay from an inferior amplitude of 1 m during the relative stability of the minimum level until 20 m in two months, in April – May. From 1961 to 1980, the maximum annual amplitude reached 34 m in 1980 while the minimal annual amplitude felt to 10 m in 1977. The maximum absolute amplitude have reached 40 m during this period.

From 1973 to 2006, the mean water inflow from the Bistrița and Bistricioara rivers were of 1.46 km³/year (INHGA, 2008) (tab. 2); from 1991 to 2006, the mean water outflow from the sluice were of 1.66 km³/year. The years 2005 and 2006 were particularly humid years with mean inflow of 1.76 and respectively 2.04 km³/year, and a mean outflow of 2.09 and respectively 2.17 km³/year. For 2005 and 2006, on the average, the Bistrița inflow represents 83% of the river inflow. In July and August 2005, the Bistricioara inflow was greater representing 33% and 25% of the river inflow.

Tab. 2 Mean annual water load and maximum water replacement time (hydrologic data, INHGA)

	Mean annual water inflow (km ³ /an)	Mean annual water outflow (km ³ /an)	Maximum water replacement time (day)
1973-2006	1.46	1.66*	287
2005	1.76	2.09	237
2006	2.04	2.17	206

* 1991-2006

Calculation of replacement time of water can be useful to understand water mass movement. According to the general equation, $\tau_w = V_{\text{lake}}/V_{\text{inflow}}$, the so-calculated replacement time of water corresponds to a maximum value because of water exploitation is not considered. From 1991 to 2006, the mean maximum replacement time of water was of 287 days, and of 237 and 206 days respectively for 2005 and 2006 (tab. 2).

The Bicaz lake displays dimictic (Apopei, 1983) and mesotrophic characteristics (Mazareanu et al., 1983). The date of sampling surveys have been chosen according to

lake seasons: at the beginning of summer stratification (June-July), at the end of maximum summer stratification (October) and at the spring overturn (April) (Apopei, 1983). Because of its considerable length, three sampling sites have been chosen, from upstream to downstream: (i) a upper site (#1), in front of Hangu, at about 10 km down to the Bistrița river confluence with the lake, (ii) a middle site (#2), in front of Secu, and (iii) a down site (#3) at a cross point between Potoci, the dam and the sluice (fig. 1).

The 2005 and 2006 hydrographs of the lake exhibit two periods of river high water per year in spring and summer, and a period of river low water in winter (fig. 3): with maximum in April-May and August in 2005, and in April and June in 2006.

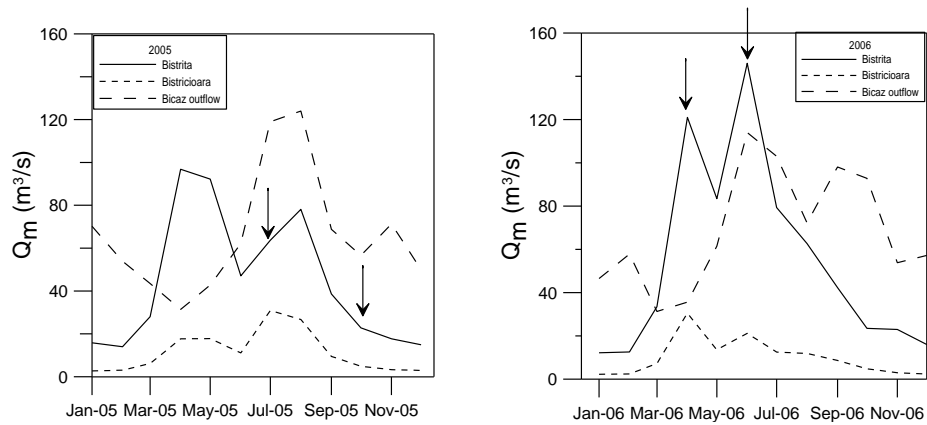


Fig. 3 Hydrographs of the Bicaz lake for years 2005 and 2006. Arrows indicate the sampling surveys

Characteristics of lake hydrology during our surveys has been carried out:

- July 2005: after an important river inflow and low outflow;
- October 2005: after an important river inflow as well as an important outflow;
- April 2006: during important river inflow and very low outflow;
- June 2006: during an important river inflow and important outflow, the lake overflowed by the top of the dam.

Measured maximum water depths at each site for each survey are presented in table 3. The depth measured during the June 2006 survey will be used as a reference depth as the water level of the lake is known (513 m high).

Sampling and analytical procedures

Samples were collected in July 2005 (July 6th, only at the down site, A-3), October 2005 (25 & 26, B-1, B-2, B-3), April 2006 (12 & 14, C-1, C-2, C-3) and June 2006 (24

& 25, D-1, D-2, D-3) from a small motor boat. Water column collection was made with a vertical water sampler (transparent acrylic tube) linked to a graduated nylon rope. We analyzed major-, minor- and some trace elements in filtered and bulk water. Samples were filtered on site with 0.45 μm cellulose acetate membranes that were first rinsed with the sample. Aliquots for cations (major and trace elements) and nutrients were acidified to pH=2 with Suprapur grade nitric acid (Merck). Samples were stored at about 4°C until analysis in polypropylene bottles.

Tab. 3 Maximum measured depth of the lake during sampling survey

Survey	Site 1	Site 2	Site 3
July 2005			86 m
October 2005	34 m	59 m	78 m
April 2006	29 m	57 m	73 m
June 2006	36 m	64 m	88 m

Electric conductivity, pH and temperature were measured locally in the boat. Alkalinity was measured by titrimetry (Gran method calculation) on the sampling day. Major cation (Na, K, Ca, Mg) concentrations were determined by atomic absorption or emission flame spectrometry while anion (Cl^- , SO_4^{2-} , NO_3^- and F^-) concentrations were measured by ionic chromatography using a chemical suppressor. ΣPO_4 was measured by colorimetry. H_4SiO_4 , Li, Rb, Sr and Ba were measured by ICP-MS.

Trace element analyses were performed by inductively coupled plasma quadrupole mass-spectrometry (ICP-MS, Perkin Elmer/Sciex Elan 6000). The sample dilution factor ranges from 2 –100 depending on element concentration. Measurements of element concentrations were performed using Rh (10 ng/ml) as internal standard to minimize drift effects of the instrument. Calibration solutions were prepared from monoelemental ICP-MS standard solutions and high purity chemical reagents (Merck). A batch of 5-7 samples was bracketed by two calibration procedures. Accuracy and precision of determinations were checked at regular intervals with water certified reference materials (NIST 1643d, NIST 1640, NRCC SLRS-4) with compositions similar to the analysed samples. (Govindaraju, 1994)

At each station, the water depth of the lake has been calculated with a monobeam echosounder.

For a better understanding we considered also the study of the Bistrița river at Galu and the Bistricioara river before the confluence with the lake.

Results

Physical and chemical properties of the lake are presented as depth profiles or binary correlation diagrams to show time distribution for one site or space distribution for one survey. Only results measured in the dissolved phase are presented here.

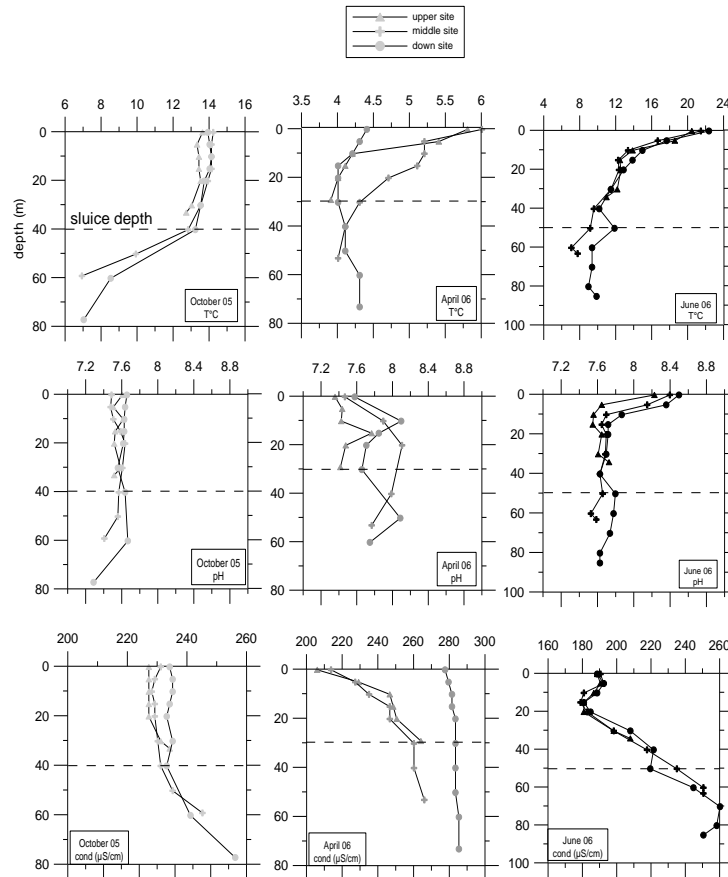


Fig. 4 Profiles of temperature, pH and electric conductivity at the three sites in October 2005, April 2006 and June 2006. The dashed line indicates the sluice depth.

1. Temperature, pH and electric conductivity

The summer thermal stratification begins in April and lasts until October (fig. 4). Lower air temperatures and wind turbulence did mix layers during October and November. From February to April, many times a partial ice cape(s) occurred at the surface of the lake or at low depth, sometimes acting as a stopper to water circulation.

The distribution of pH (fig. 4) shows the importance of biological activity in June 2006 at the three sites (basic pH in the photic zone). At the bottom of the water column, in October and April, the pH decreases at all three sites.

The maximum conductivity is observed in April, at the down site (280 $\mu\text{S}/\text{cm}$), since the minimum is observed in a particular layer in June 2006 (fig. 4) In October, the distribution of electric conductivity reveals that the water composition is homogeneous along the water column and along the lake as well. In April, the measured profiles at the upper and middle sites were very different from the down site: an increase of water conductivity from the top to approximately 30 m instead of an homogeneous water column at the down site. In June 2006, the same feature is observed at each site with a less mineralized layer below 5 m and a minimum of conductivity measured at 15 m. The conductivity increases then gradually to the bottom and achieves a value close to the maximum recorded in October.

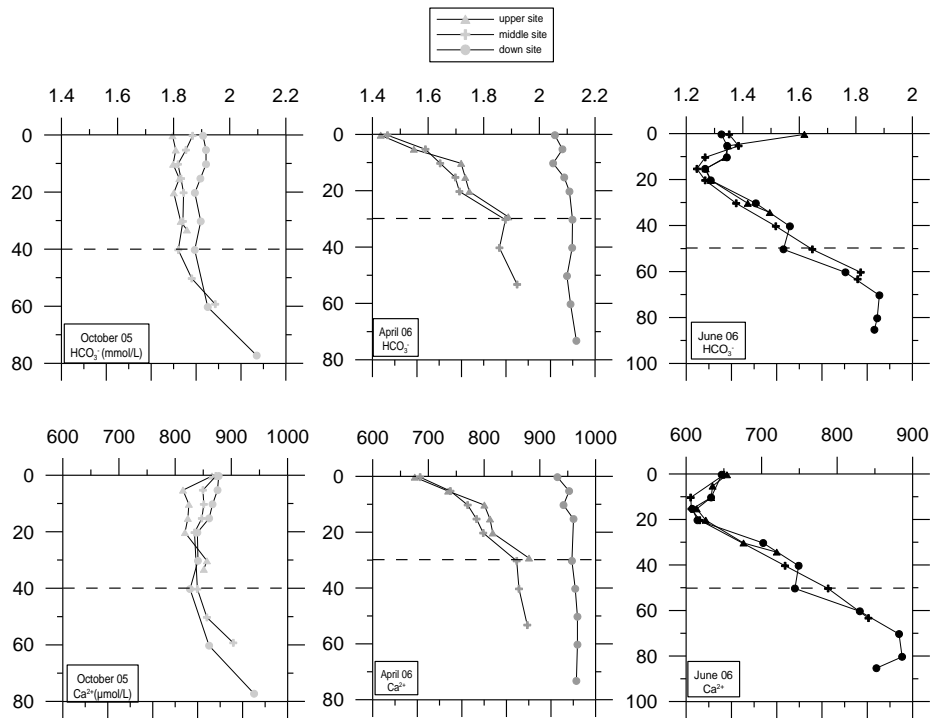


Fig. 5 Profiles of hydrogenocarbonate and calcium ion at the three sites in October 2005, April 2006 and June 2006. The dashed line indicates the sluice depth

2. Major elements and nutrients

The Bicz waters are dominated by Ca^{2+} and HCO_3^- ions (tab. 4 and fig. 5).

Tab. 4 Analytical results for major elements and nutrients measured at the three sites during the four surveys

Depth	T	pH	cond.	alk	HCO ₃ ⁻	CO ₃ ²⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	H ₄ SiO ₄	SPO ₄	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
m	°C		µS/cm	mmol/L			µmol/L								
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A-3															
0	19.8	8.68	190	1.54	1.47	33	149	36	698	199	27	1.1	82	195	32
5	17.6	8.30	213	1.63	1.60	15	158	38	750	215	57	0.7	85	199	41
10	15.8	7.99	231	1.95	1.93	9	164	44	875	232	84	0.8	87	197	52
15	14.0	7.80	228	1.86	1.85	5	162	42	845	227	100	1.0	92	197	59
20	11.8	7.71	227	1.84	1.83	4	160	42	845	226	108	0.9	92	198	62
30	9.6	7.73	209	1.63	1.62	4	159	40	764	206	108	1.2	91	197	58
40	8.0	7.62	214	1.59	1.58	3	166	41	737	212	107	0.7	97	205	56
50	7.7	7.59	228	1.79	1.78	3	181	44	828	233	98	1.0	108	224	55
60	7.7	7.60	231	1.81	1.80	3	191	44	830	240	96	1.0	109	222	59
B-1															
0	13.6	7.60	227	1.80	1.79	3	169	47	864	245	86	0.9	84	217	52
5	13.3	7.50	227	1.81	1.80	3	173	47	813	236	83	1.0	84	220	50
10	13.4	7.61	227	1.80	1.80	3	171	48	823	254	83	1.0	85	220	50
15	13.4	7.52	227	1.82	1.82	3	169	47	821	247	86	0.7	84	220	50
20	13.5	7.51	227	1.80	1.80	3	166	47	816	247	85	0.9	84	220	50
30	13.0	7.58	231	1.83	1.82	3	169	47	855	244	83	0.7	87	228	49
33	12.7	7.51	234	1.85	1.84	3	174	47	850	255	84	0.7	90	233	49
B-2															
0	14.2	7.48	231	1.87	1.86	3	166	48	871	242	81	0.9	81	211	51
5	14.1	7.47	229	1.85	1.84	3	164	48	848	241	82	0.9	81	212	51
10	14.1	7.50	228	1.82	1.81	3	164	47	850	258	85	1.0	81	213	51
15	14.1	7.58	229	1.83	1.82	3	160	47	846	239	86	0.9	81	213	50
20	13.9	7.63	229	1.84	1.83	4	167	47	833	242	90	1.1	81	214	50
30	13.5	7.60	230	1.84	1.83	3	165	47		253	79	1.1	85	221	49
40	12.8	7.56	231	1.82	1.81	3	188	47	838	267	81	1.0	88	227	49
50	9.9	7.55	235	1.87	1.86	3	187	46	855	243	98	0.2	98	221	57
59	6.9	7.40	245	1.95	1.95	2	192	45	902	243	110	0.7	107	222	58
B-3															
0	13.9	7.65	234	1.91	1.90	4	177	50	876	250	80	1.0	81	206	51
5	14.0	7.63	235	1.92	1.91	4	177	49	874	254	77	0.7	82	211	52
10	14.1	7.62	235	1.92	1.91	4	175	49	865	245	80	1.0	82	211	52
15	14.0	7.62	234	1.90	1.89	4	178	49	859	257	85	1.0	83	214	52
20	13.7	7.61	233	1.88	1.87	4	183	48	838	257	80	0.7	86	221	51

Hydrodynamics of the Bicz Lake. Selected major and trace elements

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
30	13.5	7.55	235	1.90	1.89	3	177	48	839	253	90	1.0	87	223	52
40	13.2	7.63	233	1.88	1.87	4	179	47	825	256	84	0.9	87	222	52
60	8.5	7.66	241	1.93	1.92	4	190	44	859	246	90	1.1	105	230	56
77	7.0	7.3	256	2.10	2.09	2	200	46	939	269	104	0.8	111	228	52
C-1															
0	5.8	7.35	206	1.43	1.43	1	331	40	674	203	119	1.0	267	192	63
5	5.4	7.43	229	1.55	1.55	2	385	45	734	211	112	0.6	172	208	62
10	4.2	7.42	246	1.72	1.72	2	212	46	799	243	111	0.9	137	228	60
15	4.1	7.76	248	1.74	1.73	5	210	47	809	231	109	0.9	141	229	61
20	4.0	7.47	250	1.75	1.75	2	214	49	814	234	106	0.9	146	227	61
29	3.9	7.41	264	1.89	1.89	2	222	50	879	233	107	0.9	149	234	59
C-2															
0	6.0	7.46	213	1.46	1.45	2	177	41	684	199	117	0.5	113	195	62
5	5.2		227	1.59	1.59	0	184	43	738	218	116	0.9	121	209	61
10	5.2	7.89	235	1.65	1.64	6	193	44	769	235	112	0.9	124	215	60
15	5.1		246	1.70	1.69	0	197	46	785	224	112	1.1	126	221	60
20	4.7	8.10	246	1.73	1.71	10	202	47	797	241	110	1.0	128	225	60
30	4.3		260	1.88	1.87	0	215	48	857	246	96	0.9	131	238	59
40	4.1	7.98	260	1.87	1.85	8	210	48	861	267	104	1.0	130	237	59
53	4.0	7.76	266	1.93	1.92	5	211	48	876	262	101	0.8	132	237	59
C-3															
0	4.4	7.57	277	2.06	2.05	4	208	49	930	271	98	0.6	118	243	58
5	4.3		279	2.08	2.08	0	209	49	951	270	97	1.1	118	242	59
10	4.2	8.09	281	2.07	2.05	12	211	49	941	276	97	0.8	117	248	60
15	4.0	7.84	281	2.10	2.09	7	205	50	959	278	97	1.0	117	247	60
20	4.0	7.70	283	2.12	2.11	5	209				98	0.9	118	248	60
30	4.0	7.65	283	2.13	2.12	4	209	48	956	269	96	0.7	118	247	61
40	4.1		283	2.12	2.11	0	211	49	962	264	99	1.0	119	247	61
50	4.1	8.08	283	2.12	2.10	12	210	49	966	266	101	1.1	120	247	61
60	4.3	7.74	285	2.12	2.11	5	210	49	966	274	100	1.0	119	247	61
73	4.3		285	2.13	2.13	0	212	49	964	280	99	1.0	120	248	61
D-1															
0	20.4	8.22	188	1.64	1.61	13	158	34	653	183	113	0.8	74	186	37
5	18.5	7.64	190	1.35	1.34	3	146	37	634	187	120	0.9	69	174	45
10	13.8	7.55	186	1.34	1.34	2	141	32	632	182	133	0.9	66	174	49
15	12.4	7.54	181	1.27	1.27	2	133	31	613	167	140	0.8	63	168	50
20	12.5	7.64	181	1.29	1.28	3	134	32	625	165	125	0.8	63	167	48
30	12.1	7.60	198	1.42	1.41	3	148	35	675	176	118	0.7	76	184	53
34	10.9	7.72	208	1.50	1.49	4	158	37	719	181	119	0.8	86	193	56
40	9.5	7.62	217	1.52	1.51	3	170	39	730	207	114	0.9	100	205	59

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
50	9.1	7.65	235	1.65	1.64	3	184	42	787	230	118	0.8	113	217	59
60	7.0	7.52	250	1.82	1.81	3					108	0.6	126	230	64
63	7.7	7.58	250	1.81	1.80	3	191	45	841	223	109	1.0	116	223	62
D-3															
0	22.3	8.49	188	1.36	1.32	19	147	32	646	184	100	1.0	73	192	37
5	17.6	8.35	192	1.37	1.34	14					108	1.0	73	191	42
10	14.9	7.86	188	1.35	1.34	5	141	33	632	174	118	1.0	69	181	47
15	13.8	7.71	181	1.27	1.26	3	135	32	607	175	127	0.9	66	175	47
20	12.8	7.71	184	1.29	1.28	3	136	33	614	172	119	0.9	69	176	49
30	11.4	7.69	208	1.45	1.44	3	156	36	701	193	119	1.0	87	194	59
40	10.1	7.62	221	1.57	1.56	3	171	39	748	207	120	0.9	102	206	61
50	11.8	7.8	219	1.55	1.54	4	166	38	743	210	108	0.9	94	203	55
60	9.3	7.8	244	1.77	1.76	5	183	43	829	226	104	0.6	109	219	60
70	9.3	7.7	260	1.89	1.88	5	192	45	881	254	99	0.9	114	228	61
80	8.9	7.6	258	1.88	1.87	4	189	45	885	249	99	0.9	110	226	58
85	9.8	7.6	250	1.87	1.86	4	183	44	851	238	101	1.1	105	220	56

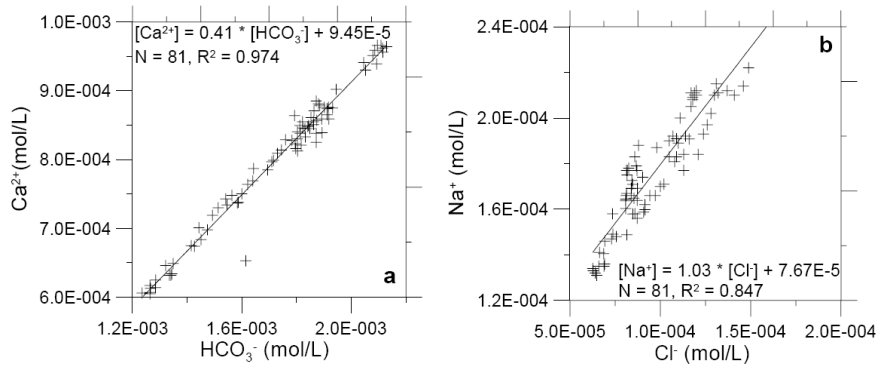


Fig. 6 Distribution of Ca^{2+} concentrations versus HCO_3^- concentrations and of Na^+ concentrations versus chloride concentrations observed in the lake from July 2005 to June 2006

Generally, Mg^{2+} and SO_4^{2+} are more abundant than Na^+ and Cl^- . Considering the whole data set, the following correlations were calculated (concentrations are expressed as mol/L) (fig. 6):

$$\text{mean lake: } [\text{Ca}^{2+}] = 0.41 [\text{HCO}_3^-] + 9.45 \times 10^{-5} \quad n = 81, R^2 = 0,974 \quad (1)$$

$$\text{mean lake: } [\text{Na}^+] = 1.03 [\text{Cl}^-] + 7.65 \times 10^{-5} \quad n = 81, R^2 = 0,847 \quad (2)$$

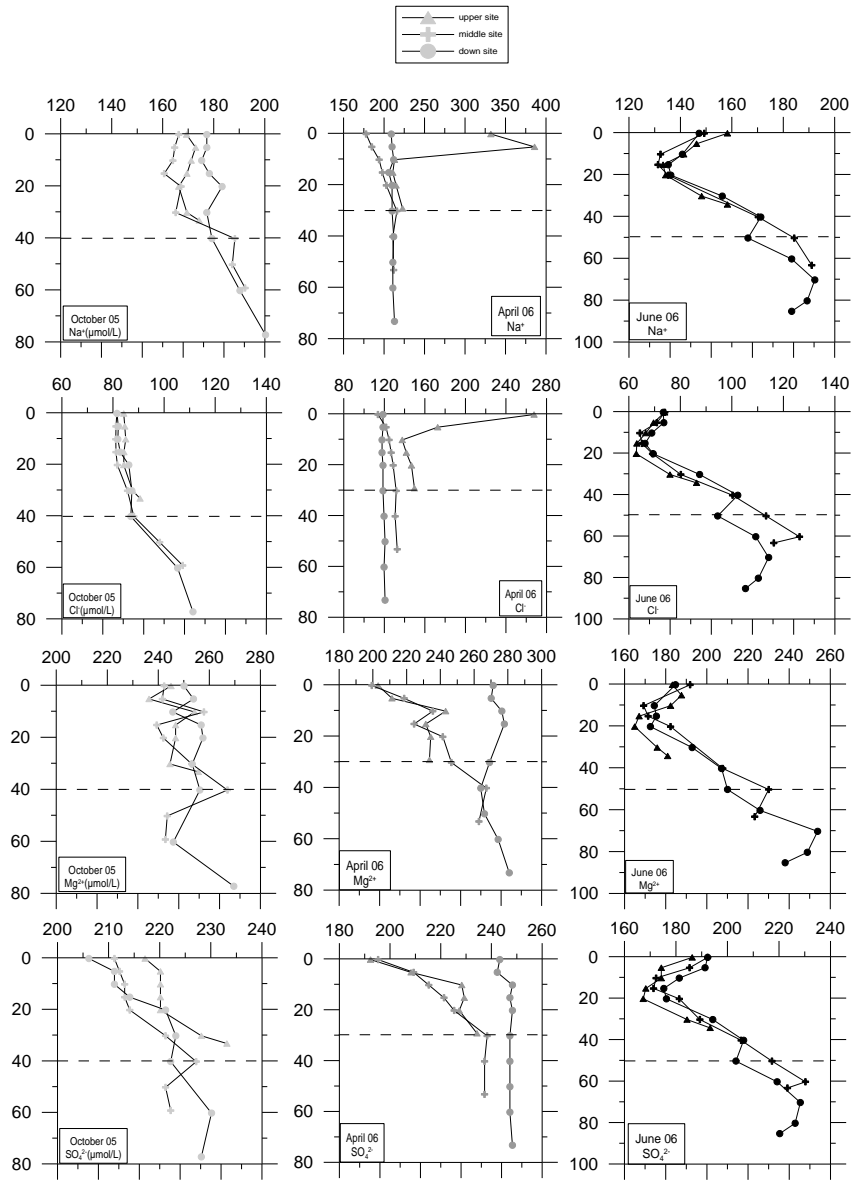


Fig. 7 Profiles of Na⁺, Cl⁻, Mg²⁺ and SO₄²⁻ at the three sites in October 2005, April 2006 and June 2006. The dashed line indicates the sluice depth

In part charges from Na^+ , Mg^{2+} and K^+ are compensated by HCO_3^- . The concentrations of major elements vary similarly to the electrical conductivity. Minimal concentrations were recorded in June 2006 at 15 m depth (D-1 15m), while maximal concentrations were recorded in April 2006 at the down site (C-3 73m). Na^+ and Cl^- have a different behaviour in April at the upper and middle sites (fig. 7).

Recorded concentrations of nitrate and orthophosphate are low, all along the year (respectively: 32-64 $\mu\text{mol/L}$ and 0.5-1.2 $\mu\text{mol/L}$). Concentrations of Si vary only slightly (77-140 $\mu\text{mol/L}$) and are minimal in October for all three sites.

3. Trace elements: F, Li, Rb, Sr, Ba

These five elements have been chosen due to the fact that they are very mobile elements and are naturally present under one oxidation state. Concentrations of fluoride and strontium are very stable (respectively: 2,83-3,90; 1,01-1,92 ($\mu\text{mol/L}$)) (tab. 5). Li, Rb and Ba exhibit the highest variability (respectively: 298-699; 9.25-20.95; 111-257(nmol/L)). Minimal concentrations were recorded in June 2006 and maximal in April 2006, excepted for fluoride (minimum at C-1 surface) and for Rb (maximum at B-3 77 m depth).

Tab. 5 Analytical results for trace elements measured at the three sites during the four surveys

Depth m	F $\mu\text{mol/L}$	Li nmol/L	Rb nmol/L	Sr $\mu\text{mol/L}$	Ba nmol/L
0	1	2	3	4	5
A-3					
0	3.1	426	10.14	1.30	149
5	3.2	453	11.86	1.43	165
10	3.1	451	10.51	1.51	185
15	3.1	428	9.96	1.43	178
20	3.1	491	10.14	1.42	176
30	3.1	394	11.86	1.30	168
40	3.1	408	12.13	1.34	167
50	3.2	453	13.01	1.56	192
60	3.2	427	12.10	1.46	180
B-1					
0	3.3	537	11.21	1.61	195
5	3.4	539	12.72	1.57	186
10	3.5	519	12.11	1.51	188
15	3.4	557	12.10	1.58	194
20	3.2	557	12.07	1.58	194
30	3.3	541	11.61	1.55	195
33	3.5	617	13.05	1.64	228
B-2					

Hydrodynamics of the Bicz Lake. Selected major and trace elements

0	1	2	3	4	5
0	3.4	501	11.17	1.58	204
5	3.4	487	11.85	1.64	206
10	3.5	532	11.70	1.50	181
15	3.5	519	12.10	1.59	196
20	3.5	557	11.74	1.64	209
30	3.6	562	11.71	1.62	198
40	3.6	599	12.50	1.57	194
50	3.5	518	12.33	1.58	194
59	3.4	499	18.28	1.77	206
B-3					
0	3.5	493	11.28	1.65	216
5	0.0	517	10.59	1.57	206
10	3.4	495	11.07	1.58	217
15	3.5	563	11.65	1.63	225
20	3.5	545	12.55	1.74	230
30	3.5	598	12.12	1.70	224
40	3.5	526	12.89	1.57	208
60	3.3	555	15.42	1.50	206
77	3.5	600	20.95	1.45	193
C-1					
0	2.8	385	10.74	1.20	190
5	3.0	487	11.48	1.27	209
10	3.1	525	11.62	1.44	235
15	3.2	502	12.72	1.47	247
20	3.2	471	12.68	1.50	248
29	3.3	549	13.70	1.76	257
C-2					
0	3.1	434	11.04	1.21	195
5	3.1	418	11.01	1.30	210
10	3.2	476	11.59	1.45	224
15	3.2	488	12.34	1.49	234
20	3.2	535	12.41	1.49	242
30	3.3	579	10.65	1.44	226
40	3.4	605	11.59	1.69	238
53	3.4	610	11.02	1.63	219
C-3					
0	3.5	623	11.28	1.90	230
5	3.4	685	10.35	1.85	219
10	3.7	699	10.85	1.90	224
15	3.7	630	10.81	1.82	227
20	3.9	653	11.40	1.86	240
30	3.7	610	10.40	1.92	237
40	3.7	657	11.23	1.89	243
50	3.7	580	11.37	1.87	240
60	3.7	637	10.75	1.87	229

0	1	2	3	4	5
73	3.7	638	9.69	1.85	225
D-1					
0	3.3	422	10.52	1.29	122
5	3.2	377	11.54	1.10	119
10	3.2	366	10.06	1.11	116
15	2.9	370	11.84	1.12	127
20	3.1	330	10.25	1.10	116
30	3.2	369	10.26	1.20	134
34	3.3	388	11.43	1.25	140
D-2					
0	3.3	386	9.42	1.28	130
5	3.2	364	10.64	1.27	136
10	3.2	298	9.90	1.02	111
15	3.2	315	10.55	1.01	117
20	3.1	334	9.89	1.01	119
30	3.2	353	10.38	1.18	130
40	3.3	387	11.40	1.31	155
50	3.4	530	11.59	1.53	195
60	3.4	519	11.77	1.57	212
63	3.5	531	12.16	1.57	208
D-3					
0	3.1	363	9.25	1.24	116
5	3.1	448	9.48	1.27	126
10	3.0	361	10.12	1.16	115
15	3.4	331	10.80	1.13	121
20	3.3	319	10.35	1.10	121
30	3.4	382	10.58	1.24	152
40	3.5	468	11.47	1.44	175
50	3.5	434	10.39	1.31	153
60	3.7	502	10.07	1.55	182
70	3.7	544	10.03	1.55	192
80	3.7	546	10.79	1.59	194
85	3.7	470	10.49	1.57	181

Discussion

Two main questions about hydrodynamics of the lake can be asked. (1) Is a stable summer stratification developed, and is it stable enough to have an individualization of an epilimnion and a hypolimnion ? (2) What is the origin of elements present in the lake, knowing that a maximum replacement time of water of 206 to 237 days can be calculated (tab. 2) ?

1. Stratification of the lake and currents

The temperature profiles show that the thermocline begins to develop in July 2005, between 20 and 40 m depth, and is well marked in October 2005, at 40 m depth (fig. 8a). Data for June 2006 confirm this mechanism. In October 2005, water is colder and more mineralized in the hypolimnion. The epilimnion exhibits a homogeneous composition in Ca^{2+} , HCO_3^- , Cl^- , K^+ and Rb . At the same depth (40 m), slight differences in composition are recorded (Na^+ , Mg^{2+} , sulphate, Li). This is also the depth of the sluice.

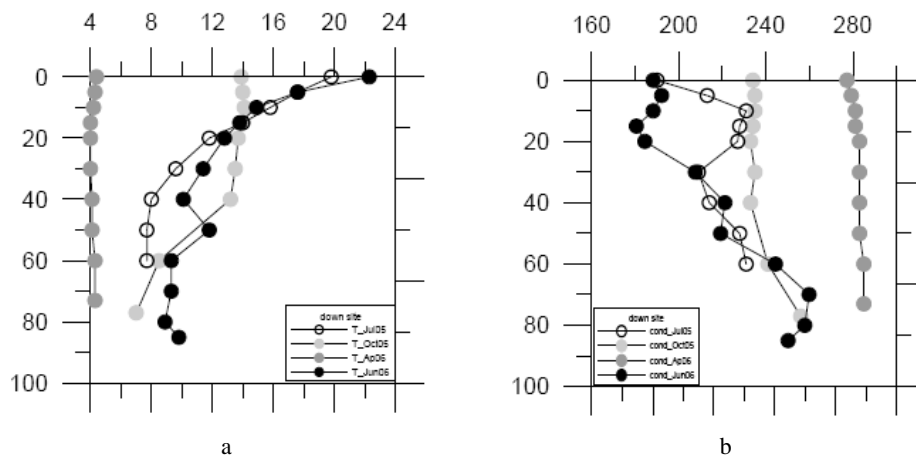


Fig. 8 Profiles of temperature (a) and electrical conductivity (b) measured at the down site for the four surveys

In April 2006, data evidence an input of diluted waters at the surface of the upper and middle sites. This diluted waters are warmer than the lake and richer in Na and chloride (fig. 7). For the middle site, the mineralization remains constant under 30 m depth. The down site exhibits a homogeneous composition in major elements (fig. 4, 5 and 7). In June 2006, a less mineralized layer is recorded on the top of the water column, at all three sites, with a minimum concentration recorded at 15 m depth. Another specific layer is observed at approximately 50 m depth with less mineralized waters (fig. 4, 5, 7, 9). This layer is present at both the middle and the down site.

Superficial currents recorded in April and June 2006 originated from the river inflow (Bistrița and Bistricioara) whose temperature and composition, i. e. density, are different from that of lake water.

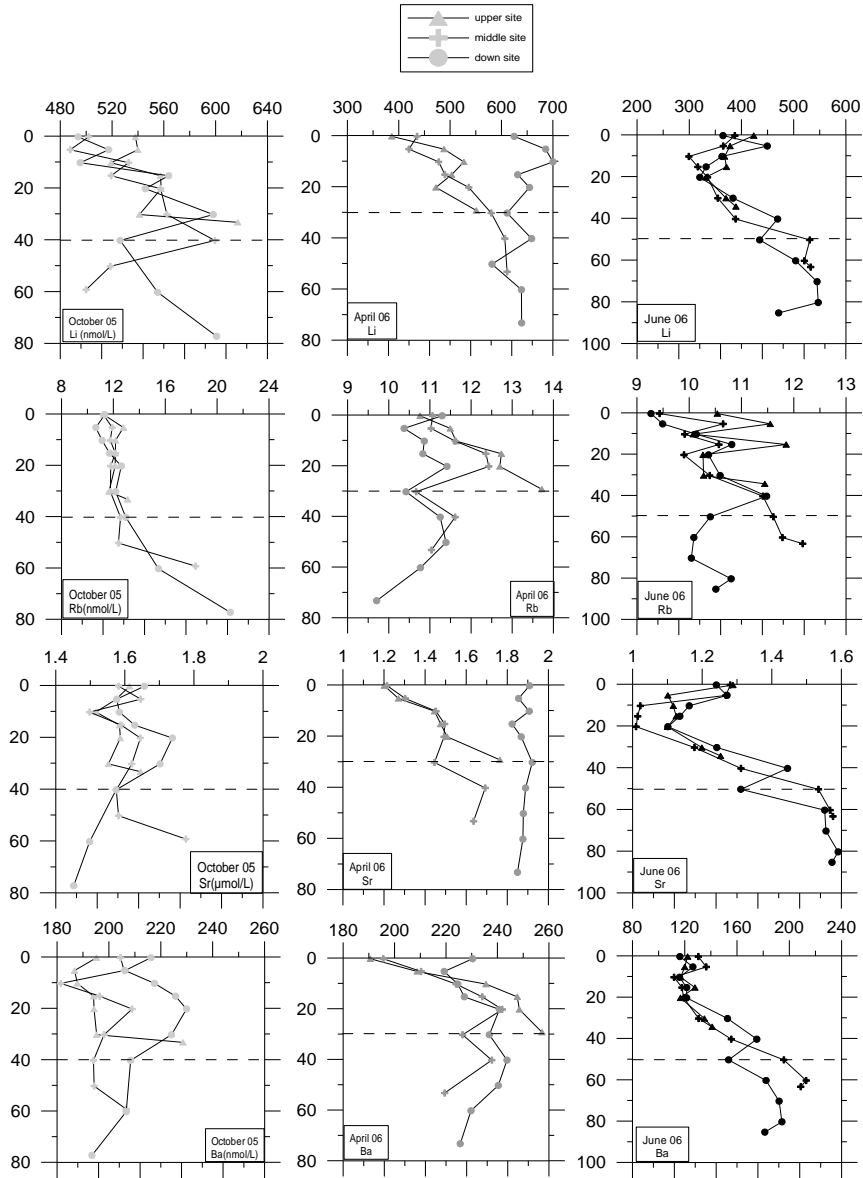


Fig. 9 Profiles of Li, Rb, Sr and Ba at the three sites in October 2005, April 2006 and June 2006. The dashed line indicates the sluice depth

In April, the current disappeared at the middle site. In June 2006, the river layer remains un-mixed until the site 3. Vertical advection and diffusion are not efficient enough to erase the difference in chemical composition even for the few meters of the top waters.

This result involves the fact that the velocity of river inflow is high enough to limit exchange between river and lake waters. In July 2005, an equivalent layer was recorded at the down site (fig. 8b).

Deep current may originate from the sluice drawing off. This current carries waters with a different composition and also limits the renewing of deeper waters which stay confined at the bottom of the water column.

It is possible that the remaining of the river layer at the down site is linked to the presence of the deep current allowing a complicated superposition of horizontally moving layers.

2. Origin of elements and mixing of waters

Elements present in the lake waters originated from the weathering and mechanical erosion of the Bistrița and the Bistricioara watershed (river input) and from the water/sediment interaction within the lake (lake fingerprint). The lake fingerprint will be observed in waters which have resided a long time in the lake without additional river input. The more characteristic point is the down site sampled at the end of winter time, a time when river inflow is very low (precipitation occurs mainly as snow), an ice stopper limits water circulation, and the hydroelectric outflow is low. We assume that C-3 at 73 m depth represents the lake end-member. The composition of the lake varies according to river input. The quality and quantity of river input varies also according to season. The more diluted recharge waters have been recorded in June 2006, at the point D-1 at 15 m depth. If no other process is involved in the distribution of two species, their concentrations must be aligned on a straight line corresponding to the mixing of these two kind of waters.

Dominant ions: Ca^{2+} and HCO_3^-

The C-3/D-1 mixing equation for these two species is as follows

$$\text{C-3/D-1 mixing: } [\text{Ca}^{2+}] = 0.40 [\text{HCO}_3^-] + 1.17 \times 10^{-4} \quad (3)$$

which is very similar to equation (1). The mean river water line follows the equation

$$\text{mean river: } [\text{Ca}^{2+}] = 0.27 [\text{HCO}_3^-] + 2.29 \times 10^{-4} \quad n = 6, R^2 = 0.949 \quad (4)$$

and indicates that the lake waters are richer in calcium compared to HCO_3^- than river waters (fig. 10). The Bistrița samples are on the mean lake waters line. The main contribution of the Bistrița river (mean of 83%) and the weathering of lake sediments explain the distribution of these factors.

Na/Cl

Na^+ and Cl^- distribution involves an additional source namely an anthropogenic one. In April 2006, the diluted waters entering the lake were particularly rich in Na^+ and Cl^- . This anthropogenic fingerprint, probably linked to road salting, is still noticeable in June 2006 (fig. 11). Two kinds of mixing explain the distribution of these elements in the lake: (i) a spring mixing between an anthropogenic end-member (C-1 surface) and diluted recharge waters (D-1 15 m depth), (ii) a summer mixing between a lake end-member (C-3 73 m depth) and summer river inflow comprising either 83% of Bistrița and 17% of Bistrițioara input (July 2005 composition), or 67% of Bistrița and 33% of Bistrițioara input (July 2005 composition) (fig. 11).

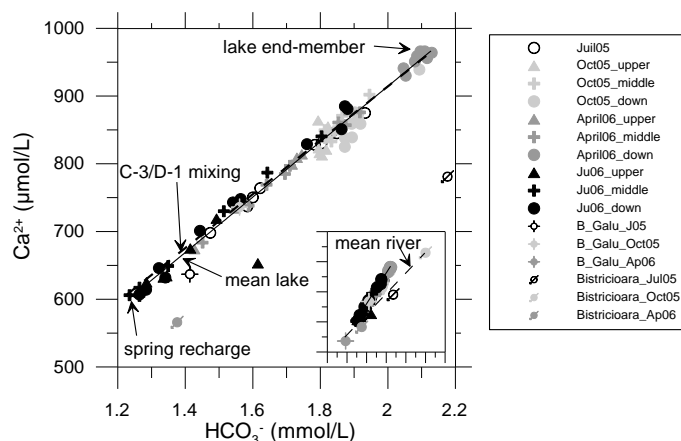


Fig. 10 Distribution of Ca^{2+} concentrations versus HCO_3^- concentrations observed in the lake and in the rivers from July 2005 to June 2006. Identification of mixing condition.

The anthropogenic end-member is characterized by a high concentration of Na^+ and Cl^- and a Na/Cl ratio close to one, just like in salt. During weathering, as rocks contain little chloride, the Na/Cl ratio increases. It is noticeable that not only the April waters from the upper and middle site recorded the anthropogenic input but even the down site, supposed to represent the lake end-member. The anthropogenic input is still noticeable at the down site in June (July 2005 and June 2006) and begin to be remarkable at the beginning of the snowy season (October 2005, surface waters). The Na/Cl anthropogenic input is important enough to be detectable all the year long.

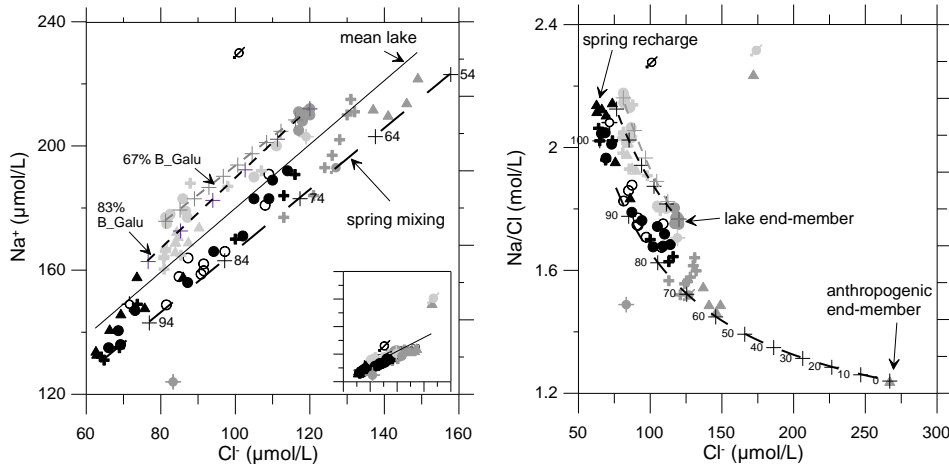


Fig. 11 Distribution of Na^+ versus Cl^- and of Na/Cl ratio versus chloride observed in the lake and in the rivers from July 2005 to June 2006. Identification of mixing condition

Ca/Li

As calcium is the dominant cation, we compared the Li distribution, a purely mobile, small size ion, to Ca distribution in order to determine its origin. The C-3/D-1 mixing line nearly overlaps the mean lake water line according to (fig. 12)

$$\text{mean lake: } [\text{Ca}] = 975 [\text{Li}] + 3,20 \times 10^{-4} \quad n = 81, R^2 = 0.806 \quad (5)$$

$$\text{C-3/D-1 mixing: } [\text{Ca}] = 1108 [\text{Li}] + 2.57 \times 10^{-4} \quad (6)$$

The mean river water line exhibits a richer fingerprint mainly because of the Bistricioara river

$$\text{mean river: } [\text{Ca}] = 504 [\text{Li}] + 3.61 \times 10^{-4} \quad n = 6, R^2 = 0.966 \quad (7)$$

Between the spring recharge and the lake end-member Ca and Li increase but the Ca/Li ratio is always higher than the mean river ratio (fig. 12b). During the water/sediments interaction within the lake, the Ca/Li ratio decreases but is still superior to the Ca/Li ratio of rivers in October, when weathering is the dominant process occurring in the watershed. In April, the input of river waters with a low Ca/Li ratio is noticeable in the upper and middle site and also at the down site, probably because of the important difference of concentration between lake and rivers (important concentration gradient), and due to the rapid diffusion of Li.

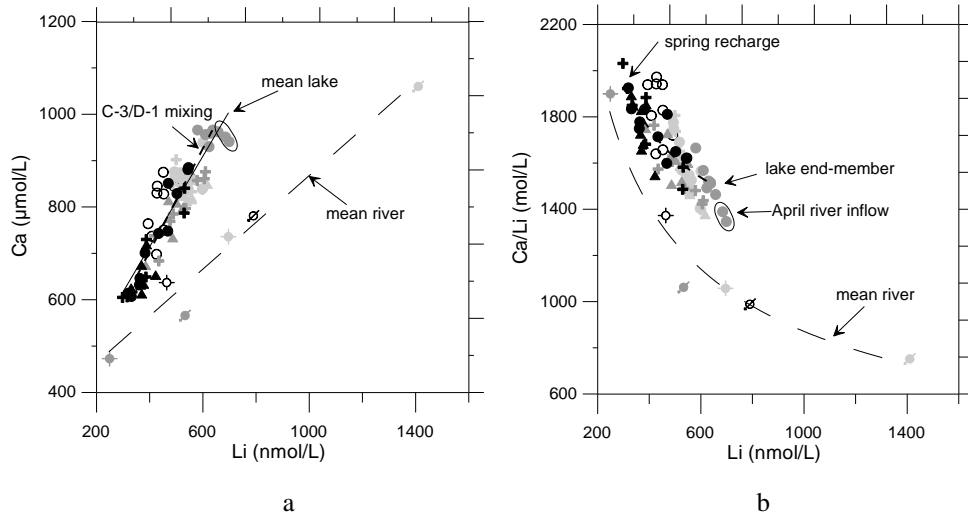


Fig. 12 Distribution of Ca versus Li (a) and of Ca/Li ratio versus Li (b) observed in the lake and in the rivers from July 2005 to June 2006. Identification of mixing condition.

Ca/Ba

The C-3/D-1 mixing line is different from the mean lake water line (fig. 13)

$$\text{mean lake: } [\text{Ca}] = 2120 [\text{Ba}] + 4.00 \times 10^{-4} \quad n = 81, R^2 = 0.676 \quad (8)$$

$$\text{C-3/D-1 mixing: } [\text{Ca}] = 3310 [\text{Ba}] + 2.18 \times 10^{-4} \quad (9)$$

The mean river water line is almost parallel to the mean lake water but exhibits a different fingerprint with increased Ba content

$$\text{mean river: } [\text{Ca}] = 1940 [\text{Ba}] + 3.23 \times 10^{-4} \quad n = 6, R^2 = 0.986 \quad (10)$$

The poor concordance between the mixing line and the mean lake water line is mainly due to samples of the October 2005 at down site and of the April 2006 at upper site as well as to the top column of the middle site. In October 2005, waters at the down site exhibit the Bistricioara fingerprint of July (in July 2005, Bistricioara inflow represented 33% of the river inflow), the Bistricioara which is richer in Ba than the Bistrița. In April 2006, at the upper site and at the top of the water column of the middle site, the April river flow is very much noticeable, much more than for Li. Data on filtered and bulk samples show that Ba is partly carried to the lake linked on particles, while in the lake, Ba is in the dissolved phase. Particles act as a reservoir for Ba,

reservoir which does not exist for Li. The diffusion of Ba has also altered the top waters of the down site.

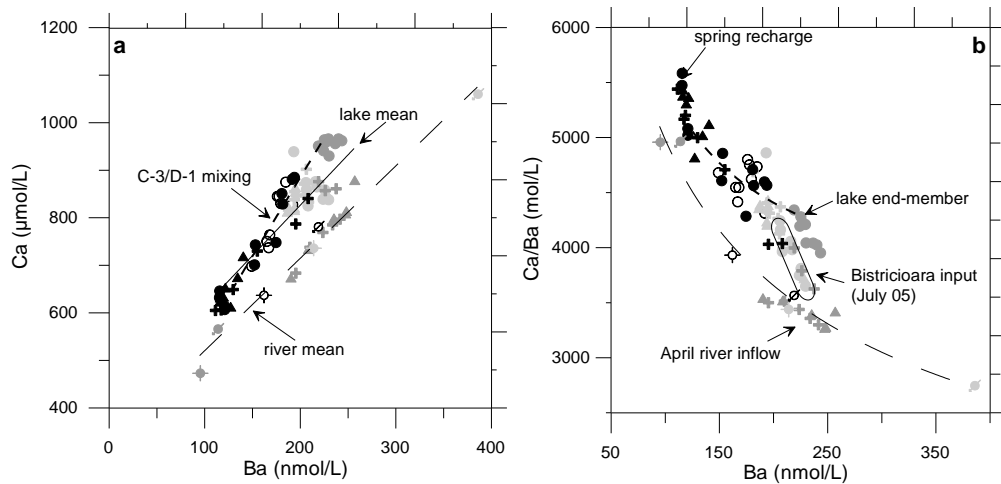


Fig. 13 Distribution of Ca versus Ba and of Ca/Ba ratio versus Ba observed in the lake and in the rivers from July 2005 to June 2006. Identification of mixing condition.

Ca/Sr

The C-3/D-1 mixing line, the mean lake water line and the mean river water line are nearly concordant (fig. 14a) which implies a common origin of these two species.

$$\text{mean lake: } [\text{Ca}] = 415 [\text{Sr}] + 1.85 \times 10^{-4} \quad n = 81, R^2 = 0.882 \quad (11)$$

$$\text{C-3/D-1 mixing: } [\text{Ca}] = 426 [\text{Sr}] + 1.75 \times 10^{-4} \quad (12)$$

$$\text{mean river: } [\text{Ca}] = 456 [\text{Sr}] + 1.18 \times 10^{-4} \quad n = 6, R^2 = 0.992 \quad (13)$$

The Ca/Sr ratio records a quite different mechanism (fig. 14b): for a given Sr concentration various Ca/Sr ratios were measured. Saturation index calculations show that calcite precipitation may occur in some samples. Because Sr is less incorporated during calcite precipitation, the variability of the Ca/Sr ratio can be linked to the Ca/Sr fractionation during calcite precipitation.

K/Rb

The C-3/D-1 mixing line roughly describes the K/Rb distribution in the lake (fig. 15a). The mean lake and the mean river water lines display no significance. The lake end-member is richer in K than the spring recharge but not richer in Rb. From October 2005 to the lake end-member (April 2006), an important decrease of Rb is recorded (fig. 15b).

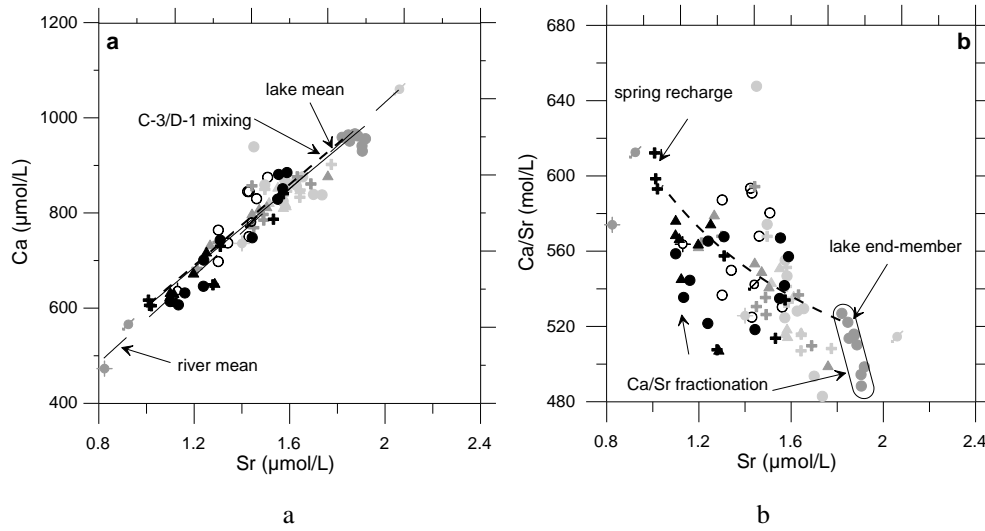


Fig. 14 Distribution of Ca versus Sr (a) and of Ca/Sr ratio versus Sr (b) observed in the lake and in the rivers from July 2005 to June 2006. Identification of mixing condition

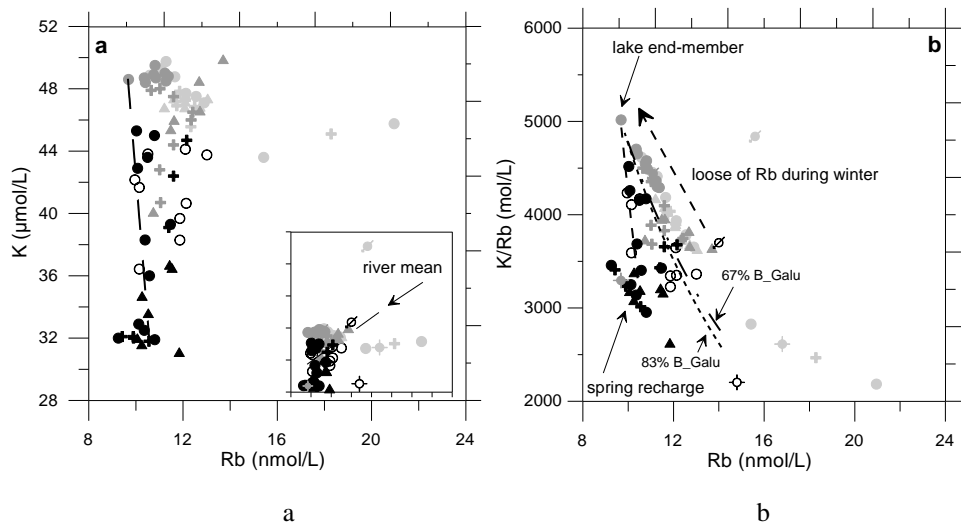


Fig. 15 Distribution of K versus Rb (a) and of K/Rb ratio versus Rb (b) observed in the lake and in the rivers from July 2005 to June 2006. Identification of mixing condition

These winter loose cannot be explained by any biological uptake or solid phase precipitation. Data on bulk samples show that an important part of Rb, mainly at the down site, is linked to particles. The decrease in dissolved Rb concentration may correspond to a scavenging on particles (adsorption on oxi-hydroxide, clay or organic matter?).

Conclusion

Results on the 2005 and 2006 surveys demonstrate that the water column of the Bicaz lake exhibits a summer stratification, may be delayed by the high river inflow of June-July. Water circulation within the lake seems to be more laminar than turbulent according to major components which underline the presence of several layers at the upper, middle and down site. In July 2005 and June 2006, a superficial layer exhibits a river fingerprint, whereas a deep layer is evidenced at the sluice depth. In October 2005, some elements seem to attest the presence of a superficial current at the 20 m depth (Na, Sr, Ba, fig. 7 and 9), as the sluice drawing off is not visible.

The water column structure of a lake is a key parameter controlling biogeochemical processes. The persistence of a river layer until the down site and the presence of a deep current made of a mix between river waters and bottom waters from the upper site may prevent the development of stable redox conditions. So the cycling of iron which plays an important role in the transport of trace elements in lake may not occur.

In such a dynamic system the renewing of water linked to these currents is also fundamental. Estimation of the renewing time of water in a lake used for hydroelectric production is not that simple. The approximate time of 206 to 237 days we have calculated are consistent with our data for October 2005. Barium data for the down site exhibit the fingerprint of the Bistricioara river whose inflow was more important three months before. This may involve that waters stay at least three months in the lake during summer time. Some waters may transit faster (in the deep current) or more slowly (under the deep current).

These results evidence that prediction of trace element behaviour in the lake of Bicaz is critical. A further paper will present results on these species.

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