Available online at http://geology.uaic.ro/auig/
Analele Stiintifice ale Universitatii "Al. I. Cuza" din Iasi
Seria Geologie 60 (2) (2014) 55–80

AUI GEOLOGIE

Geochemical and hydrodynamic control of trace element transport in a reservoir: impact of interflow layer

Nathalie GASSAMA[1], Constantin COCÎRȚĂ[1], Haino Uwe KASPER[2]

[1] EA 6293 GéHCO Géohydrosystèmes Continentaux, Université François-Rabelais de Tours, 37200 Tours, France
[2] Institut für Geologie und Mineralogie, Universität zu Köln, Germany

Abstract

Concentration of trace elements both in the water column (dissolved phase and acid-soluble suspended particles) and in sediments (bulk and acid-soluble particles) was followed for one year in a water reservoir (the Bicaz reservoir) used for electricity production. This study investigated the impact of river inflows, outflows and the position of the outflow for the cycling and the transport of these elements along this water reservoir. Time series results reveal that river inflow supplies mainly reducing waters. In the water column, the stable Al/Fe ratio (from 0.8 to 1.5) recorded in acid-soluble suspended particles suggests the formation of similar amorphous phases during the year, phases that could be stabilized by organic ligands. In sediments, these amorphous phases are no more recorded. In the water column, some trace elements are strongly associated with Al-Fe amorphous phases (Rb, Cs, Co, Cu, Zn, Pb, Th); others are independent (Sr, Sn, As, Sb, U). In sediments, Co, Y, Zn, Ga, Cr, Ni, V, Rb, and Ba are associated with phases containing Fe, Al, K, Mg, P and Ti. The reservoir acts as a moderate sink for Fe, V, Cr, Co, Cu; it acts alternately as a sink and a source for Zn. Among the elements studied, only Mn and Ni are significantly stored. Rb shows particular affinity for Fe oxide which is not recorded in literature. Our results show the importance of the outflow depth on the transport of trace elements within a reservoir.

Keywords: reservoir, Al-Fe particles, trace elements, redox condition, interflow layer, water column, sediments.

1. Introduction

The transport of trace elements in aquatic systems depends mainly on the biogeochemical behavior of iron (Sigg, 1985; Balistrieri et al., 1992; Viollier et al., 1995; Taillefert and Gaillard, 2002; Hamilton-Taylor et al., 2005). Some trace elements can be scavenged

---

Corresponding author's e-mail: constantin.cocirta@univ-tours.fr

by particulate or colloidal iron oxyhydroxides. Some can be buried in sediments with settling particles and then stored or released depending on the physico-chemical conditions occurring at the sediment-water interface. In natural lakes, organic matter from tributaries and authigenic biomass production, together with thermal stratification, regulate the redox conditions of the water column. These conditions determine the behavior of iron. In reservoirs, the size of river inflows and outflows, together with the position of the outflow, disturbs the potential stratification of the water column and consequently the biogeochemical processes within the reservoir (Han et al., 2000; Fontane et al., 2000; Casamitjana et al., 2003; Rueda et al., 2007). However, the behavior of iron and of associated trace elements is difficult to predict due to the movement of water.

The Izvorul Muntelui-Bicaz reservoir (henceforth called Bicaz) in Romania (Fig. 1) is an impoundment that collects waters from the Bistriţa watershed, which is a mining district rich in polymetallic sulfide and manganese ore deposits (Munteanu et al., 2004). The watershed is mainly composed of crystalline rocks, whereas the reservoir lies on carbonaceous rocks (flysch). There has been little mineral processing on site. There have been no mining activities for several years, but tailings are still exposed to weathering. Mining activities may have added to high natural background concentrations of trace elements in river waters. For health reasons, it is important to determine whether the reservoir acts as a sink for trace elements, as a permanent sink or periodically as a source, depending on the physico-chemical conditions prevailing in the reservoir (Becker et al., 2001; Holmström and Öhlander, 2001; Moncur et al., 2006; Munk and Faure, 2004; Sánchez España et al., 2008). The Bicaz reservoir experiences summer and winter thermal stratification (Apopei, 1983). In a previous study, data on major and selected trace elements were used to describe mixing of waters (Gassama et al., 2012). Two specific layers were determined: an intrusion layer originating from the river inflow, and a layer (velocity current) at the outflow depth. Water transit time may vary considerably according to depth and season: some waters may transit fast (i.e. the deep current) and some very slowly (below the deep current). In addition, mixing will vary depending on the contrast in density and velocity of the water layers. These contrasting water movements may have a significant impact on biogeochemical processes (Casamitjana et al., 2003; Rueda et al., 2007). This work was undertaken (i) to characterize the water quality pertaining to trace elements, (ii) to assess the redox status along the water column at different seasons, and (iii) to determine the impact of the interflow current on the transport and speciation of trace elements within the reservoir. Four surveys were carried out between July 2005 and June 2006, scheduled at periods when water mixing was expected to occur. Because of the reservoir's elongated shape (31.1 km), three sampling sites were selected along a longitudinal transect (Fig. 1). Samples from the water column were collected to study both the dissolved phase and the amorphous phases of suspended particles (acid soluble phases, ASP). To ensure the preservation of amorphous phases, we worked on bulk solution instead of sediment traps, particularly where phase ageing modifies the trace element content (Viollier et al., 1997; Lamborg et al., 2008). A core of sediments was collected at each site in October 2007 to study bulk composition and amorphous phases (i.e. ASP).

2. Hydrological characteristics of the reservoir

The hydrographic basin of the Bicaz reservoir is located in a mountainous area which has a continental climate with an average annual temperature of 7 to 7.5°C in the reservoir area (Erhan, 1988). The main tributaries (Fig. 1) of the reservoir are the Bistriţa River with a mean discharge of 1.25 km^3/year, and the Bistricioara River with a discharge of 0.21 km^3/year. Other tributaries are negligible due to a mean annual discharge of 0.016 km^3/year. The years 2005 and 2006 were particularly wet, resulting in a mean inflow of 1.76 and 2.04 km^3/year respectively, and a mean outflow of 2.09 and 2.17 km^3/year respectively (INHGA, 2008).

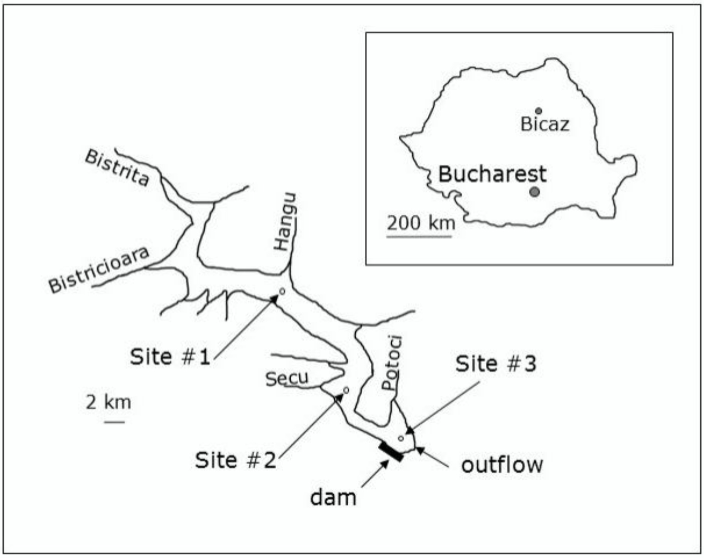

Fig. 1 Location of the Bicaz reservoir and collection sites.

Water outflow occurs through an outlet tunnel located about 45 m below the maximum level of the reservoir, between the Potoci bay and the dam (Fig. 1). During the surveys, the outflow depth varied from 30 to 50 m (centre of the outflow) depending on water level.

Data (temperature, electrical conductivity, major and selected trace elements) from the 2005 and 2006 surveys demonstrate that the water column of the Bicaz reservoir exhibits both winter and summer stratification (Gassama et al., 2012). Summer stratification starts in June-July and is marked in October (Fig. 2). During winter, low temperatures induce a winter thermal stratification with occasional ice. In October 2005, an intrusion layer formed by river waters rapidly dipped, supplying the deep current at the outflow depth (30 to 50 m), which limited the deepening of the thermocline. In April 2006, an intrusion layer became less pronounced at the downstream site, and a weak deep current (at a depth of about 30 m) restricted exchanges between the top and bottom of the water column. In June 2006, a stable intrusion layer (at a depth of 10 to 20 m) and a deep current (at a depth of 40 to 60 m) were recorded. This intrusion layer was recorded at about the same depth in July 2005.

3. Sampling and analytical procedures

Water sampling

Samples were collected in July 2005 (only at site #3, A3 profile), October 2005 (B series: B1, B2 and B3), April 2006 (C1, C2 and C3), and June 2006 (D1, D2 and D3). Sampling of the water column was made with a vertical water sampler (transparent acrylic tube) attached to a graduated nylon rope. The water column was sampled at depths of 0, 5, 10, 15, 20 m and then every 10 m down to the bottom (minus approximately 2 m). Major, minor (nutrients, F, Fe and Mn) and selected trace elements (Li, Be, Al, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Sn, Sb, Ba, Pb, Th, U and Cs) were analyzed in filtered and unfiltered water. Samples were filtered on site with 0.45 µm cellulose acetate membrane filters, which had previously been rinsed with the sample. Aliquots for cation and nutrient determinations were acidified to pH=2 with Suprapur grade nitric acid (Merck). Samples were stored in polypropylene bottles at ca. 4°C until analysis. For unfiltered water samples, additional acid was added in the laboratory prior to analysis.

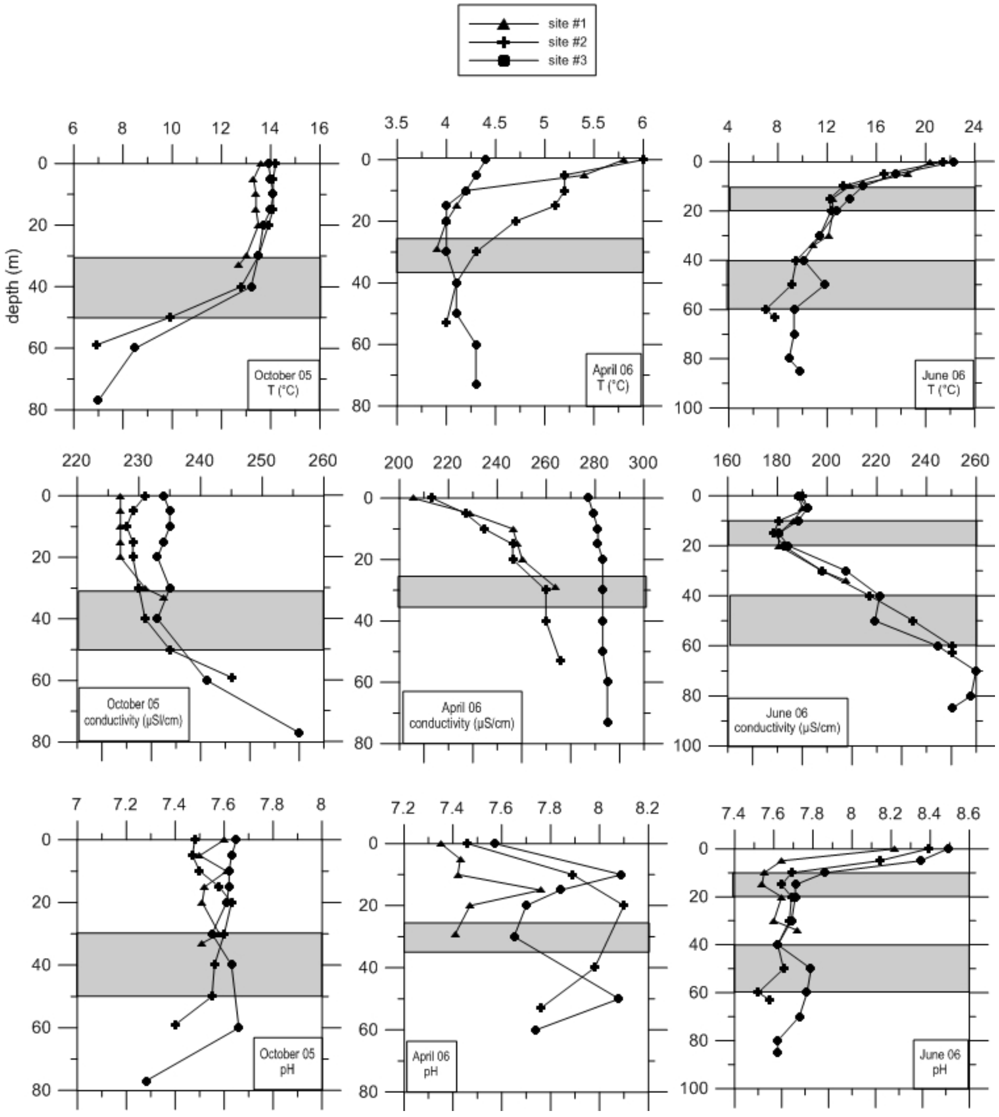

Fig. 2 Profiles of T, electrical conductivity and pH measured in the water column in October 2005, April 2006 and June 2006, at each site. Specific water layers are indicated in grey. In October 2005, the thermocline is at the deep layer depth. In June 2006, it is at the intrusion layer depth.

Concentrations measured in filtered water samples corresponded to the true dissolved phase plus colloidal fraction concentrations. Element concentrations in suspended particles were determined by the difference between concentrations measured in unfiltered (here called "total" concentration) and in filtered ("dissolved" concentration) water samples. The concentration in particulate matter calculated in this way (ASP: acid soluble phases) corresponds to elements present in amorphous phases, which are acid soluble, in carbonates, and to elements adsorbed on stable solids such as clays. For solubility reasons, silicate minerals and stable sulfides were not taken into account.

ICP-MS and X-ray fluorescence analyses were performed in Cologne, others in Tours.

Sediment sampling

One sediment core (approximately 50 cm in length) was recovered at each site in October 2007 using a gravity corer equipped with a crystal-clear PVC tube (Uwitec, corer 90 mm). Once ashore, cores were cut every 3 cm with a plastic cutter and stored in plastic bags. The sediment cores were sufficiently compact to sample the first centimeters without any difficulty.

Solution analyses

Electrical conductivity, pH and temperature were measured immediately on site in the boat. Alkalinity was determined by titrimetry (Gran method calculation) on the sampling day. Major cation (Na, K, Ca and 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. Silicium and trace elements were measured by inductively coupled plasma quadrupole mass-spectrometry (ICP-MS, Perkin Elmer/Sciex Elan 6000). Organic carbon was measured using a Shimadzu carbon analyser (TOC-VCSH/ASIV/TNM). Data on major elements and nutrients are available in Gassama et al. (2009). Silicium, dissolved and particulate organic carbon, and trace elements are presented in Table 1.

Sediment analyses

Major elements in sediments were analyzed using X-ray fluorescence with a Philips PW2400 spectrometer following the "oxiquant" procedure. Seventy-two natural rocks and clays were used as certified reference materials (CRMs) for calibration.

A soft digestion of sediment samples was carried out at room temperature for 10 days, using a solution of 0.01 mol/L of Suprapur grade HNO_3 (Merck) (25 mL of acid for 2 g of dry sediments). Using this procedure, only amorphous and carbonated minerals are dissolved. These solutions were analyzed using ICP-MS. First, a TotalQuant (semiquantitative) analysis was performed to encompass the concentration range of samples. Secondly, based on these data, element concentrations were measured using as internal standards Ru-Re 10 $ng.ml^{-1}$ added to blanks, samples and calibration standards to minimize drift effects of the spectrometer.

Calibration solutions were prepared with high purity chemical reagents (Merck Suprapur, Perkin Elmer and High-Purity Standards as single and/or multi-element solutions). A batch of 5 to 7 samples was bracketed by two calibration procedures. Accuracy and precision of determinations were checked with well-defined CRMs (Govindaraju, 1994; Dulski, 2001).

Identification of solid phases in sediments

Mineral composition was determined by powder X-ray diffraction (XRD) using a Rigaku diffractometer (Rigaku Corporation, Tokyo, Japan) (47 bulk samples). All samples were run at 40 kV, 15 mA, using Cu-Kα radiation (1.53 Å), with a scan speed of 7.2°/min, between 3.0 and 44.0° with a step size of 0.03°. The American Mineralogist Crystal Structure Database (AMCSD) was used to identify mineral phases from the diffractograms.

Tab. 1 Concentrations of selected elements measured in the water column

	depth	Si		Al		Fe		Mn		Li		Rb		Cs		Sr		Ba		V		Cr	
	m	µmol/L		µmol/L		µmol/L		µmol/L		µmol/L		nmol/L		nmol/L		µmol/L		nmol/L		nmol/L		nmol/L	
		diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP
July 2005																							
#3	0	26.7	0.0	2.01	0.54	0.00	0.20	0.03	0.02	0.43	0.03	10.14	1.08			1.30	0.07	149.1	0.5	4.59	1.49	4.13	16.25
	5	56.6	0.0	2.01	0.35	0.00	0.26	0.04	0.01	0.45	0.03	11.86	0.04			1.43	0.00	165.0	0.0	4.89	0.73	2.60	3.90
	10	83.5	0.0	1.28	0.97	0.00	0.59	0.02	0.04	0.45	0.05	10.51	0.25			1.51	0.00	184.8	2.4	4.50	0.65	0.00	10.38
	15	99.9	1.9	1.16	0.44	0.00	0.17	0.01	0.02	0.43	0.02	9.96	0.68			1.43	0.01	177.8	9.9	3.81	0.27	2.38	1.42
	20	108.3	0.0	0.95	0.57	0.00	0.45	0.01	0.26	0.49	0.00	10.14	0.34			1.42	0.01	176.0	4.5	2.32	1.85	0.13	3.77
	30	107.9	4.3	1.17	5.06	0.08	1.04	0.04	0.04	0.39	0.05	11.86	0.11			1.30	0.07	168.0	20.8	3.24	3.83	2.77	11.19
	40	106.5	1.4	1.11	1.43	0.00	1.00	0.03	0.08	0.41	0.01	12.13	0.00			1.34	0.03	166.9	16.8	2.93	1.92	2.44	0.00
	50	98.4	8.7	0.66	1.16	0.01	0.42	0.02	0.09	0.45	0.04	13.01	0.00			1.56	0.00	192.0	16.2	2.51	1.71	2.40	0.00
	60	95.8	6.4	0.72	1.01	0.05	0.63	0.01	0.13	0.43	0.13	12.10	0.27			1.46	0.04	179.5	24.4	2.51	1.32	2.83	0.00
October 2005																							
#1	0	85.6	0.0	1.14	0.85	0.00	0.49	0.03	0.08	0.54	0.00	11.21	0.48	0.02	0.01	1.61	0.00	194.9	0.0	0.00	0.00	0.00	0.00
	5	82.8	4.5	1.05	1.12	0.00	0.71	0.02	0.11	0.54	0.00	12.72	0.00	0.02	0.02	1.57	0.00	186.5	0.0	1.28	4.04	0.00	0.00
	10	83.3	5.7	1.09	1.25	0.00	0.76	0.01	0.11	0.52	0.02	12.11	0.35	0.01	0.03	1.51	0.02	187.5	7.4	0.00	3.26	0.00	5.79
	15	85.5	0.0	1.32	0.78	0.00	1.30	0.01	0.11	0.56	0.00	12.10	0.57	0.01	0.02	1.58	0.04	193.8	0.0	0.00	3.46	0.00	4.35
	20	85.1	1.9	1.08	1.13	0.00	0.88	0.01	0.12	0.56	0.00	12.07	0.00	0.01	0.04	1.58	0.00	194.0	1.2	0.00	0.00	0.00	0.00
	30	83.4	2.4	1.14	2.54	0.00	2.13	0.32	0.29	0.54	0.00	11.61	1.37	0.02	0.02	1.55	0.00	195.0	0.9	0.00	0.00	0.00	0.00
	33	83.7	2.8	1.86	2.43	0.16	2.76	1.11	0.00	0.62	0.00	13.05	0.00	0.03	0.03	1.64	0.00	228.3	0.0	0.00	0.00	0.00	0.00
#2	0	81.2	3.2	1.26	0.80	0.00	0.49	0.04	0.05	0.50	0.03	11.17	0.77	0.03	0.01	1.58	0.04	204.2	7.8	0.33	2.26	0.00	0.00
	5	81.8	7.1	1.14	1.21	0.27	0.45	0.04	0.08	0.49	0.07	11.85	0.26	0.02	0.02	1.64	0.00	205.5	7.6	0.33	0.98	0.00	0.00
	10	85.4	2.6	1.05	1.50	0.00	1.34	0.02	0.11	0.53	0.02	11.70	0.29	0.02	0.02	1.50	0.04	181.2	25.2	0.41	0.53	0.00	0.00
	15	86.4	1.8	1.11	1.29	0.00	0.72	0.03	0.11	0.52	0.04	12.10	0.29	0.01	0.05	1.59	0.04	196.2	18.7	0.00	2.55	0.00	0.00
	20	89.8	0.0	1.18	1.61	0.00	0.87	0.04	0.14	0.56	0.00	11.74	0.54	0.02	0.03	1.64	0.00	208.7	2.7	0.00	8.19	0.00	1.25
	30	79.2	6.0	1.20	1.72	0.00	0.96	0.02	0.31	0.56	0.02	11.71	0.81	0.02	0.04	1.62	0.05	197.8	24.6	0.00	7.73	0.00	4.92
	40	80.5	5.6	1.62	2.63	0.45	2.16	0.15	0.78	0.60	0.00	12.50	1.02	0.02	0.06	1.57	0.15	193.8	53.9	0.00	10.68	0.00	10.23
	50	98.1	0.2	0.79	2.41	0.00	1.35	0.05	0.22	0.52	0.00	12.33	0.29	0.02	0.03	1.58	0.06	194.0	28.3	0.00	4.63	0.00	4.27

	depth	Si		Al		Fe		Mn		Li		Rb		Cs		Sr		Ba		V		Cr	
	m	µmol/L		µmol/L		µmol/L		µmol/L		µmol/L		nmol/L		nmol/L		µmol/L		nmol/L		nmol/L		nmol/L	
		diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP
	59	109.8	4.6	0.46	3.82	0.00	2.32	0.02	0.36	0.50	0.00	18.28	2.05	0.02	0.08	1.77	0.00	206.4	24.5	1.18	3.80	0.00	0.00
#3	0	79.5	3.8	0.91	0.87	0.00	0.82	0.02	0.07	0.49	0.04	11.28	0.06	0.02	0.04	1.65	0.00	215.9	0.0	2.36	3.57	0.00	0.00
	5	77.1	1.5	0.86	0.97	0.00	0.50	0.02	0.07	0.52	0.07	10.59	0.60	0.02	0.04	1.57	0.00	205.9	2.1	4.40	0.00	2.13	0.00
	10	80.2	0.3	0.86	1.15	0.08	0.74	0.02	0.08	0.49	0.10	11.07	0.11	0.02	0.02	1.58	0.00	217.3	0.0	3.85	0.00	0.00	0.00
	15	84.6	1.1	1.02	1.05	0.32	0.26	0.02	0.09	0.56	0.00	11.65	0.01	0.02	0.03	1.63	0.03	225.4	0.0	5.38	0.00	7.08	0.00
	20	79.9	8.0	1.17	1.24	0.12	0.83	0.02	0.20	0.55	0.04	12.55	0.15	0.02	0.02	1.74	0.00	229.6	0.0	6.48	0.00	3.56	0.00
	30	90.1	3.7	1.18	1.75	0.17	0.94	0.02	0.32	0.60	0.02	12.12	0.66	0.02	0.05	1.70	0.04	223.9	0.0	7.50	0.00	8.40	0.00
	40	84.3	7.7	2.30	1.03	1.09	0.41	0.27	0.17	0.53	0.09	12.89	0.00	0.06	0.00	1.57	0.06	208.1	0.0	4.67	0.00	4.13	0.00
	60	98.9	2.6	0.49	1.95	0.00	1.53	0.02	0.19	0.55	0.01	15.42	0.00	0.02	0.06	1.50	0.07	206.4	0.0	1.41	0.54	2.51	0.00
	77	104.1	11.2	0.36	2.78	0.00	1.74	0.02	1.72	0.60	0.05	20.95	2.25	0.02	0.08	1.45	0.47	193.2	24.1	0.00	2.98	0.00	0.00
April 2006																							
#1	0	119.3	14.4	1.54	17.91	0.59	16.87	1.75	1.23	0.39	0.14	10.74	4.04	0.05	0.20	1.20	0.07	190.3	61.7	9.46	17.00	4.25	8.25
	5	112.0	11.0	0.82	15.60	0.25	15.75	1.82	1.31	0.49	0.06	11.48	3.31	0.03	0.23	1.27	0.13	208.5	56.2	7.64	14.21	5.31	5.50
	10	110.6	11.2	0.84	13.73	0.36	14.14	1.90	1.35	0.53	0.09	11.62	2.27	0.03	0.19	1.44	0.13	235.2	40.1	7.75	14.59	4.73	7.37
	15	109.5	17.2	1.03	15.92	0.60	15.54	2.05	1.53	0.50	0.11	12.72	3.83	0.02	0.23	1.47	0.17	247.4	65.9	7.50	16.06	22.52	0.00
	20	106.4	0.7	0.89	7.75	0.46	5.84	2.30	0.00	0.47	0.20	12.68	0.00	0.02	0.15	1.50	0.32	248.2	0.0	6.18	4.59	5.56	2.88
	29	106.6	36.4	0.65	29.54	0.20	25.91	2.56	1.81	0.55	0.17	13.70	7.99	0.02	0.43	1.76	0.05	257.0	98.5	5.03	28.74	4.17	20.63
#2	0	116.5	10.6	1.13	15.74	0.57	15.45	1.67	1.20	0.43	0.06	11.04	4.54	0.02	0.21	1.21	0.08	195.3	66.1	5.54	19.36	3.69	8.96
	5	115.6	12.1	1.26	20.48	0.60	19.58	1.70	1.34	0.42	0.22	11.01	7.06	0.04	0.30	1.30	0.07	210.0	58.7	6.34	17.18	5.81	7.88
	10	112.2	4.1	1.29	13.65	0.93	13.67	1.78	1.00	0.48	0.12	11.59	3.45	0.03	0.19	1.45	0.00	223.6	53.7	5.97	13.88	4.92	4.40
	15	111.6	15.0	1.14	17.84	0.67	16.64	1.64	1.31	0.49	0.16	12.34	4.06	0.04	0.26	1.49	0.01	233.8	47.3	6.56	16.33	5.58	10.56
	20	110.5	6.8	1.17	14.42	0.56	13.31	1.68	1.14	0.53	0.09	12.41	3.00	0.02	0.23	1.49	0.15	241.6	54.6	6.30	12.84	4.96	7.00
	30	95.9	19.5	0.80	13.78	0.50	11.19	1.38	1.10	0.58	0.03	10.65	4.32	0.03	0.21	1.44	0.26	226.1	50.4	3.81	11.96	0.00	10.62
	40	104.1	6.7	0.85	10.80	0.35	10.30	1.40	1.05	0.61	0.01	11.59	2.28	0.04	0.14	1.69	0.08	237.5	37.9	7.46	4.46	0.13	16.60
	53	101.3	10.7	0.69	10.78	0.20	9.96	1.39	1.18	0.61	0.04	11.02	4.10	0.03	0.16	1.63	0.11	219.2	75.4	1.98	12.96	0.00	9.38
#3	0	97.6	0.0	0.61	1.42	0.00	1.10	0.06	0.22	0.62	0.02	11.28	0.25	0.02	0.00	1.90	0.00	230.0	6.7	4.55	0.00	0.00	0.00
	5	97.1	0.0	0.41	1.84	0.00	1.35	0.04	0.29	0.68	0.00	10.35	0.99	0.02	0.01	1.85	0.00	219.0	20.9	2.91	0.00	0.00	0.00
	10	96.9	3.5	0.43	2.71	0.00	2.07	0.02	0.33	0.70	0.00	10.85	1.45	0.02	0.05	1.90	0.15	224.3	30.8	1.47	5.30	0.00	4.21
	15	97.3	4.4	0.44	2.93	0.00	2.21	0.02	0.38	0.63	0.02	10.81	1.21	0.00	0.06	1.82	0.18	226.8	34.2	2.25	6.19	0.00	4.58

	depth	Si		Al		Fe		Mn		Li		Rb		Cs		Sr		Ba		V		Cr	
	m	µmol/L		µmol/L		µmol/L		µmol/L		µmol/L		nmol/L		nmol/L		µmol/L		nmol/L		nmol/L		nmol/L	
		diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP
	20	98.4	0.0	0.44	3.34	0.00	2.42	0.01	0.39	0.65	0.00	11.40	0.20	0.00	0.06	1.86	0.14	240.5	5.5	5.10	0.00	0.00	1.54
	30	95.5	4.1	0.43	3.06	0.00	2.43	0.02	0.45	0.61	0.00	10.40	1.86	0.01	0.06	1.92	0.05	236.5	14.9	4.10	2.34	0.00	3.54
	40	99.1	0.0	0.42	3.17	0.00	2.47	0.03	0.52	0.66	0.00	11.23	1.12	0.01	0.05	1.89	0.08	243.4	17.0	3.08	3.47	0.00	1.88
	50	101.0	0.0	0.43	3.13	0.00	2.44	0.03	0.58	0.58	0.08	11.37	1.08	0.00	0.08	1.87	0.17	240.0	24.6	2.53	3.00	0.90	0.00
	60	99.5	1.1	0.42	4.73	0.00	3.85	0.07	0.65	0.64	0.06	10.75	1.94	0.01	0.08	1.87	0.12	229.4	36.0	1.69	6.20	0.00	4.94
	73	98.8	4.3	0.37	7.68	0.00	6.28	0.07	0.79	0.64	0.09	9.69	3.69	0.02	0.12	1.85	0.23	225.2	39.2	4.24	8.29	0.00	8.13
June 2006																							
#1	0	113.2	0.0	2.70	3.58	0.00	3.12	0.04	0.19	0.42	0.04	10.52	0.90	0.04	0.09	1.29	0.00	121.6	0.8	4.88	2.42	0.00	1.83
	5	120.4	22.5	2.61	16.80	0.16	12.15	0.09	0.73	0.38	0.08	11.54	6.05	0.05	0.28	1.10	0.06	119.4	44.9	4.77	11.92	0.00	7.94
	10	132.8	8.3	2.23	9.41	0.23	6.60	0.03	0.40	0.37	0.02	10.06	2.27	0.03	0.12	1.11	0.05	116.3	24.4	3.06	6.91	0.00	1.46
	15	139.9	6.1	8.23	6.53	4.63	4.17	0.30	0.26	0.37	0.01	11.84	1.58	0.11	0.11	1.12	0.00	127.2	20.9	9.13	4.28	4.67	0.87
	20	124.8	30.7	2.14	21.69	0.54	12.83	0.04	0.71	0.33	0.19	10.25	6.20	0.05	0.35	1.10	0.00	116.2	50.3	5.40	14.25	0.00	9.67
	30	118.2	29.0	1.60	20.05	0.22	13.80	0.03	0.59	0.37	0.13	10.26	5.51	0.03	0.26	1.20	0.12	134.4	46.1	4.28	13.98	0.77	10.63
	34	119.2	20.9	1.59	18.36	0.16	12.87	0.03	0.55	0.39	0.17	11.43	4.55	0.02	0.27	1.25	0.13	140.4	43.6	2.18	15.16	0.00	8.33
#2	0	109.4	0.0	2.55	1.48	0.00	0.68	0.02	0.05	0.39	0.04	9.42	0.50	0.04	0.02	1.28	0.00	129.8	0.0	4.28	0.00	0.00	0.00
	5	127.2	0.0	4.78	0.19	1.38	0.15	0.10	0.01	0.36	0.00	10.64	0.19	0.06	0.00	1.27	0.03	135.9	0.0	5.18	2.02	0.23	1.29
	10	128.2	4.2	2.31	7.11	0.37	4.27	0.04	0.24	0.30	0.05	9.90	2.20	0.03	0.12	1.02	0.08	111.2	20.2	1.12	9.42	0.00	3.65
	15	125.1	7.5	2.03	11.39	0.28	7.56	0.03	0.39	0.32	0.00	10.55	2.43	0.02	0.20	1.01	0.08	117.3	26.5	2.83	10.33	0.00	5.50
	20	120.1	20.5	1.87	12.70	0.55	8.29	0.03	0.39	0.33	0.08	9.89	2.98	0.03	0.17	1.01	0.12	118.6	36.1	2.55	12.23	0.00	6.75
	30	123.1	2.6	1.53	6.36	0.00	4.25	0.02	0.23	0.35	0.05	10.38	0.89	0.02	0.13	1.18	0.06	130.0	19.0	5.01	3.46	0.00	1.40
	40	114.3	12.0	1.33	6.84	0.06	4.72	0.02	0.25	0.39	0.05	11.40	1.37	0.02	0.12	1.31	0.12	155.0	35.0	3.24	6.64	0.00	4.70
	50	118.5	0.3	1.27	6.01	0.24	4.11	0.02	0.22	0.53	0.04	11.59	1.66	0.03	0.11	1.53	0.01	195.3	1.5	4.61	4.95	0.90	2.77
	60	108.1	6.8	0.83	5.89	0.21	4.06	0.02	0.24	0.52	0.05	11.77	1.56	0.02	0.14	1.57	0.13	212.4	7.7	3.83	6.03	0.00	4.58
	63	109.1	3.7	1.03	5.40	0.16	3.58	0.08	0.35	0.53	0.06	12.16	1.78	0.02	0.11	1.57	0.17	208.2	21.4	4.18	5.05	1.02	2.48
#3	0	99.9	9.8	2.33	1.15	0.00	0.99	0.02	0.04	0.36	0.06	9.25	0.68	0.02	0.03	1.24	0.07	115.7	30.1	3.38	2.87	0.00	0.00
	5	108.3	2.6	2.18	1.52	0.00	1.49	0.01	0.05	0.45	0.02	9.48	0.71	0.02	0.03	1.27	0.02	125.6	15.2	4.08	1.98	0.00	0.00
	10	118.1	18.3	2.12	4.83	0.16	3.83	0.02	0.16	0.36	0.10	10.12	1.08	0.02	0.09	1.16	0.07	115.5	37.0	3.16	5.87	0.00	0.83
	15	127.2	5.8	2.15	5.93	0.35	4.71	0.03	0.20	0.33	0.04	10.80	1.54	0.02	0.09	1.13	0.00	120.9	19.0	6.24	5.16	0.52	9.06
	20	118.7	7.6	1.82	7.98	0.85	5.50	0.03	0.26	0.32	0.04	10.35	1.79	0.03	0.11	1.10	0.00	120.8	20.6	3.57	8.13	0.00	7.88

depth	Si		Al		Fe		Mn		Li		Rb		Cs		Sr		Ba		V		Cr	
m	µmol/L		µmol/L		µmol/L		µmol/L		µmol/L		nmol/L		nmol/L		µmol/L		nmol/L		nmol/L		nmol/L	
	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP
30	119.1	0.0	1.41	3.32	0.01	2.87	0.02	0.13	0.38	0.04	10.58	0.00	0.03	0.05	1.24	0.00	152.1	2.1	3.00	3.95	0.06	2.63
40	119.5	0.0	2.23	2.61	0.71	2.55	0.05	0.12	0.47	0.00	11.47	0.00	0.05	0.04	1.44	0.00	174.6	1.9	4.81	3.06	0.62	4.06
50	108.2	5.6	1.79	3.45	0.11	3.13	0.02	0.14	0.43	0.02	10.39	0.70	0.02	0.05	1.31	0.00	153.0	20.1	2.89	4.18	1.10	1.70
60	104.0	10.0	1.12	3.07	0.18	2.84	0.02	0.15	0.50	0.01	10.07	1.80	0.05	0.03	1.55	0.04	181.6	29.9	3.44	3.73	1.87	4.21
70	98.5	7.9	0.86	2.60	0.00	2.48	0.02	0.14	0.54	0.02	10.03	1.15	0.02	0.05	1.55	0.10	191.6	26.3	3.24	2.49	0.00	4.42
80	98.6	8.8	0.87	2.41	0.00	2.09	0.03	0.16	0.55	0.08	10.79	1.23	0.03	0.02	1.59	0.14	193.8	27.7	3.59	2.39	4.85	0.00
85	101.4	10.1	0.98	4.25	0.08	3.37	0.08	0.36	0.47	0.09	10.49	1.80	0.03	0.06	1.57	0.01	180.7	29.5	2.75	4.49	6.60	0.00

Tab. 1 Concentrations of selected elements measured in the water column (*continuation*)

	depth	Co		Ni		Cu		Zn		Cd		Pb		As		Sb		Th		U		COD	COP
	m	nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		pmol/L		nmol/L		mg/L	mg/L
		diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP		
July 2005																							
#3	0	1.22	0.81	10.34	45.15	19.89	14.56	141.96	1.33	0.09	0.20	0.26	2.99	16.03	0.00	0.42	0.29	0	4	1.50	0.00	2.46	
	5	1.58	0.05	15.81	5.52	37.99	15.82	154.87	0.00	0.26	0.35	1.86	3.99	12.25	0.00	0.53	0.45	4	4	1.66	0.00	2.55	
	10	1.46	0.39	17.53	0.24	31.76	23.02	117.15	97.43	0.32	0.68	1.03	8.69	9.49	0.00	0.46	0.21	0	9	1.38	0.09	2.80	
	15	1.12	0.58	14.89	1.84	21.81	4.77	135.49	4.07	0.33	0.20	0.73	3.47	7.88	0.00	0.47	0.00	0	9	1.49	0.00	2.30	
	20	1.15	0.93	11.41	4.38	20.87	3.64	98.16	13.86	0.15	0.00	0.23	1.15	8.33	0.00	0.39	0.08	0	9	1.52	0.00	2.25	
	30	1.20	0.88	11.94	11.62	28.53	22.21	133.81	105.49	0.26	0.08	2.18	3.62	9.68	0.00	0.54	1.02	4	13	1.50	0.16	2.29	
	40	1.27	0.92	15.74	0.00	29.23	1.84	153.66	31.77	0.22	0.15	1.80	1.71	7.97	0.84	0.61	0.00	9	22	1.81	0.00	2.50	
	50	1.14	0.32	14.75	0.60	21.83	3.81	96.10	26.94	0.09	0.11	0.24	1.65	9.08	0.00	0.53	0.10	0	22	1.96	0.00	2.05	
	60	1.44	0.54	14.41	5.08	21.64	6.91	86.06	264.94	0.13	0.04	0.30	2.18	7.65	0.40	0.53	0.00	0	13	1.91	0.04	2.24	
October 2005																							
#1	0	1.46	0.05	6.10	1.18	36.13	0.00	101.84	7.24	0.12	0.00	0.66	0.11	10.29	0.00	0.49	0.10	0	9	2.70	0.00	2.14	5.74
	5	1.19	0.58	7.65	0.12	36.01	0.76	106.13	3.24	0.10	0.20	1.53	10.49	10.32	0.00	0.52	0.00	4	0	2.70	0.00	2.14	1.94

	depth	Co		Ni		Cu		Zn		Cd		Pb		As		Sb		Th		U		COD	COP
	m	nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		pmol/L		nmol/L		mg/L	mg/L
		diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP		
	10	1.09	1.02	10.29	2.13	43.56	0.36	111.40	18.53	0.15	0.02	3.61	16.48	8.26	4.30	0.57	0.11	4	0	2.62	0.14	3.00	0.72
	15	1.36	0.49	7.95		32.09	0.00	104.99	0.00	0.01	0.23	1.36	1.79	8.34	2.76	0.54	0.00	0	4	2.85	0.00	2.24	1.29
	20	1.19	0.76	6.42	2.13	28.67	4.00	95.93	28.53	0.00	0.18	0.43	1.61	8.94	1.78	0.48	0.21	0	13	2.64	0.08	2.42	1.97
	30	1.82	1.68	7.97	3.95	29.37	2.90	104.99	25.29	0.06	0.09	0.53	2.04	8.25	1.67	0.62	0.00	0	9	2.73	0.00	2.23	4.32
	33	3.75	0.69	13.88		49.83	0.00	181.41	0.00	0.17	0.01	3.69	0.00	10.72	0.00	0.78	0.00	4	15	3.06	0.00	1.99	2.98
#2	0	1.36	0.92	11.21	4.91	88.64	0.00	101.32	0.00	0.02	0.04	0.66	1.03	8.68	1.01	0.87	0.00	4	0	2.53	0.08	2.32	7.96
	5	1.24	0.59	11.80	1.92	30.91	0.00	88.16	0.00	0.04	0.00	0.54	0.66	11.13	0.00	0.62	0.09	4	0	2.60	0.20	2.17	6.45
	10	1.12	0.93	10.17	7.27	28.05	5.21	80.48	16.31	0.13	0.28	0.44	1.90	10.44	0.00	0.54	0.03	0	9	2.75	0.06	2.13	5.84
	15	1.17	0.63	12.31		29.41	0.00	86.69	8.00	0.12	0.00	0.43	0.46	10.58	0.00	0.57	0.05	4	0	2.75	0.00	2.16	7.76
	20	1.20	1.04	11.65	4.65	30.96	0.00	88.65	2.39	0.11	0.04	0.39	0.70	9.84	2.46	0.57	0.05	4	0	2.90	0.00	2.16	2.04
	30	1.27	1.12	11.82	6.63	28.71	0.87	86.71	76.04	0.16	0.00	0.46	1.89	9.68	0.96	0.66	0.00	0	4	2.84	0.03	2.16	1.59
	40	1.49	3.53	15.47	9.32	30.30	6.37	109.99	54.00	0.20	0.00	0.38	1.49	8.68	2.86	0.55	0.11	0	9	2.65	0.33	2.03	2.01
	50	1.27	1.20	10.94	3.65	28.36	5.26	96.04	29.19	0.02	0.12	0.28	2.77	8.81	0.49	0.50	0.00	0	13	2.42	0.00	2.15	3.76
	59	1.48	1.08	13.49	2.11	25.17	2.56	87.30	16.34	0.02	0.04	0.25	1.73	8.54	1.50	0.48	0.00	1	24	2.27	0.00	2.25	2.71
#3	0	1.20	0.92	11.57	4.56	26.36	0.55	114.50	0.00	0.03	0.14	0.06	1.84	9.57	0.36	0.58	0.16	0	4	2.63	0.07	2.30	2.98
	5	1.31	0.42	10.08	3.37	27.23	1.73	104.08	0.00	0.00	0.00	0.48	6.43	9.37	0.00	0.62	0.00	4	9	2.53	0.00	2.50	3.84
	10	1.34	0.61	7.97	8.07	26.55	6.11	103.90	8.44	0.05	0.00	0.58	1.08	9.45	0.00	0.64	0.23	4	4	2.57	0.00	2.31	2.22
	15	1.54	0.58	12.01	2.28	28.72	0.00	102.19	0.00	0.12	0.00	0.53	0.50	9.64	0.51	0.65	0.00	4	0	2.73	0.00	2.22	13.45
	20	1.34	0.90	10.83	11.43	37.17	0.00	125.29	0.00	0.00	0.10	1.53	0.00	11.13	0.00	0.89	0.00	4	0	2.80	0.00	2.14	6.40
	30	1.70	0.93	15.93	5.09	32.80	0.00	109.32	12.45	0.11	0.00	0.97	0.10	10.96	0.00	0.60	0.00	4	4	2.88	0.00	2.17	2.07
	40	2.38	0.75	11.97	8.16	29.35	4.42	108.67	13.34	0.11	0.00	0.67	0.42	11.23	0.00	0.52	0.02	4	4	2.70	0.00	2.56	5.39
	60	1.44	0.66	16.10	2.75	21.64	18.07	96.50	33.81	0.03	0.07	0.24	2.16	9.27	0.00	0.49	0.56	1	11	2.21	0.00	2.06	19.64
	77	1.48	1.41	17.24	5.52	20.00	4.06	102.55	10.78	0.00	0.12	0.12	0.99	10.04	1.35	0.32	0.11	0	9	2.17	0.13	2.12	1.78
April 2006																							
#1	0	5.40	11.00	25.38	13.15	40.02	36.15	88.04	137.80	0.06	0.28	0.18	12.42	12.59	10.50	0.97	0.24	34	302	2.58	0.18	15.43	
	5	4.28	11.84	23.44	7.24	39.86	46.30	112.71	144.78	0.20	0.28	0.16	19.71	10.60	14.90	1.17	0.10	22	315	3.13	0.03	6.46	
	10	4.04	10.15	23.78	4.75	32.18	32.09	89.57	110.74	0.09	0.14	0.00	13.32	11.95	12.17	1.10	0.04	22	272	3.26	0.18	2.84	
	15	4.77	11.81			32.97	33.60	93.13	114.18	0.10	0.23	0.01	12.22	12.49	13.55	1.18	0.00	17	319	3.39	0.26	2.81	

	depth	Co		Ni		Cu		Zn		Cd		Pb		As		Sb		Th		U		COD	COP
	m	nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		pmol/L		nmol/L		mg/L	mg/L
		diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP		
	20	5.02	0.03	22.96	0.00	33.03	0.98	90.00	66.19	0.10	0.00	0.34	2.17	12.53	0.00	1.22	0.00	26	73	3.60	0.00	2.76	
	29	4.85	14.61	29.93	21.94	33.29	109.16	89.26	168.46	0.11	0.41	0.32	16.61	13.91	15.56	1.24	0.24	17	457	3.47	0.25	16.14	
#2	0	4.77	11.37	24.34	4.39	32.97	29.34	78.37	107.92	0.11	0.14	0.37	11.29	11.35	11.83	1.07	0.08	30	280	2.68	0.00	24.37	
	5	4.21	11.78	25.63	6.85	32.25	30.45	83.49	116.54	0.09	0.16	0.53	10.43	12.45	8.60	1.01	0.11	34	396	2.92	0.02	4.89	
	10	4.34	9.99	26.45	6.17	36.15	59.74	91.97	91.59	0.09	0.17	0.78	8.30	11.49	9.78	1.02	0.00	26	267	3.00	0.00	3.84	
	15	4.17	10.18	28.97	3.42	31.65	24.94	90.32	88.73	0.06	0.02	0.61	8.05	12.04	8.62	1.13	0.02	26	392	3.19	0.11	5.98	
	20	4.33	9.06	29.74	10.66	29.73	21.81	85.19	95.32	0.08	0.24	0.56	9.65	11.33	12.19	1.12	0.15	30	254	3.27	0.17	3.02	
	30	3.09	8.16	24.03		25.98	20.66	81.00	73.89	0.15	0.03	0.38	5.61	11.35	8.30	0.96	0.27	22	233	3.05	0.19	5.51	
	40	2.66	7.47	8.65	23.61	26.82	19.42	90.67	46.15	0.06	0.07	0.00	5.77	12.89	6.19	1.13	0.03	0	233	3.17	0.13	7.35	
	53	2.77	7.23	8.45	14.92	27.75	19.18	83.77	70.45	0.07	0.12	0.00	7.51	10.14	9.80	1.05	0.08	13	254	3.04	0.22	10.39	
#3	0	1.29	1.12	5.84	3.80	25.29	2.68	86.32	15.88	0.04	0.04	0.00	1.12	9.12	0.00	0.84	0.08	0	13	2.90	0.10	1.78	
	5	1.22	1.19	6.51	1.96	25.68	1.89	91.13	14.13	0.24	0.00	0.11	2.45	9.89	0.37	0.99	0.00	4	13	2.81	0.00	1.90	
	10	1.34	1.63	7.09	7.10	23.26	6.67	90.38	19.73	0.07	0.05	0.00	2.49	9.76	0.00	0.90	0.00	0	26	2.87	0.20	4.56	
	15	1.25	2.25	7.24	3.49	23.28	5.00	78.80	31.15	0.06	0.00	0.00	2.15	8.88	0.03	0.86	0.00	0	30	2.88	0.23	4.40	
	20	1.37	1.87	8.01	7.60	21.18		84.30	22.98	0.04	0.12	0.00	3.55	9.94	0.00	0.98	0.24	0	22	2.78	0.07	4.45	
	30	1.22	2.34	5.48	7.77	21.94	5.76	78.69	15.91	0.00	0.11	0.00	1.66	8.61	1.00	0.99	0.00	0	30	2.86	0.09	4.78	
	40	1.10	3.04	8.06	2.32	21.21	7.62	79.99	15.70	0.04	0.00	0.00	2.51	8.64	1.59	0.92	0.01	0	43	2.85	0.17	17.36	
	50	1.17	2.22	7.10	1.99	22.54	7.15	77.82	27.64	0.04	0.07	0.00	1.62	7.92	2.18	0.98	0.00	0	43	2.76	0.19	5.17	
	60	1.27	3.55	10.17	5.48	21.23	10.05	76.40		0.04	0.06	0.00	3.34	8.36	2.17	0.90	0.05	0	62	2.83	0.16	3.15	
	73	1.46	5.26	5.43		21.55	71.54	78.28	44.26	0.00	4.07	0.00	4.38	9.02	1.25	0.86	0.08	4	78	3.02	0.00	17.13	
June 2006																							
#1	0	1.60	1.57	5.14	2.65	34.96	0.00	63.45	17.36	0.03	0.04	0.00	0.60	9.86	0.58	0.72	0.00	13	26	1.53	0.00	2.43	8.91
	5	2.04	6.45	11.91	19.72	55.71	28.60	231.34	45.36	0.14	0.01	1.62	25.07	11.12	4.36	1.03	0.40	17	142	1.70	0.11	3.16	8.32
	10	1.34	3.43	5.93	8.87	30.14	9.85	77.64	41.35	0.07	0.10	0.00	3.43	8.44	3.80	0.71	0.07	30	91	1.59	0.06	2.48	12.67
	15	3.92	2.36	13.49	6.61	42.84	2.99	115.18	20.10	0.00	0.04	2.48	2.39	10.89	0.40	0.77	0.00	138	125	1.76	0.00	2.11	8.28
	20	1.49	7.06	5.40	23.35	33.71	20.07	75.11	83.14	0.02	0.23	0.00	5.81	10.77	1.49	0.90	0.00	52	371	1.69	0.12	2.33	9.61
	30	1.32	7.21	10.41	18.63	29.62	17.61	72.22	71.53	0.02	0.03	0.22	12.11	8.29	2.11	0.90	0.00	39	384	1.87	0.01	2.51	9.36
	34	1.14	7.70	3.27	26.21	27.01	14.76	72.01	60.47	0.05	0.00	0.00	3.95	8.64	0.00	0.80	0.00	34	440	2.02	0.03	2.50	11.93

	depth	Co		Ni		Cu		Zn		Cd		Pb		As		Sb		Th		U		COD	COP
	m	nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		nmol/L		pmol/L		nmol/L		mg/L	mg/L
		diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP	diss.	ASP		
#2	0	1.02	1.15	3.85	0.46	21.70	0.00	68.09	2.08	0.00	0.00	0.00	0.00	8.16	0.00	0.62	0.09	4	17	1.52	0.00	1.87	8.44
	5	2.00	0.03	4.28	0.00	32.61	1.05	78.64	16.67	0.06	0.00	0.66	0.02	9.20	1.86	0.74	0.00	22	9	1.60	0.00	1.04	11.96
	10	1.02	2.90	1.65	9.79	29.65	3.67	67.31	30.27	0.00	0.00	0.00	2.01	7.57	1.63	0.57	0.10	22	116	1.40	0.04	2.29	7.37
	15	1.19	4.72	2.57	12.50	27.76	10.51	69.54	35.78	0.00	0.07	0.00	2.75	9.13	0.00	0.70	0.00	39	207	1.54	0.03	2.53	12.70
	20	1.27	4.75	1.74	20.85	29.51	16.40	67.62	45.43	0.00	0.16	0.00	4.66	7.84	1.59	0.74	0.00	43	151	1.60	0.08	2.31	14.18
	30	1.12	2.55	3.27	8.48	25.89	4.89	72.02	12.69	0.04	0.00	0.00	1.09	7.93	0.10	0.67	0.00	13	95	1.88	0.00	1.59	22.30
	40	1.10	2.60	2.32	11.87	26.69	10.03	65.49	154.41	0.00	0.16	0.00	1.75	6.59	1.95	0.85	0.00	30	106	2.16	0.20	2.13	10.10
	50	1.32	2.14	4.75	7.41	27.94	7.19	66.99	21.58	0.00	0.12	0.00	1.10	8.48	1.17	0.88	0.11	22	108	2.79	0.00	2.05	11.14
	60	1.02	2.66	4.53	13.08	26.88	8.78	70.67	23.97	0.00	0.12	0.00	1.54	6.99	4.07	0.89	0.16	13	121	2.85	0.24	0.43	10.37
	63	1.29	2.12	4.96	7.36	27.15	5.93	70.35	16.22	0.00	0.12	0.00	0.88	7.78	3.56	0.90	0.00	22	73	2.90	0.01	2.07	15.46
#3	0	1.19	0.12	2.49	7.34	21.03	2.42	61.22	16.14	0.00	0.00	0.00	0.57	5.11	2.60	0.71	0.00	0	17	1.46	0.00	2.12	7.89
	5	1.29	0.15	2.83	5.35	23.07	4.44	69.04	11.27	0.00	0.00	0.00	1.03	7.41	0.13	0.69	0.00	9	13	1.51	0.00	1.54	12.68
	10	0.88	1.83	3.07	12.81	26.79	6.55	67.22	29.16	0.00	0.00	0.00	2.52	7.25	2.80	0.67	0.09	22	22	1.42	0.11	2.10	9.98
	15	1.07	3.04	2.49	13.18	28.75	8.06	74.80	28.71	0.00	0.20	0.00	2.73	9.76	0.32	0.76	0.00	26	52	1.54	0.00	2.20	12.03
	20	1.75	2.55	4.62	15.67	33.70	14.72	100.11	25.75	0.08	0.00	0.20	3.99	7.42	1.19	0.77	0.09	30	99	1.55	0.06	2.33	8.34
	30	1.05	1.43	4.12	9.62	23.18	4.69	62.35	24.57	0.00	0.02	0.00	3.28	7.10	0.00	0.91	0.02	17	34	1.97	0.00	1.90	8.73
	40	1.56	1.14	3.53	9.49	26.83	4.11	78.78	6.41	0.01	0.08	0.00	1.67	9.12	0.00	0.97	0.00	30	34	2.36	0.00	2.02	9.18
	50	1.15	1.40	4.75	8.16	25.78	3.92	69.62	17.91	0.07	0.00	0.00	1.73	8.94	0.00	0.79	0.05	17	39	2.09	0.00	2.08	9.44
	60	1.29	0.73	5.26	8.84	23.20	6.22	68.95	23.93	0.04	0.09	0.00	1.50	7.61	1.64	0.92	0.00	22	26	2.50	0.18	2.07	23.10
	70	1.37	0.54	4.50	4.89	24.88	2.53	65.34	22.21	0.03	0.00	0.00	1.14	8.00	1.33	0.77	0.16	9	30	2.52	0.12	2.05	8.84
	80	1.22	0.87	11.34	1.35	21.94	4.04	63.52	19.99	0.00	0.00	0.00	1.11	7.78	1.00	0.88	0.07	9	30	2.34	0.21	2.02	15.18
	85	1.34	1.32	12.16	0.88	21.64	8.11	63.19	29.81	0.00	0.07	0.00	1.63	7.22	2.09	0.86	0.07	13	52	2.17	0.28	2.03	

4. Results

Water conductivity ranged from 180 to 280 µS/cm, and pH ranged from 7.2 to 8.5 (Fig. 2). No data on dissolved oxygen were monitored. For hydrological reasons, the concentration of samples taken in early April (2006) from site #3 derived mainly from the interaction between water and the reservoir basin (small input in winter because of snow precipitation and a relatively long residence time of water) and reflected the carbonaceous nature of the reservoir basin. In June (2005 and 2006, Fig. 2), the pH profile reflected the primary activity in the reservoir.

At all seasons, the dominant water type was Ca-HCO_3 (Gassama et al., 2009). Compared to rivers, reservoir waters were rich in Ca. The saturation index (SI) was calculated using PHREEQC Version 2 with the WATEQ4F database (Parkhurst and Appelo, 1999; Ball and Nordstrom, 1991). A few samples were slightly oversaturated with respect to calcite (A3 surface, 5, 10 m depth; C2 20 m; C3 10, 50 m depth; D1 surface; D2 surface; D3 surface) and the others were close to equilibrium: July 2005 (A), $-0.57 < SI < 0.59$; October 2005 (B), $-0.71 < SI < -0.30$; April 2006 (C), $-1.00 < SI < 0.05$; June 2006 (D), $-0.66 < SI < 0.37$. Also calcite precipitation was not influencing trace element solubility.

4.1 Water column

Major constituents of acid soluble phases

Aluminum, iron and manganese occurred more in the ASP than in the dissolved phase at each season (Tab. 2), except for Al at site #3 in July 05 and Mn at sites #1 and #2 in April (Fig. 3). For a given site and season, Al, Fe, and in many cases Mn, showed a similar pattern of distribution in the ASP fraction. Correlation calculations (Tab. 3) yielded a very stable Al/Fe ratio, from 0.8 to 1.5 (Fig. 4), in these acid soluble phases. Fe/Mn ratios ranged between 8 and 9 in April (site #1 and #3), and between 18 and 20 in June 2006 (at the three sites).

In October, at the end of summer (a period of little rainfall and high biomass production), river waters input mainly particulate Fe, Al and Mn (Fig. 3). The high increase in dissolved Fe and Mn recorded at the level of the current (Fig. 3) implied the presence of anoxic waters in this layer. At site #3, the decrease in ASP content was linked to the reduction of Fe and Mn. No deep current was revealed by data on organic carbon (dissolved and particulate) (Fig. 3).

In April (period of no to low thermal stratification and low authigenic biomass production), a very large quantity of water enters the reservoir because of rainfall and snow melt, with a high load of particles (Tab. 1). At site #3, the water column was homogeneous and oxic (no dissolved Fe or Mn) (Figs. 2 & 3), which is characteristic of dimictic lakes during this season (spring overturn). Although the lake waters were oxic, the slow rate of oxidation of Mn(II) revealed input of reducing waters from rivers (high concentration of dissolved Mn) (site #1 & #2) (Fig. 3). We can assume that the reducing characteristic of these waters was linked to a high load of organic matter and of oxygen-consuming substances. Between sites #2 and #3, the decrease in particle load may be due to sedimentation or to delayed arrival.

In June (beginning of thermal stratification and rise in biomass production), there was an input of Fe and Mn amorphous particles from the river. A concentration peak was recorded at a depth of 20 m (for both ASP and dissolved phases) (Fig. 3), indicating an anoxic intrusion layer. Data on major elements suggest that a deep current occurred at a depth of 50 m (Fig. 2), whereas ASP and dissolved Fe and Mn suggest a specific layer at 40 m (Fig. 3) where water was more reductive. The deep current originated from the outflow, which was then at a depth of 45 m depth. This seemed to slow down the settling of particles, creating a thin layer enriched in particles and slightly reductive because of the organic load of the river (Odulo et al., 1997).

Tab. 2 Proportion of element presents in acid soluble phases of suspended particles compared to total (dissolved + acid soluble forms) concentration measured in the water column, at each season and for one year

	Si	**Al**	**Fe**	**Mn**	**Li**	**Rb**	**Cs**	**Sr**	**Ba**	**Ca**	**V**	**Cr**	**Co**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**	**As**	**Sb**	**Th**	**U**	**Corg**
A-July 05																							
min-max	0-8	15-81	93-100	21-96	0-23	0-10		0-5	0-12	0-8	7-54	37-100	3-45	1-81	6-44	1-75	21-70	49-92	0-10	16-65	50-100	0-10	
mean	2%	45%	98%	64%	8%	3%		2%	5%	3%	30%	76%	31%	28%	26%	28%	47%	78%	2%	36%	88%	2%	
median	1%	43%	100%	65%	7%	2%		1%	5%	2%	34%	80%	34%	26%	24%	20%	48%	84%	0%	36%	100%	0%	
B-October 05																							
min-max	0-10	31-89	27-100	0-99	0-17	0-11	0-86	0-25	0-22	0-10	28-100	100-100	3-70	2-51	1-46	3-47	0-100	10-97	0-34	0-54	0-100	0-11	19-91
mean	4%	57%	91%	77%	4%	4%	61%	3%	4%	5%	84%	100%	37%	27%	12%	16%	63%	69%	8%	16%	64%	2%	60%
median	3%	54%	100%	82%	3%	2%	67%	1%	1%	4%	100%	100%	39%	25%	12%	14%	71%	79%	4%	17%	89%	0%	60%
C-April 06																							
min-max	0-25	70-98	93-100	0-97	0-34	0-39	0-100	0-18	0-28	0-16	36-87	34-100	1-78	11-100	3-88	13-76	0-100	86-100	0-58	1-22	74-100	0-7	
mean	7%	91%	98%	61%	12%	18%	83%	6%	15%	4%	66%	80%	65%	37%	41%	42%	60%	98%	30%	10%	94%	4%	
median	5%	92%	98%	44%	12%	18%	88%	6%	15%	3%	68%	91%	71%	33%	43%	47%	62%	100%	41%	8%	95%	5%	
D-June 06																							
min-max	0-20	4-93	10-100	6-96	0-37	0-38	0-92	0-11	0-30	0-9	28-89	16-100	2-87	7-92	3-37	3-70	6-100	4-100	1-37	3-28	29-100	0-11	72-96
mean	7%	70%	92%	83%	11%	14%	70%	4%	13%	4%	57%	90%	57%	63%	21%	27%	84%	94%	18%	12%	74%	3%	84%
median	6%	75%	96%	88%	11%	12%	79%	4%	14%	5%	58%	100%	62%	68%	20%	25%	100%	100%	17%	11%	78%	2%	83%
1 year																							
min-max	0-25	4-98	10-100	0-99	0-37	0-39	0-100	0-25	0-30	0-16	7-100	16-100	1-87	1-100	1-88	1-76	0-100	4-100	0-58	0-65	0-100	0-11	
mean	5%	70%	94%	73%	9%	11%	71%	4%	10%	4%	62%	86%	51%	43%	26%	29%	66%	86%	16%	15%	79%	3%	
median	4%	75%	99%	83%	7%	9%	79%	3%	11%	3%	65%	100%	49%	35%	21%	25%	68%	96%	12%	12%	89%	1%	

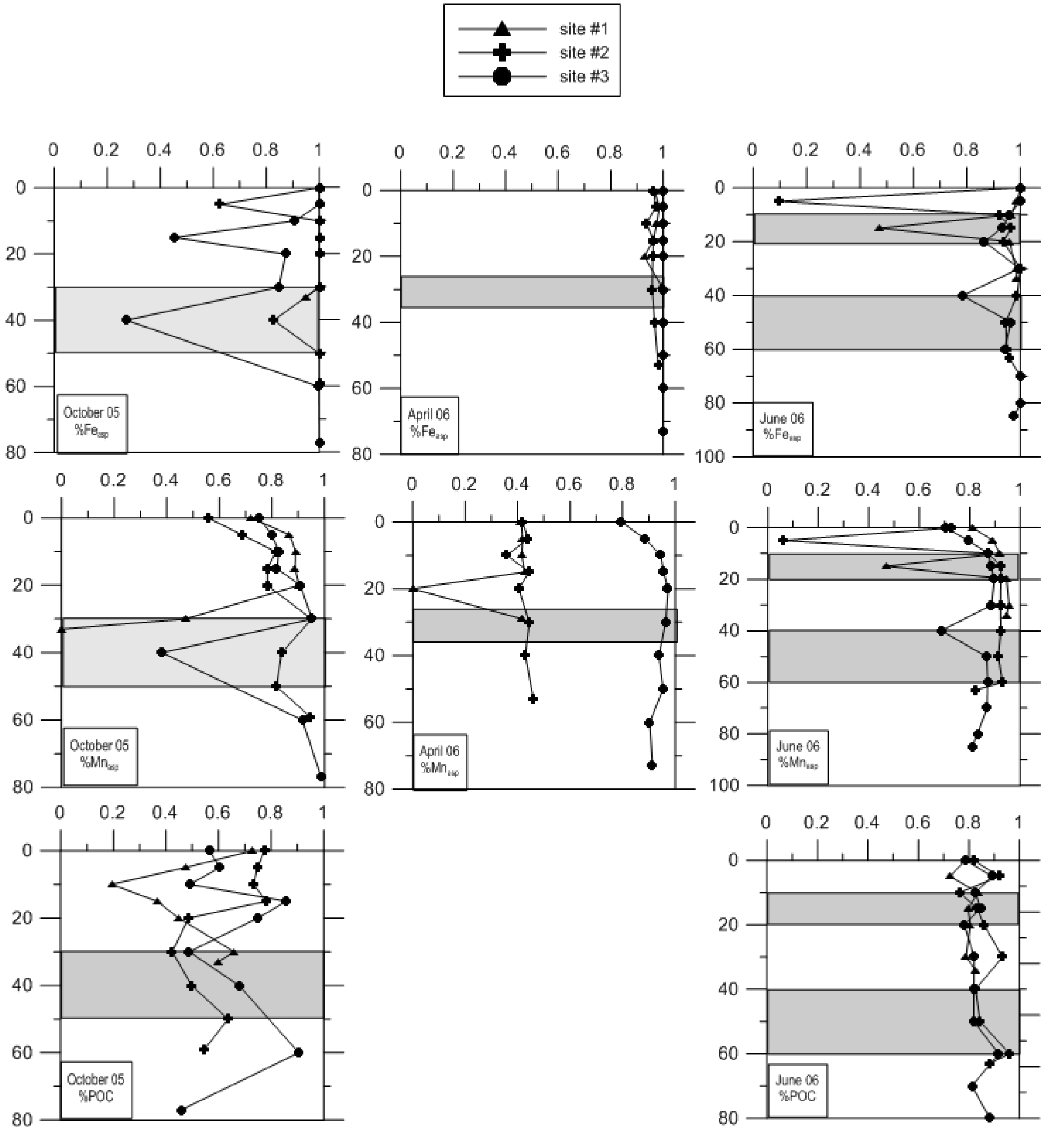

Fig. 3 Proportion of particulate acid soluble phase relative to total concentration (dissolved phase + ASP) measured in bulk water for Fe, Mn and carbon, at each site and each season.

Trace elements

The selected trace elements can be divided into two groups, the first comprising alkali (Li, Rb and Cs) and alkaline earth elements (Sr and Ba), and the second comprising transition elements as well as As, Sn, Sb, Pb, Th and U. Elements of the first group (group 1) are very mobile and exist naturally in an oxidation state. Elements of the second group (group 2) exist in several oxidation states, and their solubility mainly depends on redox water characteristics.

Tab. 3 Calculated correlations between Al, Fe, Mn and Si in the dissolved and in acid soluble phases (concentrations in mol/L). Not considered samples are indicated between brackets

Al/Fe in the dissolved phase		**Al/Fe in ASP of suspended particles**	
		A3 (30 m)	$[Al] = 1.2 [Fe] + 2\cdot10^{-7}$ $R^2 = 0.752$
		B1	$[Al] = 0.8 [Fe] + 5\cdot10^{-7}$ $R^2 = 0.772$
		B2	$[Al] = 1.2 [Fe] + 4\cdot10^{-7}$ $R^2 = 0.845$
		B3	$[Al] = 1.1 [Fe] + 4\cdot10^{-7}$ $R^2 = 0.796$
C1 (0 m)	$[Al] = 0.8 [Fe] + 6\cdot10^{-7}$ $R^2 = 0.870$	C1	$[Al] = 1.1 [Fe] - 5\cdot10^{-7}$ $R^2 = 0.963$
C2	$[Al] = 0.9 [Fe] + 5\cdot10^{-7}$ $R^2 = 0.732$	C2	$[Al] = 1.0 [Fe] + 1\cdot10^{-6}$ $R^2 = 0.944$
		C3	$[Al] = 1.2 [Fe] + 2\cdot10^{-7}$ $R^2 = 0.997$
		D1	$[Al] = 1.5 [Fe] - 6\cdot10^{-7}$ $R^2 = 0.967$
		D2	$[Al] = 1.5 [Fe] + 1\cdot10^{-7}$ $R^2 = 0.994$
		D3	$[Al] = 1.5 [Fe] - 9\cdot10^{-7}$ $R^2 = 0.970$

Al/Mn in the dissolved phase		**Al/Mn in ASP of suspended particles**	
		B2 (30 & 40 m)	$[Al] = 9 [Mn] + 4\cdot10^{-7}$ $R^2 = 0.994$
C2	$[Al] = 1 [Mn] - 1\cdot10^{-6}$ $R^2 = 0.954$		
		C3	$[Al] = 9 [Mn] - 7\cdot10^{-7}$ $R^2 = 0.810$
D1	$[Al] = 24 [Mn] + 1\cdot10^{-6}$ $R^2 = 0.973$	D1	$[Al] = 31 [Mn] - 2\cdot10^{-6}$ $R^2 = 0.865$
		D2 (bottom)	$[Al] = 31 [Mn] - 4\cdot10^{-7}$ $R^2 = 0.976$
		D3 (bottom)	$[Al] = 30 [Mn] - 7\cdot10^{-7}$ $R^2 = 0.825$

Fe/Mn in ASP of suspended particles		**Fe/Si in ASP of suspended particles**	
C1	$[Fe] = 9 [Mn] + 5\cdot10^{-6}$ $R^2 = 0.793$	C1	$[Fe] = 0.5 [Si] + 8\cdot10^{-6}$ $R^2 = 0.925$
C3	$[Fe] = 8 [Mn] - 8\cdot10^{-7}$ $R^2 = 0.819$		
D1	$[Fe] = 20 [Mn] - 4\cdot10^{-7}$ $R^2 = 0.860$	D1	$[Fe] = 0.4 [Si] + 3\cdot10^{-6}$ $R^2 = 0.930$
D2	$[Fe] = 18 [Mn] - 1\cdot10^{-7}$ $R^2 = 0.840$		
D3 (bottom)	$[Fe] = 20 [Mn] + 1\cdot10^{-7}$ $R^2 = 0.849$		

Al/Si in the dissolved phase		**Al/Si in ASP of suspended particles**	
A3	$[Al] = -0.01 [Si] + 3\cdot10^{-6}$ $R^2 = 0.718$		
B2	$[Al] = -0.03 [Si] + 4\cdot10^{-6}$ $R^2 = 0.793$		
		C1	$[Al] = 0.6 [Si] + 8\cdot10^{-6}$ $R^2 = 0.964$
C2	$[Al] = 0.03 [Si] - 2\cdot10^{-6}$ $R^2 = 0.769$		
		D1	$[Al] = 0.6 [Si] + 4\cdot10^{-6}$ $R^2 = 0.977$

Mn/Si in the dissolved phase		**Mn/Si in ASP of suspended particles**	
C2	$[Mn] = 0.02 [Si] - 6\cdot10^{-7}$ $R^2 = 0.796$	C2 (30 m)	$[Mn] = 0.03 [Si] + 9\cdot10^{-7}$ $R^2 = 0.864$
		D1	$[Mn] = 0.02 [Si] + 2\cdot10^{-7}$ $R^2 = 0.863$

A: July 2005; B: October 2005; C: April 2006; D: June 2006.

The elements of group 1 were mainly measured in the dissolved phase (Tab. 2), except Cs, which was mainly found in ASP; Sr was the most soluble. These elements could thus be sorted according to their “affinity” for the amorphous particulate phase: Cs > Ba, Rb, Li > Sr. This sequence is in accordance with previous studies (Kinninburgh and Jackson, 1981). The highest ASP fraction was recorded in April and June, mostly at sites #1 and #2. Several elements of group 2 (Tab. 2) occurred mainly in ASP (V, Cr, Cd, Pb, Th); some were mainly in dissolved form (As, Sb and U), the others were ubiquist (Co, Ni, Cu, Zn). For both groups, the ASP forms were mainly associated with amorphous iron or manganese phases (Tab. 4, Fig. 5). In June, there were more correlations between iron and trace elements.

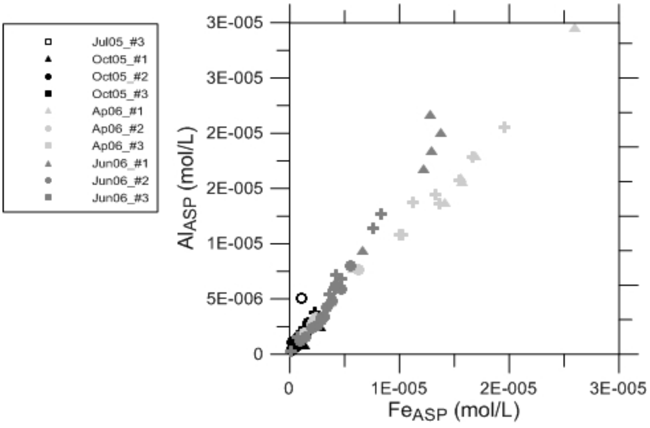

Fig. 4 Relationship between Al and Fe in acid soluble particles at each season.

4.2 Sediments

Mineral phases

Quartz, illite-type argillaceous minerals, feldspar (e.g. albite), halloysite, talc, jacobsite and a mixed Fe-Ti oxide were identified by XRD sediment analysis (C. Grosbois, *person. com*. 2011). Mineralogical composition did not vary from one site to another or from top to bottom of a core. No sulfide mineral was measurable by this method, but SEM observation identified some secondary pyrites as framboids (C. Grosbois, *person. com*. 2011).

Bulk composition

Correlations calculated on bulk sediments (XRF data, Tab. 5) revealed the presence of some clay-oxide aggregates composed of Fe, Al, K, Mg, P, Ti, and several trace elements (Co, Y, Zn, Ga, Cr, Ni, V, Rb and Ba). These elements were slightly anti-correlated to Si, which could be due to the proportion of quartz and feldspar in the sediments (dilution effect). These elements were also anti-correlated to carbonaceous phases (here identified by Ca and Sr). The last three samples at the bottom of the core at site #1 presented a distinctive signature. We assumed that they represented terrigenous input from the watershed. To assess the impact of physico-chemical processes occurring within the reservoir, these points were used as a reference (see part 5.5).

Amorphous phases

In the amorphous phases, none of the correlations observed in suspended particles was recorded (Tab. 5), except the link between Mn and Co.

5. Discussion

5.1 Redox characteristics in the reservoir – Fe and Mn

From the relative distributions of Fe_{diss}/Fe_{asp} and of Mn_{diss}/Mn_{asp} (Fig. 3), it is possible to determine the relative redox characteristics of reservoir waters. In addition,

Tab. 4 Calculated correlations between trace elements and iron in the dissolved and in acid soluble phases. Concentrations are expressed in mol/L. Not considered samples are indicated between brackets

	Fe - in ASP of suspended particles			**Fe - dissolved phase**		**Fe - in ASP of suspended particles**	
Li	C2	$[Fe] = 42\ [Li] + 1\cdot10^{-5}\ R^2 = 0.815$	**Co**			C1	$[Fe] = 1140\ [Co] + 4\cdot10^{-6}\ R^2 = 0.810$
	D1	$[Fe] = 52\ [Li] + 5\cdot10^{-6}\ R^2 = 0.710$				C2	$[Fe] = 1828\ [Co] - 3\cdot10^{-6}\ R^2 = 0.879$
Rb	B3	$[Fe] = 500\ [Rb] + 6\cdot10^{-7}\ R^2 = 0.738$				C3	$[Fe] = 1140\ [Co] - 1\cdot10^{-7}\ R^2 = 0.932$
	C1	$[Fe] = 2141\ [Rb] + 8\cdot10^{-7}\ R^2 = 0.976$		D1	$[Fe] = 1651\ [Co] - 2\cdot10^{-6}\ R^2 = 0.897$	D1	$[Fe] = 1763\ [Co] + 3\cdot10^{-7}\ R^2 = 0.984$
	C3	$[Fe] = 1307\ [Rb] + 9\cdot10^{-7}\ R^2 = 0.781$				D2	$[Fe] = 1732\ [Co] - 3\cdot10^{-7}\ R^2 = 0.957$
	D1	$[Fe] = 1958\ [Rb] + 2\cdot10^{-7}\ R^2 = 0.917$				D3	$[Fe] = 1332\ [Co] + 1\cdot10^{-6}\ R^2 = 0.874$
	D2	$[Fe] = 2641\ [Rb] + 5\cdot10^{-8}\ R^2 = 0.818$	**Ni**			D1	$Fe] = 479\ [Ni] + 2\cdot10^{-6}\ R^2 = 0.898$
Sr	C1	$[Fe] = -59\ [Sr] + 2\cdot10^{-5}\ R^2 = 0.798$				D2	$[Fe] = 381\ [Ni] + 7\cdot10^{-7}\ R^2 = 0.858$
Ba	C1	$[Fe] = 208\ [Ba] + 4\cdot10^{-6}\ R^2 = 0.890$	**Cu**			C1	$[Fe] = 171\ [Cu] + 8\cdot10^{-6}\ R^2 = 0.921$
	D1	$[Fe] = 240\ [Ba] + 1\cdot10^{-6}\ R^2 = 0.912$				C2 (10 m)	$[Fe] = 713\ [Cu] - 3\cdot10^{-6}\ R^2 = 0.848$
Cs	B2	$[Fe] = 24368\ [Cs] + 3\cdot10^{-7}\ R^2 = 0.703$				D1	$[Fe] = 351\ [Cu] + 5\cdot10^{-6}\ R^2 = 0.761$
	C1	$[Fe] = 59279\ [Cs] + 2\cdot10^{-6}\ R^2 = 0.823$				D2	$[Fe] = 467\ [Cu] + 1\cdot10^{-6}\ R^2 = 0.823$
	C2	$[Fe] = 57378\ [Cs] + 2\cdot10^{-6}\ R^2 = 0.815$				D3	$[Fe] = 321\ [Cu] + 1\cdot10^{-6}\ R^2 = 0.735$
	C3	$[Fe] = 38676\ [Cs] + 5\cdot10^{-7}\ R^2 = 0.788$	**Zn**			C1	$[Fe] = 171\ [Zn] - 6\cdot10^{-6}\ R^2 = 0.887$
	D1	$[Fe] = 42697\ [Cs] + 3\cdot10^{-7}\ R^2 = 0.882$				C2	$[Fe] = 127\ [Zn] + 3\cdot10^{-6}\ R^2 = 0.724$
	D2	$[Fe] = 38885\ [Cs] - 3\cdot10^{-7}\ R^2 = 0.899$				C3 (60 m)	$[Fe] = 128\ [Zn] - 4\cdot10^{-7}\ R^2 = 0.716$
	D3	$[Fe] = 38317\ [Cs] + 9\cdot10^{-7}\ R^2 = 0.823$				D1	$[Fe] = 166\ [Zn] + 1\cdot10^{-6}\ R^2 = 0.818$
V	C1	$[Fe] = 824\ [V] + 3\cdot10^{-6}\ R^2 = 0.986$		D3	$[Fe] = 25\ [Zn] - 2\cdot10^{-6}\ R^2 = 0.847$	D2 (40 m)	$[Fe] = 176\ [Zn] + 1\cdot10^{-7}\ R^2 = 0.733$
	D1	$[Fe] = 864\ [V] + 9\cdot10^{-7}\ R^2 = 0.974$	**Cd**			C1	$[Fe] = 35236\ [Cd] + 8\cdot10^{-6}\ R^2 = 0.903$
	D2	$[Fe] = 571\ [V] + 8\cdot10^{-7}\ R^2 = 0.816$	**Pb**	C2	$[Fe] = 720\ [Pb] + 3\cdot10^{-7}\ R^2 = 0.874$	D1 (5&30 m)	$[Fe] = 2143\ [Pb] + 1\cdot10^{-6}\ R^2 = 0.777$
	D3	$[Fe] = 663\ [V] + 3\cdot10^{-7}\ R^2 = 0.830$				D2	$[Fe] = 1710\ [Pb] + 1\cdot10^{-6}\ R^2 = 0.862$
Cr	C3	$[Fe] = 514\ [Cr] + 1\cdot10^{-6}\ R^2 = 0.755$				D3	$[Fe] = 1063\ [Pb] + 1\cdot10^{-6}\ R^2 = 0.730$
	D1	$[Fe] = 1035\ [Cr] + 3\cdot10^{-6}\ R^2 = 0.926$	**Th**			B2	$[Fe] = 65718\ [Th] + 8\cdot10^{-7}\ R^2 = 0.727$
	D2	$[Fe] = 1059\ [Cr] + 7\cdot10^{-7}\ R^2 = 0.780$				C1	$[Fe] = 50579\ [Th] + 1\cdot10^{-6}\ R^2 = 0.955$
						C2	$[Fe] = 44330\ [Th] + 1\cdot10^{-6}\ R^2 = 0.791$
						C3	$[Fe] = 44458\ [Th] + 9\cdot10^{-7}\ R^2 = 0.838$
						D1	$[Fe] = 23139\ [Th] + 4\cdot10^{-6}\ R^2 = 0.713$
						D2	$[Fe] = 40520\ [Th] + 1\cdot10^{-7}\ R^2 = 0.878$

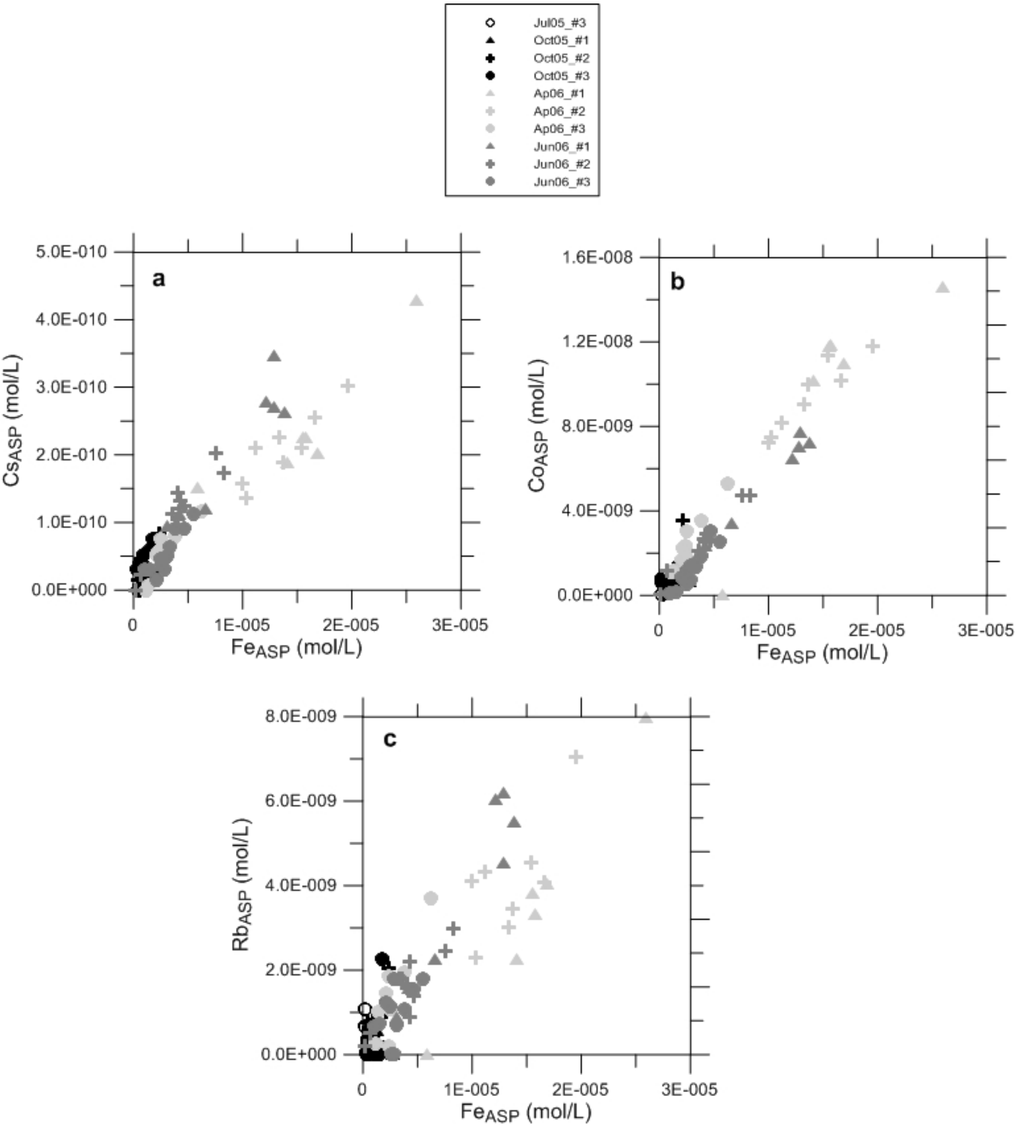

Fig. 5 Relationship observed at each season (concentration expressed as mol/L)in the ASP particlesa) between Cs and Fe, b) between Co and Fe, c) between Rb and Fe.

because the kinetics of Mn(IV) reduction is faster than that of Fe(III) (Davison, 1993), pE calculations (Ball and Nordstrom, 1991) were made for Mn(II)/Mn(IV) equilibrium (Tab. 6). Results show that authigenic organic matter production was low enough to have oxidizing reservoir waters at all seasons. Reductive water layers originated from the river load, implying a high content of organic matter and oxygen-consuming substances in river waters. Furthermore, the behavior of Fe and Mn oxides was not regulated by thermal stratification of the water column but by the river inflow (quality and quantity), the reservoir level (both the height of the water column and the outflow depth), withdrawal, and the intrusion layer. Because of the barrier formed by the deep current, waters at the bottom of the water column stayed isolated, but still oxidizing, from June to early winter overturn (minimum of 11.6 for a circum-neutral pH).

5.2 Nature of acid soluble phases in suspended particles

The link between Al and Fe content in ASP was recorded at each site and during each season (Tab. 4), always with a very good R^2 value. The Al/Fe ratio was very stable during transport in the reservoir, even though redox conditions changed. This implies that Al and Fe were in the same phase and that their contents were controlled by stoichiometric ratio, which suggests the existence of a specific mineral (amorphous) phase. By contrast, the variability of the Fe/Mn ratio suggests that Mn was present in various mineral phases and/or adsorbed on particles.

In lakes, Fe (hydr)oxides consist of iron (≥30 wt%) and small amounts of P, Ca, N, Mn, Si, S, Mg and C (Davison and De Vitre, 1992). The proportions of cations other than iron depend on the physico-chemical parameters prevailing in the lake, on the origin of particles (pedogenic/aquagenic) and on the production of aquagenic organic matter (Tipping et al., 1981; Buffle et al., 1989; Perret et al., 2000). The nature of organic matter also influences the shape of particles (Perret et al., 2000). In the Bicaz reservoir, no P or Ca was measured in acid soluble phases of suspended particles. Furthermore, the prevailing redox conditions in the reservoir suggest that authigenic organic matter production was very low. The anoxic layer always came from the river inflow. Particulate matter sampled in the reservoir mainly originated from the weathering of soils and rocks and was modified during transport in the river and then when entering the reservoir.

Tab. 5 Calculated correlations between several elements in main solid phases (XRF) and in acid soluble phases (soft digestion + ICP-MS) present in sediments. Concentrations are expressed in mol/g of dry sediment

Main phases in sediments		**Acid soluble phases in sediments**	
All sites	$[Al] = 2.4\,[Fe] + 1\cdot10^{-3}\ R^2 = 0.843$	All sites**	$[Mn] = 6906\,[Co] - 1\cdot10^{-6}\ R^2 = 0.849$
All sites	$[Fe] = 25\,[P] + 3\cdot10^{-4}\ R^2 = 0.685$		
All sites	$[Fe] = 1.6\,[K] - 3\cdot10^{-4}\ R^2 = 0.756$		
All sites	$[Fe] = 1404\,[Co] + 2\cdot10^{-4}\ R^2 = 0.941$		
All sites	$[Fe] = 1484\,[Y] + 2\cdot10^{-5}\ R^2 = 0.859$		
All sites*	$[Fe] = 115\,[Zn] + 6\cdot10^{-4}\ R^2 = 0.785$		
All sites*	$[Fe] = 1790\,[Ga] + 4\cdot10^{-4}\ R^2 = 0.784$		
All sites**	$[Fe] = 2.3\,[Mg] - 2\cdot10^{-4}\ R^2 = 0.834$		
All sites	$[Ca] = -53\,[Ti] + 6\cdot10^{-3}\ R^2 = 0.837$		
site #1*+2	$[Fe] = 11\,[Ti] - 1\cdot10^{-4}\ R^2 = 0.734$		
site #1+2	$[Fe] = 403\,[Cr] + 4\cdot10^{-5}\ R^2 = 0.907$		
site #3	$[Fe] = 563\,[Cr] - 4\cdot10^{-4}\ R^2 = 0.855$		
site #1*+2	$[Fe] = 423\,[Ni] + 5\cdot10^{-4}\ R^2 = 0.825$		
site #3	$[Fe] = 499\,[Ni] + 3\cdot10^{-4}\ R^2 = 0.787$		
site #1+2	$[Fe] = 312\,[V] + 1\cdot10^{-4}\ R^2 = 0.865$		
site #1+2	$[Fe] = 411\,[Rb] + 1\cdot10^{-4}\ R^2 = 0.885$		
site #1*+2	$[Fe] = 153\,[Ba] + 3\cdot10^{-4}\ R^2 = 0.839$		

* without the bottom of the core from site#1 which exhibits a particular signature

**without the bottom of the core from site#3.

Tab. 6 Estimation of extremum values of pe from Mn2+/MnO2 equilibrium, in the water column, and of saturation index for caclcite and siderite, at the bottom of the water column. Thermodynamic data are from Wateq4f.

	pe caculation				**SI calculation**	
	Mn^{2+}/ birnessite range	**Mn^{2+}/ pyrolusite range**	**depth of min.**	**depth of max.**	**(bottom of the water column) pe from pyrolusite, Fe_{Tot} calcite**	**siderite**
Jul. 05 site#3	12.0-14.4	10.9-13.3	surface	60 m	-0.49	-7.92
Oct.05 site#1	12.7-14.7	11.6-13.6	bottom	20 m	-0.49	-7.46
Oct.05 site#2	13.5-14.7	12.4-13.6	40 m	bottom	-0.64	-8.97
Oct.05 site#3	13.1-14.9	12.0-13.8	40 m	bottom	-0.71	-8.88
Ap.06 site#1	12.0-12.9	10.9-11.7	15 m	surface	-0.70	-5.75
Ap.06 site#2	11.4-12.7	10.3-11.6	20 m	bottom	-0.35	-6.73
Ap.06 site#3	13.2-14.4	12.1-13.3	bottom	20 m	-0.32	-8.82
Jun.06 site#1	12.7-14.2	11.6-13.0	surface	10 & 30 m	-0.46	-8.15
Jun.06 site#2	12.5-14.5	11.4-13.4	5 m	30 to 60 m	-0.51	-8.14
Jun.06 site#3	12.6-14.2	11.5-13.1	surface	30 m	-0.42	-8.38

Metal (hydr)oxides may exist as crystalline minerals, as short-range order or amorphous precipitates, which are partly present as coatings on clay minerals and/or organic compounds. The nature of Fe oxides in soils depends on the Fe content of the parent rocks and on the environmental conditions (such as water-logging, temperature, organic content). Numerous reports provide evidence for the coprecipitation of Al in Fe (hydr)oxides (Cornell and Schwertmann, 2003). Aluminum can be incorporated into ferrihydrite, goethite and hematite, but it seems that two phases are formed (one Fe oxide and one Al oxide) when more than 25-30 mol% of Al is added (Bazilevskaya et al., 2011; Manceau and Gates, 2013). The Al phase is gibbsite, and the Fe phase depends on ageing. In addition, experiments show that microbial Fe(III) reduction rates decrease significantly with increasing Al substitution of ferrihydrite (Ekstrom et al., 2010). The Al substitution seems to stabilize natural ferrihydrite.

In the Bicaz reservoir, the proportion of Al in Fe (hydr)oxides was significantly higher than what was recorded in laboratory experiments. This apparent discrepancy could be linked to the presence of organic matter, which both inhibits the crystallization of oxides and stabilizes the amorphous particles. This organic matter may mainly originate from soil leaching. In June, the flow of water was faster than at any other seasons. Also, the different Al/Fe ratios recorded in October and April (≈ 1) and in June (1.5) may be linked to the ageing of particles (corresponding to a loss of Al when the flow is slower) and/or to the concentration and nature of organic matter (mature/fresh; more fresh in June). The apparent link between Al-Fe particles and Cs suggests the association of Al-Fe (hydr)oxides with clays. In aquatic systems, Cs is mainly associated with clay minerals and can be linked to exchangeable or interlayer sites (Evans et al., 1983; Loring, 1991; N'guessan et al., 2009). The presence of Cs in the soluble phase depends on the stability of clay particles (detrital particles) and to its location in minerals (exchangeable or not). This may explain the increase in Cs/Fe, in ASP, recorded during the transport of particles in the reservoir (Tab. 4), while the concentration of Fe_{ASP} decreased because of sedimentation (Tab. 1).

Tab. 7 Trace element solubility and association with Al-Fe amorphous phases of suspended particles.

% asp/total	**> 70%**	**< 30%**	**30-70%**
Group 1	Cs	Li, Rb, Sr, Ba	-
Group 2	Cr, Pb, Th	Cu, Zn, As, Sb, U	V, Co, Ni, Cd
Associated to Al-Fe$_{asp}$*	**Strongly (more than 5/10 profiles)**	**Independent (no correlation)**	**Intermediate (1 to 5/10 profiles)**
Group 1	Rb, Cs	Sr	Li, Ba
Group 2	Co, Cu, Zn, Pb, Th	Sn, As, Sb, U	V, Cr, Ni, Cd

* Based on numbers of observed correlations (see Table 3).

5.3 Behavior of acid soluble particles during diagenesis

Results for sediments show that acid soluble phases of suspended particles were transformed during diagenesis. Trace elements were always linked to Fe and Al, but in more complex phases comprising Fe, Al, K, Mg, P, Ti and several trace elements (Co, Y, Zn, Ga, Cr, Ni, V, Rb and Ba). The Fe/X ratio was often smaller in these phases than in ASP (Tabs. 4 & 5).

Although a significant Ca^{2+} - CO_3^{2-} upward diffusion originating from sediments was recorded, carbonate phases do not act as a control of trace element solubility, even for elements such as U.

5.4 Speciation of trace elements in the water column

Among the selected trace elements, based on criteria of solubility and association (direct or by coating) with Fe oxide, several types of behavior can be considered (Tab. 7).

- Low soluble elements strongly (Cs, Pb, Th) or moderately (Cr) associated with Fe oxides.
- Elements that were soluble and independent of Fe oxides: As, Sb, U.
- Soluble elements moderately (Li, Ba) or strongly (Rb, Cu, Zn) associated with Fe oxides.
- Elements moderately soluble and moderately (V, Ni, Cd) or strongly (Co) associated with Fe oxides.

Numerous studies of seasonally anoxic lakes suggest that trace element speciation is often basin-specific, particularly for elements that have affinities for Fe and Mn oxides, sulfides and organic matter (Hamilton-Taylor et al., 2005; Viollier, 1995). Here, trace elements are mainly controlled by association with amorphous Al/Fe phase. By contrast, As, Sb and U, which were mainly in oxyanion forms, remained in the dissolved phase (Tab. 2) and were little affected by the presence of oxide particles, as observed by Brandenberger et al. (2004). While Ba solubility control by Fe oxide association has already been reported (e.g. Violler et al., 1995; 1997), the interesting finding is the association of Li and Rb with iron oxides, which has rarely been discussed in the literature (pour Rb: Pichler and Veizer, 1999) but observed experimentally (Kinniburgh et al., 1975; van Beinum et al., 2005). During winter (from October 2005 to April 2006 at site #3), the lower Rb concentration in the dissolved phase (Fig. 5c) may have been linked to Fe precipitation.

5.5 Storage of trace elements in sediments

To assess the storage of an element in the reservoir sediments, we calculated the X/Zr ratio, Zr being a very insoluble element, in the sediments (XRF data). This ratio was normalized to a reference, namely, the last three centimeters of core #1, thought to represent the terrigenous signature: $(X/Zr)_{sed}/(X/Zr)_{ref}$. In core #1 (Tab. 8), the recorded Ca and Sr enrichment may be linked to particulate input from the flysch (reservoir basin). The largest enrichment factors were recorded in core #2 for Fe, Mn, V, Cr, Co, Ni, Zn, Rb and Cu. Manganese and nickel seem to be stored mainly in sediments, whereas for the other elements, ratios did not significantly differ from 1.

Tab. 8 Ratio (X/Zr)/(X/Zr)ref calculated in core samples. See text for details.

corr. depth cm	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	Na_2O	P_2O_5	V	Cr	Co	Ni	Zn	Ga	Rb	Sr	Nb	Ba	Y	Cu
core #1																						
4.5	1.4	1.4	1.6	1.7	1.2	1.4	**2.4**	1.5	0.9	1.4	1.7	1.7	1.6	**2.1**	1.0	1.5	1.7	**2.2**	1.3	1.2	1.6	1.1
7.5	1.4	1.4	1.5	1.6	1.2	1.4	**2.7**	1.4	0.9	1.3	1.6	1.5	1.5	1.5	1.0	1.3	1.5	**2.3**	1.5	1.1	1.5	**3.6**
10.5	1.4	1.6	1.7	1.8	1.4	1.6	1.3	1.6	0.9	1.6	1.8	1.7	1.8	2.0	1.3	1.4	1.8	1.6	1.6	1.4	1.7	1.6
13.5	1.5	1.5	1.8	1.9	1.5	1.7	**3.1**	1.8	1.0	1.4	1.9	1.9	1.7	**2.1**	1.2	1.5	1.9	**2.6**	1.8	1.3	1.9	1.4
20	1.4	1.5	1.7	1.9	1.4	1.6	1.5	1.7	1.0	1.5	1.9	1.8	1.8	1.9	1.5	1.6	1.9	1.6	1.8	1.4	1.8	1.2
28.5	1.4	1.2	1.3	1.4	1.2	1.2	**3.4**	1.2	0.9	1.2	1.4	1.4	1.3	1.2	1.0	0.9	1.3	**2.8**	1.2	0.9	1.3	0.9
31.5	1.3	1.3	1.3	1.5	1.2	1.2	**2.9**	1.3	0.9	1.2	1.5	1.4	1.4	1.4	1.3	1.2	1.4	**2.5**	1.5	1.0	1.3	1.2
34.5	1.4	1.4	1.5	1.6	1.2	1.4	**3.3**	1.5	0.9	1.3	1.7	1.6	1.4	1.5	1.2	1.3	1.6	**2.8**	1.3	1.0	1.6	1.2
41.5	1.3	1.1	1.2	1.3	1.2	1.2	**3.2**	1.2	1.0	1.0	1.3	1.2	1.2	1.1	0.9	1.1	1.2	**2.6**	1.2	0.9	1.1	1.0
43	1.1	1.1	1.2	1.2	1.1	1.2	1.3	1.3	1.1	1.1	1.3	1.3	1.2	1.1	1.2	1.3	1.3	1.3	1.2	1.2	1.3	1.2
46	0.9	0.9	0.8	0.8	0.9	0.8	0.7	0.7	0.9	0.9	0.7	0.7	0.8	0.9	0.8	0.7	0.7	0.7	0.8	0.8	0.7	0.8
core #2																						
1.5	1.5	1.5	1.6	1.6	**2.2**	1.4	0.6	1.5	0.9	1.4	1.9	1.7	1.7	1.7	1.1	1.4	1.8	1.2	1.7	1.4	1.5	1.1
4.5	1.6	1.7	1.9	**2.2**	**4.8**	1.7	0.8	1.9	0.9	2.0	**2.2**	**2.1**	**2.2**	**2.3**	1.8	1.8	**2.1**	1.4	2.0	1.6	1.9	1.8
7.5	1.6	1.6	1.9	**2.1**	**4.0**	1.7	0.8	1.8	1.0	1.8	**2.1**	1.9	**2.1**	**2.6**	1.8	1.8	2.0	1.3	1.7	1.5	1.9	1.9
10.5	1.5	1.6	1.8	**2.1**	**3.3**	1.6	0.9	1.7	0.9	1.8	**2.1**	1.9	**2.1**	**2.4**	1.7	1.8	2.0	1.3	1.9	1.5	1.8	2.0
16.5	1.5	1.6	1.8	**2.1**	**4.2**	1.6	1.0	1.7	0.9	1.9	**2.2**	1.8	**2.2**	**2.5**	**2.2**	1.7	2.0	1.4	1.9	1.5	2.0	**2.2**
25.5	1.5	1.6	1.8	2.0	**4.2**	1.6	0.7	1.7	0.9	1.7	2.0	1.9	2.0	**2.1**	1.7	1.7	2.0	1.3	1.7	1.5	1.8	1.9
28.5	1.5	1.6	1.7	1.8	**3.3**	1.5	0.9	1.6	0.9	1.7	1.8	1.8	1.9	1.8	1.6	1.5	1.8	1.3	1.9	1.5	1.7	1.8
37.5	1.5	1.6	1.8	2.0	**4.9**	1.6	1.3	1.7	0.9	1.8	1.9	1.9	2.0	**2.1**	1.6	1.7	1.9	1.6	1.4	1.5	1.9	**5.1**
45.5	1.5	1.6	1.8	1.9	**3.0**	1.6	0.7	1.7	0.9	1.6	2.0	1.9	1.9	**2.1**	1.4	1.6	1.9	1.3	2.0	1.4	1.7	1.8
core #3																						
1.5	1.5	1.4	1.6	1.7	**3.0**	1.5	**2.1**	1.5	0.9	1.5	1.8	1.8	1.7	2.0	1.0	1.5	1.8	2.0	1.3	1.2	1.7	1.5
7.5	1.4	1.3	1.4	1.4	**2.6**	1.2	**2.5**	1.3	0.9	1.3	1.5	1.5	1.3	1.6	0.9	1.1	1.4	**2.1**	1.4	1.1	1.3	1.4
13.5	1.4	1.4	1.6	1.8	**4.8**	1.5	**2.5**	1.5	0.9	1.7	1.7	1.9	1.7	**2.1**	1.5	1.6	1.7	1.9	1.6	1.3	1.8	1.7
22.5	1.5	1.5	1.6	1.6	**4.1**	1.4	1.2	1.5	0.9	1.5	1.8	1.8	1.7	**2.1**	1.3	1.3	1.7	1.4	1.5	1.4	1.5	1.8
28.5	1.5	1.5	1.6	1.6	**4.7**	1.4	2.3	1.5	0.9	1.5	1.9	1.8	1.6	1.8	1.0	1.5	1.7	1.9	1.6	1.3	1.6	1.6
31.5	1.5	1.5	1.7	1.8	**4.4**	1.5	1.4	1.6	0.9	1.6	1.9	1.9	1.7	**2.2**	1.4	1.5	1.8	1.5	1.5	1.3	1.6	**2.2**
34.5	1.6	1.6	1.7	1.7	**3.1**	1.5	1.1	1.7	0.9	1.4	**2.1**	1.9	1.7	1.8	1.2	1.4	1.9	1.5	1.8	1.4	1.6	**4.5**
41.5	1.5	1.4	1.4	1.3	**2.2**	1.3	**2.2**	1.4	0.9	1.1	1.7	1.6	1.3	1.5	0.7	1.1	1.6	**2.1**	1.5	1.0	1.2	1.5
43.5	1.4	1.4	1.4	1.3	**2.9**	1.1	1.6	1.3	0.8	1.1	1.6	1.5	1.3	1.5	0.8	1.4	1.5	1.6	1.3	1.2	1.2	1.3
46	1.5	1.4	1.5	1.4	1.9	1.3	1.6	1.4	0.9	1.2	1.8	1.7	1.4	1.7	0.7	1.2	1.6	1.8	1.6	1.2	1.2	1.4

▨ slightly enriched

■ slightly depleted

bold enriched with reference to the average of the last three samples from core #1

6. Conclusion

During the period under study, the reservoir seemed to act as a permanent sink for Mn and Ni, as a slight sink for Fe, V, Cr, Co, Cu, and as a moderate source and/or sink for Zn (Tab. 8).

Several experimental studies have shown that the coagulation efficiency of natural particles increases with increasing calcium concentration and decreases with increasing fulvic and dissolved organic matter concentrations (Tipping and Higgins, 1982; Ali et al., 1984; Gallegos and Menzel, 1987; Weilenmann et al., 1989; Wilkinson et al., 1997). Together with the oxic status of water, the Ca concentration and the nature and concentration of organic matter prevailing in the reservoir may favor the storage of elements associated with particles, but no direct link was identified.

It is difficult to establish an element budget in reservoirs, because water mixing is complex and time of water transit depends on the position in the water column and on season. For example, waters below the deep current remain in the reservoir longer than those at the outlet depth. However, some trace elements associated with Fe oxide particles were stored in the Bicaz reservoir along the water flow.

River inflow, water withdrawal and the position of the outlet play an important role in the biogeochemical processes in the Bicaz reservoir. As long as this reservoir is mesotrophic, it will act as a sink for numerous trace elements. Its eutrophication will lead to the occurrence of an anoxic hypolimnion at the end of summer and thus to the removal of Fe-associated trace elements from sediments by reduction of Fe oxide particles. Because of the deep position of the outlet, this removal from sediments to the soluble phase would alter the quality of the outflow waters. Under these environmental conditions, with a reservoir at the end of a watershed in a major mining area, it is important to limit biomass production in order for the reservoir to act as a sink for trace elements. This sink mainly concerns elements linked to Fe oxide particles.

Acknowledgements

The authors would like to thank the Laboratoire de Géochimie des Eaux (Paris 7 – IPG Paris) and particularly Eric Viollier for the loan of core devices. We are grateful to Cécile Grosbois (GéHCO) for XRD analyses and SEM observations. The GéEAC (Université de Tours, France) partially supported this study.

References

Ali, W., O'Melia, C.R., Edzwald, J.K., 1984. Colloidal stability of particles in lakes: measurement and significance. Wat. Sci. Technol, **17**, 701–712.

Apopei, V., 1983. Caracterizarea hidrologica a zonei lacului. In: Miron, I. (ed.). (1983). Lacul de acumulare Izvorul Muntelui – Bicaz. Monografie limnologica. Editura Academiei RSR, Bucuresti, 44–62.

Balistrieri, L.S., Murray, J.W., Paul, B., 1992. The biogeochemical cycling of trace metals in the water column of lake Sammamish, Washington: Response to seasonally anoxic conditions. Limnol. Oceanogr., **37**, 3, 529–548.

Ball, J.W., Nordstrom, D.K., 1991. WATEQ4F - User's manual with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural waters. U.S. Geological Survey Open-File Report 90-129, 185p.

Bazilevskaya, E., Archibald, D.D., Aryanpour, M., Kubicki, J.D., Martinez, C.E., 2011. Aluminium coprecipitates with Fe (hydr)oxides: does isomorphous substitution of Al^{3+} for Fe^{3+} in goethite occur? Geochim. Cosmochim. Acta, **75**, 4667–4683.

Becker, A., Klöck, W., Friese, K., Schreck, P., Treutler, H.-C., Spettel, B., Duff, M.C., 2001. Lake Süßer See as a natural sink for heavy metals from copper mining. J. Geochem. Explor., **74**, 205–217.

Brandenberger, J., Louchouarn, P., Herbert, B., Tissot, P., 2004. Geochemical and hydrodynamic controls on arsenic and trace metal cycling in a seasonally stratified US sub-tropical reservoir. Appl. Geochem., **19**, 1601–1623.

Buffle, J., De Vitre, R.R., Perret, D., Leppard, G.G., 1989. Physico-chemical characteristics of a colloidal iron phosphate species formed at the oxic-anoxic interface of a eutrophic lake. Geochim. Cosmochim. Acta, **53**, 399–408.

Casamitjana, X., Serra, T., Colomer, J., Baserba, C., Pérez-Losada, J., 2003. Effects of the water withdrawal in the stratification patterns of a reservoir. Hydrobiologia, **504**, 21–28.

Cornell R.M., Schwertmann U., 2003. The Iron Oxides: Structure, Properties, Reactions, Occurences, and Uses. Wiley-VCH, 703p.

Davison, W., 1993. Iron and manganese in lakes. Earth-Science Reviews **34**, 2, 119–163.

Davison, W., De Vitre R., 1992. Iron particles in freshwater. In: Buffle, J., van Leeuwen, H.P., (eds.). Environmental Particles, **1**, 315–355.

Dulski, P., 2001. Reference materials for geochemical studies: New analytical data by ICP-MS and critical discussion of reference values. Geostandard Newsletter, The Journal of Geostandards and Geoanalysis, **25**, 1, 87–125.

Ekstrom, E.B., Learman, D.R., Madden, A.S., Hansel, C.M., 2010. Contrasting effects of Al substitution on microbial reduction of Fe(III) (hydr)oxides. Geochim. Cosmochim. Acta, **74**, 7086–7099.

Erhan, E., 1988. Potentialul climatic al Masivului Ceahlău. Analele Stiintifice ale Universitatii “Al. I. Cuza” Iasi, Geologie - Geografie, **XXXIV**.

Evans, D.W., Alberts, J.J., Clark III, R.A., 1983. Reversible ion-exchange fixation of cesium-137 leading to mobilization from reservoir sediments. Geochim. Cosmochim. Acta, **47**, 6, 1041–1049.

Fontane, D.G., Labadie, J.W., Loftis, B.O., 1981. Optimal control of reservoir discharge quality through selective withdrawal. Wat. Resour. Res., **17**, 6, 1594–1604.

Gallegos, C.L., Menzel, R.G., 1987. Submicron size distributions of inorganic suspended solids in turbid waters by Photon Correlation Spectroscopy. Wat. Ressources Res., **23**, 596–602.

Gassama, N., Cocirta, C., Kasper, H.U., 2009. Hydrodynamics of the Bicaz lake. Considerations based on selected major and trace elements. Analele Stiintifice ale Universitatii “Al. I. Cuza” Iasi, Geologie, **LV**, 1, 39–64.

Gassama, N., Cocirta, C., Kasper, H.U., 2012. Use of major and selected trace elements to describe mixing processes in a water reservoir. C.R. Geoscience, **344**, 25–32.

Govindaraju, K., 1994. Compilation of working values and sample description for 383 geostandards. Geostandards Newsletter, Special Issue, **XVIII**, 1–158.

Hamilton-Taylor, J., Smith, E.J., Davison, W., Sugiyama, M., 2005. Resolving and modelling the effects of Fe and Mn redox cycling on trace metal behaviour in a seasonally anoxic lake. Geochim. Cosmochim. Acta, **69**, 8, 1947–1960.

Han, B.-P., Armengol, J., Garcia, J.C., Comeerma, M., Roura, M., Dolz, J., Straskraba, M., 2000. The thermal structure of Sau Reservoir (NE: Spain): a simulation approach. Ecol. Model., **125**, 109–122.

Holmström, H., Öhlander, B., 2001. Layers rich in Fe- and Mn-oxyhydroxides formed at the tailings-pond water interface, a possible trap for trace metals in flooded mine tailings. J. Geochem. Explor., **74**, 189–203.

INHGA, 2008. Monthly (2005 & 2006) and multi-annual (1973-2006) Q_{mean} measured on the Bistriţa river (Frumosu station) and on the Bistricioara river (Bistricioara city station). Monthly (2005 & 2006) and multi-annual (1991-2006) Q_{mean} measured at the sluice of Bicaz. Contract # 136/2008, Institutul National de Hidrologie si Gospodarire a Apelor, Bucharest.

Kinniburgh, D.G., Skyers, J.K., Jackson, M.L., 1975. Specific adsorption of trace amounts of calcium and strontium by hydrous oxides of iron and aluminium. Soil Sci. Amer. Proc., **39**, 464–470.

Kinniburgh, D.G., Jackson, M.L., 1981. Cation adsorption to hydrous metal oxides and clays. In: Anderson, M.A., Rubin, A.J. (Eds). Adsorption of Inorganics at solid-liquid interface. Ann Arbor Sci. Publi., Ann Arbor, Mich., 91–160.

Lamborg, C.H., Buesseler, K.O., Lam, P.J., 2008. Sinking fluxes of minor and trace elements in the North Pacific Ocean measured during the VERIGO program. Deep-Sea Research II, **55**, 1564–1577.

Loring, D.H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments. ICES J. Mar. Sci., **48**, 101–115.

Manceau, A., Gates, W.P., 2013. Incorporation of Al in iron oxyhydroxides: implication for the structure of ferrihydrite. Clay Minerals, **48**, 3, 481–489.

Moncur, M.C., Ptacek, C.J., Blowes, D.W., Jambor, J.L., 2006. Spatial variations in water composition at the northern Canadian lake impacted by mine drainage. Appl. Geochem., **21**, 1799–1817.

Munk, L.A., Faure, G., 2004. Effects of pH fluctuations on potentially toxic metals in the water and sediment of the Dillon Reservoir, Summit County, Colorado. App. Geochem., **19**, 1065–1074.

Munteanu, M., Marincea, S., Kasper, H.U., Zak, K., Alexe, V., Trandafir, V., Saptefrati, G., Mihalache, A., 2004. Black chert-hosted manganese deposits from the Bistritei Mountains, Eastern Carpathians (Romania): petrography, genesis and metamorphic evolution. Ore Geology Reviews, **24**, 45–65.

N’guessan, Y.M., Probst, J.-L., Bur, T., Probst, A., 2009. Trace elements in stream bed sediments from agricultural catchments (Gascogne region, S-W France): Where do they come from? Sci. Total Environ., **407**, 2939–2952.

Odulo, A., Swanson, J.C., Mendelsohn, D., 1997. The steady flow between reservoirs with different density and level over a sill. Cont. Shelf Res., **17**, 13, 1561–1580.

Parkhurst, D.L., Appelo, C.A.J., 1999. User’s guide to PHREEQC (version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312p.

Perret, D., Gaillard, J.-F., Dominik, J., Atteia, O., 2000. The diversity of natural hydrous iron oxides. Environ. Sci. Technol., **34**, 354–3546.

Pichler, T., Veizer, J., 1999. Precipitation of Fe(III) oxyhydroxide deposits from shallow-water hydrothermal fluids in Tutum Bay, Ambitle Island, Papua New Guinea. Chem. geol., **162**, 15–31.

Rueda, F.J., Fleenor, W.E., de Vicente, I., 2007. Pathways of river nutrients towards the euphotic zone in a deep-reservoir of small size: Uncertainty analysis. Ecol. Model., **202**, 345–361.

Sánchez España, J., López Pamo, E., Santofimia Pastor, E., Diez Ercilla, M., 2008. The acidic mine pit lakes of the Iberian Pyrite Belt: An approach to their physical limnology and hydrogeochemistry. Appl. Geochem., **23**, 1260–1287.

Sigg, L, 1985. Metal transfer mechanisms in lakes; the role of settling particles. In: Stumm, W. (ed.). Chemical processes in Lakes. Wiley, New York, 283–310.

Taillefert, M., Gaillard, J.-F., 2002. Reactive transport modeling of trace elements in the water column of a stratified lake: iron cycling and metal scavenging. J. Hydrol., **256**, 16–34.

Tipping, E., Woof, C., Cooke, D., 1981. Iron oxide from a seasonally anoxic lake. Geochim. Cosmochim. Acta, **45**, 9, 1411–1419.

Tipping, E., Higgins, D.C., 1982. The effect of adsorbed humic substances on the colloid stability of haematite particles. Coll. Surf., **5**, 85–92.

van Beinum, W., Hofmann, A., Meeussen, J.C.L., Kretschmar, R., 2005. Sorption kinetics of strontium in porous hydrous ferric oxide aggregates. I. The Donnan diffusion model. J. Colloid Interface Sci., **283**, 18–28.

Viollier, E., 1995. Geochemistry of trace elements within lacustrine environment. PhD dissertation, University Denis Diderot – Paris, 306p. (In French).

Viollier, E., Jezequel, D., Michard, G., Pepe, M., Sarazin, G., Alberic, P., 1995. Geochemical study of a crater lake (Pavin lake, France): Trace-element behaviour in the monimolimnion. Chem. Geol., **125**, 61–72.

Viollier, E., Michard, G., Jezequel, D., Pepe, M., Sarazin, G., 1997. Geochemical study of a crater lake: Pavin lake, puy de Dome, France. Constraints afforded by the particulate matter distribution in the element cycling within the lake. Chem. Geol., **142**, 225–241.

Weilenmann, U., O'Melia, C.R., Stumm, W., 1989. Particle transport in lakes: Models and measurements. Limnol. Oceanogr., **34**, 1–18.

Wilkinson, K. J., Negre, J.-C., Buffle, J., 1997. Coagulation of colloidal material in surface waters: the role of natural organic matter. J. Contam. Hydrol., **26**, 1-4, 229–243.