Anthropogenic influence on the degradation of an urban lake – The Pampulha reservoir in Belo Horizonte, Minas Gerais, Brazil

Kurt Friese [a,*], Gerald Schmidt [b,c], Jorge Carvalho de Lena [d], Herminio Arias Nalini Jr.[d], Dieter W. Zachmann [b,e]

[a] UFZ-Helmholtz Center for Environmental Research, Department Lake Research, Brückstraße 3a, D-39114 Magdeburg, Germany
[b] Institute for Environmental Geology, Technical University of Braunschweig, Germany
[c] DECHEMA e.V., Karl-Winnacker-Institut, Frankfurt/Main, Germany
[d] Department of Geology, EM, Federal University of Ouro Preto, Minas Gerais, Brazil
[e] Institute of Ecological Chemistry and Waste Analysis, Technical University of Braunschweig, Germany

ARTICLE INFO

ABSTRACT

The artificial reservoir Lagoa da Pampulha in central Brazil has been increasingly affected by sediment deposition and pollution from urban and industrial sources. This study investigates water chemistry and heavy metal concentrations and their fractionation in the lake sediment using ICP-OES, ICP-MS, and XRD analyses. Fractionation analysis was done by sequential extraction under inert gas as well as after oxidation. The lake exhibits a permanent stratification with an oxygen-free hypolimnion below 2 m depth. Nutrient concentrations are enriched for phosphorous components (SRP, PO_4). In the sediment it was not possible to detect oxygen. Carbon, sulfur, and most of the analyzed heavy metals are enriched in the top sediment layer with a pronounced downward decrease, indicating the presence of an anthropogenic influence. Statistical analysis, including correlations and a Principal Component Analysis (PCA) of depth-related total concentration data, helps to distinguish presumably anthropogenic heavy metals from geogenic components. Some samples with high element concentrations in the sediment also show elevated concentrations in their pore water. Analyses of element distribution between sediment and pore water suggest a strong bonding of heavy metals to the anoxic sediment. The trend towards elevated solubility in the pore water of oxidized samples is clear for most of the analyzed elements. Fractionation analysis reveals characteristic associations of selected elements to specific mineral bonding forms. In addition, it indicates that the behavior of heavy metals in the sediment is strongly influenced by organic substances. These substances provide buffering against oxidation, acidification, and metal release. The high nutrient loading causes reducing conditions in the lake sediment. These conditions trigger the accumulation of sediments rich in S^{2-}, which stabilizes the fixation of heavy elements. In the future, care must be taken to reduce the supply of contaminants and to prevent the release of heavy metals from sediments dredged for remediation purposes.

Introduction

The influence of industrial activity on the environment is frequently expressed in an elevated influx of pollutants in surface waters. Heavy metals pose a special problem based on their strong tendency to accumulate and the impossibility to be eliminated chemically or biologically.

In lakes the sediment may be considered the ultimate destiny of heavy metals because solid substances accumulate with time and soluble forms in contact with water may become solid material through precipitation, flocculation, adsorption, agglomeration, complexation, or by the assimilation in organic substances (e.g. intake by organisms), which is finally deposited (Calmano, 1989; Salomons and Förstner, 1984). Dissolution of metals from sediments occurs less frequently under natural circumstances, but this effect cannot be excluded, if physico-chemical conditions change. The consequences on living organisms may be serious.

The urban environments are more susceptible to the influence of anthropogenic activities than their rural counterparts. They are characterized mainly by road networks, traffic, housing, energy generation plants, industry, and waste (Virkanen, 1998; Charlesworth and Lees, 1999). Because of the variable intensity of these activities, urban soil may range from undisturbed to man-made or

* Corresponding author: Tel.: +49 391 810 9200.
  E-mail address: kurt.friese@ufz.de (K. Friese).

built-up (Kelly et al., 1996 and references therein), and this material represents the main source of chemical load to the bottom sediments of urban lakes (Virkanen, 1998). Of particular interest is the accumulation of metals in the water bodies of cities. Several studies have shown increase in metal content in aquatic environments as a consequence of urbanization (e.g. Lindström, 2001) and contamination of urban soil (Kelly et al., 1996). Also the introduction of nutrients and particulate organics is of concern in urban areas. Given the intensity with which it occurs, it may lead to eutrophication and in some cases to ecologically irreversible deterioration of the lake.

The Pampulha Lake is located in the northern part of Belo Horizonte city, the capital of Minas Gerais state, Brazil. Belo Horizonte, with 2.5 million inhabitants, is the 4th-largest Brazilian city. A large part of the catchment area of this lake (97.91 km^2) spreads over the surface of the neighbor city Contagem. The reservoir itself possesses an area of 2.7 km^2, a total water volume of 12 million m^3 (max. depth 13.3 m) and it is completely encompassed by a built city region.

The Pampulha dam was originally built up, in 1958, to store water and to prevent flooding in the region of the Pampulha stream. It was also planned as a reservoir of drinking water for the city of Belo Horizonte and as a recreation area for the population. The quickly growing population and industrialization of the area brought negative consequences which impaired the usage of the dam for its original purposes. The most obvious problem has been the silting up of the lake with an estimated input of 200,000–400,000 m^3 of sediment per annum (Cena, 2001; CPRM, 2001), a situation which got worse between 1994 and 1999 with a total income of 2 million m^3/annum. Another problem is the detraction of water quality. The eutrophication of the lake has been increasing since 1970 (Pinto Coelho, 1998), the availability of nutrients triggering such a high primary production that even with frequent withdrawal of biomass the dissolved oxygen is still being consumed. These nutrients are transported to the lake via eight small streams of which the most important and also the most polluted ones are Sarandi, Ressaca, and Agua Funda. Some measures have been adopted by local authorities to solve these problems. Among them are the "Programa de Recuperação e Desenvolvimento Ambiental da Bacia da Pampulha em Belo Horizonte (Propam)" project (www.cmbh.mg.gov.br/index. php?option=com_content&task=blogsection&id=44&Itemid=235; Rose, 2001), for which so far an amount of US$ 150 million has been spent.

The streams Sarandi and Ressaca provide together 70% of the total water income of the reservoir and their basin represents 63% of the total catchment area. A study of Rietzler et al. (2001) showed extremely high heavy metal pollution in these both streams. Potential sources for this contamination are iron and steel industries (Fe, Cr, Ni, Co), solvent and paint industries (Ni, Cr, Pb), and the land-fill dump of Belo Horizonte (Fe, Mn, Ni, Cu, Cd, Pb, Zn). The outflow is controlled by an overfall spillway, and so the water level does not vary much throughout the year (Pinto Coelho, 1998). The water from the dam flows to the Pampulha stream, which in turn flows to the Velhas River.

The geological formation of the region is assigned to the Complexo Belo Horizonte (CPRM, 2001). It is composed of granite and gneiss with parts of migmatite. The age of gneiss and migmatite amounts to 2.8 Gyr. The granites are considered to be 2.7 Gyr old. Due to intensive weathering a large and deep soil covering has formed which is mainly composed of iron and aluminum oxides and shows a brown to red color. The soil has a sandy and a clayey texture with a poor cohesion. Therefore it is susceptible to erosion.

The climate of the region can be described as tropical mountain climate with dry winter and humid summer (Köppen Cwa). The temperature shows little variation during the year with a mean maximum of 23.4 °C in February and a mean minimum of 18.5 °C in July. In contrast, the two seasons are quite clearly differentiated according to the mean precipitation values. The dry season (from April to September) shows a minimum of 13 mm in June, and the rainy season (from October to March) a maximum of 321 mm in December.

Some previous studies (Giani, 1994; Pinto Coelho, 1998) provide a good description of the lake. Its water shows strong signs of eutrophication and stratification and is very poor in oxygen. The quality of the water and its functionality are severely impaired. During our sampling work in August many dead fish were floating at the surface and no living ones could be seen.

The main goals of this work are to determine the dominant conditions in the water, the properties of the sediment, specifically its mineralogical composition and particle size distribution, the kind and concentration of heavy metals in the sediment, and their origin, either anthropogenic or geogenic.

Material and methods

For this work two sampling campaigns were carried out to include effects of the two different climatic conditions, dry winter and humid summer. The first one took place at the end of the wet season on May 8, 9, and 15, 2001, and the second one at the end of the dry season on August 7, 8, and 9, 2001. The sample stations are shown in Fig. 1 and their UTM coordinates are A (23 K 606665 7804617), B (23 K 607019 7804528), and C (23 K 607960 7805109). All of them are located in the center between the two banks. Water data are available only for the first campaign.
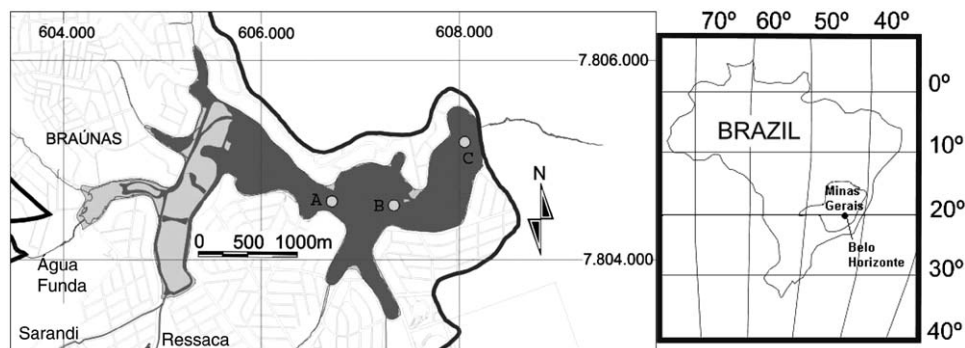

Fig. 1. Sampling points in the Pampulha reservoir. Light gray areas = islands; black line = border of catchment area.

For the water sampling new PET flasks were used. Analyses included physico-chemical parameters (T, O$_2$, pH, Eh, and electrical conductivity), main cations (Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+}), nutrients (NO$_3$–N, NO$_2$–N, NH$_4$–N, N-total, SRP, and PO$_4^{3-}$), and trace elements (Al, Fe, Mn, S, Si; As, Cd, Co, Cr, Cu, Pb, Sb, Sn, Zn). Samples were collected at each meter in depth ranging from the surface to the bottom. Physico-chemical parameters were determined in situ, using WTW instruments (WTW, Germany) and following the standard DIN specifications (DEV, 2001). The redox potential (Eh) was corrected for temperature. For the determination of trace heavy metals, samples were filtered with 0.45 µm and preserved with nitric acid (pH < 2) at 4 °C. For the determination of N species samples were also filtered and preserved with HgCl$_2$; for the determination of P samples were preserved with H$_2$SO$_4$. All the chemical analyses were conducted according to the Standard Methods for the Examination of Water and Wastewater (Greenberg et al. 1992). The concentrations of main cations (Na$^+$, Ca^{2+}, K$^+$, and Mg^{2+}) and of trace elements (Al, Fe, Mn, S, Si; As, Cd, Co, Cr, Cu, Pb, Sb, Sn, Zn) were determined using inductively coupled plasma spectrometry (ICP-OES). In all samples of surface and pore waters the concentrations of Al were below the detection limit (0.35 mg/L). The results were validated with the NIST 1643d reference material (http://georem.mpch-mainz.gwdg.de).

At each sampling station and at each sampling campaign, up to six sediment cores were collected with a gravity corer, Mondsee-corer type from UWITEC Austria (Mudroch and Azcue, 1995). The samples were collected with water on top and brought to the shore undisturbed in Polycarbonate tubes (9 cm diameter, 1 m length). The water was allowed to flow out at the top by carefully pressing up the bottom of the tubes. The sediment was then cut into slices from top to bottom (0–1, 1–2, 2–3, 3–4, 4–5, 5–7.5, 7.5–10, 10–12.5, 12.5–15, and 15–20 cm). The slices were homogenized, packed into polyethylene bags or vessels, and kept refrigerated (< 4 °C). At the second sampling campaign, one core from each sampling station was dedicated explicitly to analyses under unchanged physico-chemical conditions. While the material from other cores was eventually allowed to dry at air, the material from these cores was always kept refrigerated in an Argon atmosphere to prevent oxidation. The corresponding samples are denoted "anoxic", the others "oxidized" in the results of the sequential extraction.

The sediment samples were dried in quartz evaporating dishes at 60 °C. Some samples were separated into their different grain size fractions for analyses of trace elements because the concentration of trace elements in sediments depends on the grain size (Salomons and Förstner, 1984; Vester and Zachmann, 2003). These fractions were separated and their content of main and trace elements was determined. In this way specific differences in the enrichment in the various grain sizes may be found. In order to carry out the separation of the desired fractions, 7 g of the dry sediment was suspended in 150 mL of NH$_3$ 0.01 mol/L. To disaggregate the particles the suspension was left in an ultrasonic bath for 2 min (Bandelib Sonopuls HD 200, 200 W, 20 KHz, 130 µm amplitude, 6 mm Ti plate, 60% power). The sand fraction was separated with a stainless steel sieve (63 µm). The remaining material was separated into different silt and clay fractions (20–63, 2–20, < 2, and ≪ 2 µm) by flotation (Bachmann et al., 2001). The solid material of each grain size fraction was separated by centrifugation, dried at 60 °C and finally weighed and kept in polystyrol vials.

Analysis of mineralogy and total elemental concentrations was carried out on the untreated samples, including all grain size fractions. Because of the correlation of elemental concentrations with the grain size mentioned above, it is usually advisable to discard the sandy fraction (Salomons and Förstner,

1984). However, in this case, this fraction was so small that it could be neglected; it was usually below 1% of the total dry weight.

The mineralogical identification followed the methodology described by Zachmann (1994). The dry samples were ground in an agate mortar together with bi-distilled water to obtain a suspension. The suspension was applied to a glass plate (three plates per sample) and allowed to dry in a thin layer. One plate of each sample was then left in a desiccator filled with ethylene glycol for 24 h at 60 °C. Another sample plate was heated at 600 °C for 1 h, and the third plate was analyzed with no further treatment. All determinations were carried out by X-ray diffraction (Krischner, 1990) using a Philips PW 1730/10 instrument with a Cu tube (λ = 1.542 Å). The data evaluation was performed as described in Zachmann (1994). In general, the obtained diagrams were interpreted manually on the basis of the *Powder Diffraction File* database (JCPDS, 1967; Hanawalt method). In addition, the evaluation used clay reference materials which were prepared in the geochemical lab of the Technical University of Braunschweig (Zachmann, 1994).

Pore water was extracted with a centrifuge (diameter 26 cm, 4000 rpm) and filtered through membrane syringe filters (pore size 0.2 µm).

For fractionation analysis on the bulk sediment, a six-step sequential extraction method was applied (Jakob et al., 1990; Zachmann et al., 2009). This method is a variant of the 5-step scheme developed by Tessier et al. (1979). The following fractions were obtained: (1) exchangeable (ammonium acetate), (2) carbonatic (sodium acetate), (3) easily reducible (hydroxyl ammonium chloride), (4) less easily reducible (ammonium oxalate + oxalic acid), (5) organic/sulfidic (hot hydrogen peroxide, ammonium acetate), and (6) residual (HF digestion, see below).

For the main and trace element determination, about 200 mg of sample material was digested in open PTFE vessels with 7 mL of HNO$_3$ (65% v/v), 2 mL of HClO$_4$ (60% v/v), and 14 mL of HF (40% v/v). The vessels were heated at 140 °C for 7 h and at 180 °C until dryness. The residue was dissolved in 20 mL HNO$_3$ (1.3 mol/L) for 24 h. The dilution factor resultant from the sample weighed mass and the amount of acid was used for the calculation of the concentration in the dry mass.

Elements were determined by ICP-OES (Bausch and Lomb ARL 3520 ICP Sequential Spectrometer and Fisons Instruments Maxim) and ICP-MS (Micromass Platform ICP). The analytical methods were verified by regular participation in quality control analyses using different certified reference materials (e.g. ring experiments).

All sediment data were submitted to Principal Component Analysis (PCA) (Backhaus et al., 1996). After a careful examination of the data, an outlier (Barium) and the As concentration of one core from each sampling point were excluded. The procedure was carried out on six different data sets: (1) all data; (2) data of 1st sampling campaign; (3) data of 2nd sampling campaign; (4) data of sampling station A (both seasons); (5) data of sampling station B (both seasons), and (6) data of sampling station C (both seasons). In order to minimize the large differences among the data, a normalization procedure was performed to obtain the normalized value z_{kj} according to the equation:

$$z_{kj} = \frac{x'_{kj} - \mu_j}{\sigma_j}$$

where x'_{kj} is the ln x_{kj} (the natural logarithm of the measured value k for the element j), μ_j is the mean value of the logarithm of all measured data for the element j, and σ_j the standard deviation for the logarithm of all measured data for the element j. These

Table 1
Physico-chemical parameters, nutrient, main and trace element concentrations in the water of the Pampulha reservoir for the first campaign (May 2001); T=Temperature, DO=dissolved oxygen; Eh=redox potential, EC=electric conductivity; (Al was below detection limit).

Station	Depth (m)	T (°C)	DO (mg/L)	pH	Eh (mV)	EC (µS/cm)	Na+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	S (mg/L)	NO_3–N (mg/L)	NO_2–N (µg/L)	NH_4–N (mg/L)	N^{tot} (mg/L)	Si (mg/L)	SRP (µg/L)	PO_4 (µg/L)	Fe (mg/L)	Mn (µg/L)	Cr (µg/L)	Co (µg/L)	Cu (µg/L)	Zn (µg/L)	As (µg/L)	Cd (µg/L)	Sn (µg/L)	Sb (µg/L)	Pb (µg/L)
A	0	24.9	5.70	7.60	420	291	23.0	8.25	26.7	2.74	1.62	0.41	33	3.6	5.1	6.4	6	220	0.23	0.02	1.14	0.79	12.4	*	1.10	0.22	0.04	0.27	2.34
	1	24.0	2.69	7.42	390	293	23.9	8.18	25.5	2.59	1.97	0.05	27	3.8	4.8	6.4	7	321	<0.09	0.02	0.68	0.79	2.67	*	2.41	4.25	0.08	0.32	6.27
	2	23.6	1.76	7.35	380	295	22.7	8.00	25.6	2.54	1.61	0.10	32	3.7	4.6	6.5	5	78	0.010	<0.01	1.04	0.61	0.83	*	0.97	0.13	0.02	0.58	1.18
	3	23.5	0.56	7.36	400	298	25.9	8.15	26.3	2.59	2.53	0.12	35	3.8	5.0	6.3	6	407	<0.09	0.04	1.04	0.93	8.88	*	4.44	9.88	0.19	1.36	16.0
	4	23.4	0.34	7.31	380	297	29.3	9.14	28.0	2.72	4.36	<0.05	13	3.8	4.8	6.7	3	947	0.22	0.16	1.83	1.42	23.8	*	6.67	16.1	0.30	0.83	36.5
	5	23.3	0.30	7.30	370	298	22.6	7.72	25.1	2.48	1.56	<0.05	<6	3.9	5.0	6.5	6	171	<0.09	0.10	1.04	0.62	0.85	*	0.93	0.27	0.02	0.13	1.26
	6	22.5	0.25	7.32	360	324	24.6	7.80	26.0	2.57	2.00	<0.05	13	4.2	5.5	6.5	8	283	<0.09	0.03	0.35	0.65	3.87	*	2.28	4.44	0.10	1.09	7.00
	6.8	22.3	0.20	7.28	280	325	27.3	8.22	25.4	2.86	2.27	<0.05	<6	4.5	5.5	6.9	9	484	0.33	0.18	1.58	1.26	4.96	*	2.07	3.86	0.10	0.70	7.15
B	0	24.9	6.50	7.74	350	290	22.4	7.35	24.3	2.47	1.42	0.08	<6	3.1	6.2	6.5	470	131	0.12	0.03	0.94	0.73	1.24	18.1	1.07	0.17	0.08	0.20	0.94
	1	23.8	2.56	7.51	360	298	23.6	7.65	24.7	2.57	1.78	0.17	<6	3.2	6.7	6.7	8	205	<0.09	<0.01	0.70	0.82	3.55	*	1.91	2.63	0.08	3.38	3.18
	2	23.6	0.79	7.36	360	292	23.0	7.52	24.4	2.54	1.45	0.19	36	3.4	7.4	6.8	7	110	<0.09	<0.01	<0.03	0.65	1.65	28.4	0.95	0.12	0.03	0.36	0.71
	3	23.7	0.34	7.35	350	291	22.8	7.46	24.7	2.53	1.54	0.28	10	3.6	8.5	6.8	20	57	<0.09	0.06	<0.03	0.58	0.61	5.2	0.85	0.07	<0.01	0.11	0.41
	4	23.4	0.26	7.29	320	294	22.8	7.66	23.7	2.53	1.51	0.05	<6	3.4	5.6	6.5	480	151	<0.09	0.16	3.05	0.66	0.43	14.6	0.89	0.07	0.01	0.22	0.47
	5	23.6	0.19	7.27	290	293	22.0	8.28	25.0	2.60	2.45	0.85	7	3.5	7.2	6.5	150	<28	0.29	0.22	0.51	0.82	1.33	18.6	1.06	0.13	0.04	0.23	2.41
	6	23.4	0.28	7.25	320	293	22.1	7.75	24.8	2.46	1.41	1.03	15	5.4	16.2	6.9	60	241	0.36	0.27	0.61	0.75	1.03	9.1	1.01	0.08	<0.01	0.22	0.58
	7	23.4	0.17	7.25	140	297	22.6	7.66	24.6	2.44	1.41	0.18	<6	5.0	8.5	6.6	530	621	1.03	0.42	0.07	0.85	17.1	14.4	1.20	0.07	0.06	0.25	0.96
	8	23.0	0.22	7.12	80	322	23.6	7.87	24.6	2.49	1.55	0.48	9	6.0	10.9	5.0	490	497	0.60	0.30	0.38	0.81	0.94	15.8	1.04	0.08	0.06	0.15	2.29
	9	22.8	0.20	6.99	90	328	22.4	7.51	24.1	2.42	1.32	0.82	<6	6.4	15.2	7.4	280	991	1.70	0.46	0.45	0.90	1.13	10.8	1.15	0.07	0.03	0.30	0.56
	10	22.8	0.19	6.95	60	334	21.0	7.69	24.2	2.43	0.97	1.19	17	6.8	19.0	6.9	460	1334	3.23	0.65	0.87	1.13	0.56	5.9	1.50	0.11	0.08	0.22	0.40
	11	22.6	0.28	6.80	40	358	13.1	6.88	23.2	2.23	0.35	0.32	15	12.1	**	4.8	810	3416	9.37	1.30	1.18	1.56	0.50	9.4	2.10	0.09	0.08	0.78	0.61
C	0	22.8	0.55	6.85	130	307	21.5	7.75	25.2	2.58	1.19	<0.05	<6	4.6	6.6	6.8	60	150	1.14	0.50	0.28	0.83	0.75	4.5	1.11	0.06	0.03	0.14	0.51
	1	22.9	0.44	6.97	120	307	20.9	7.56	23.9	2.43	1.18	0.05	7	4.8	7.0	6.8	60	65	1.01	0.49	0.30	0.84	0.75	4.5	1.12	0.06	0.04	0.15	0.52
	2	22.6	0.28	6.96	110	310	20.8	7.52	24.6	2.37	1.13	<0.05	6	4.9	7.2	6.8	60	.65	1.01	0.50	0.31	0.95	1.59	6.9	1.18	0.09	0.06	0.15	0.86
	3	22.5	0.28	6.99	100	311	20.8	7.21	24.4	2.40	1.14	<0.05	7	5.1	7.2	5.7	100	242	1.39	0.53	0.24	0.85	0.43	3.6	1.10	0.07	0.03	0.13	0.48
	4	22.5	0.18	7.00	90	311	21.0	7.43	24.7	2.38	1.00	<0.05	6	5.3	7.1	6.7	170	714	1.86	0.56	0.32	0.86	3.17	8.5	1.16	0.07	0.07	0.25	0.72
	5	22.4	0.23	7.00	90	310	21.1	7.47	25.0	2.39	1.00	<0.05	<6	5.3	7.5	6.8	180	658	1.81	0.54	0.87	0.80	0.52	4.8	1.12	0.05	0.05	0.16	0.63
	6	22.6	0.18	6.99	90	310	20.9	7.57	24.8	2.40	1.05	<0.05	6	5.6	7.8	6.8	180	533	1.94	0.56	0.39	0.87	1.14	4.3	1.22	0.08	0.17	0.21	0.75
	7	22.5	0.20	7.02	90	311	20.4	7.96	24.7	2.52	1.02	<0.05	<6	5.2	7.2	4.5	170	530	1.96	0.55	0.25	0.51	0.55	5.8	0.62	<0.01	<0.01	<0.01	0.47
	8	22.6	0.18	7.00	80	310	20.1	7.58	23.9	2.41	0.96	0.05	<6	6.1	8.0	6.6	260	729	2.36	0.62	0.30	0.46	0.47	3.3	0.55	<0.01	<0.01	<0.01	0.33
	9	22.5	0.18	6.97	80	315	19.1	7.04	24.0	2.34	0.61	<0.05	<6	7.1	9.6	6.8	440	1506	4.11	0.80	0.48	0.60	1.67	9.1	0.81	<0.01	0.03	<0.01	0.63
	10	22.4	0.18	6.80	80	343	11.7	5.55	17.6	1.71	0.43	<0.05	<6	7.4	9.9	6.6	480	1059	3.10	0.61	0.31	0.47	2.03	5.9	0.57	<0.01	0.02	<0.01	0.45
	11	22.2	0.16	6.72	80	347	18.5	7.11	23.7	2.31	0.39	<0.05	<6	8.9	11.3	6.8	630	2003	5.37	0.89	0.43	0.58	0.42	3.6	0.82	<0.01	0.02	<0.01	0.34
	12	22.1	0.16	6.67	80	357	13.7	6.85	23.6	2.21	0.34	0.06	<6	8.5	10.3	6.7	740	2484	7.01	1.09	0.77	1.07	0.61	4.4	1.64	0.04	015	0.13	0.66
	13.3	22.0	0.18	6.67	80	367	12.0	6.69	23.4	2.17	0.28	0.10	<6	10.8	13.4	6.4	970	3218	9.53	1.28	0.85	1.30	0.30	2.2	1.89	0.03	0.14	0.07	0.42

* No reliable results.
** Not determined.

hydrochemical data were statistically analyzed with the SPSS software Student Version release 8.0.0 (SPSS Inc.).

Results and discussion

Water chemistry

Values for the physico-chemical parameters in water are presented in Table 1. The temperature decreases slightly from top to bottom. Values of Eh, O_2, and electrical conductivity in the water column show that there is no mixing of water in spite of this restricted variation of temperature. The pH remains around neutral. This shows the persistence of a situation which has already been registered in the literature (Giani, 1994; Pinto Coelho, 1998). Table 1 shows the concentration of nutrients, main components, and trace elements in the water obtained in the first campaign. Though the concentration of soluble reactive phosphorus (SRP) in some samples is below the limit of detection, high values preponderate in most samples (max. 970 µg/L above ground at station C), confirming the other indicators for strong eutrophication of the lake. High concentrations of Mn and Fe at stations B (max. 1.3 mg/L for Mn and 9.37 mg/L for Fe) and C (max. 1.28 mg/L for Mn and 9.53 mg/L for Fe) are observed in the deepest water layers, 1–2 m above the bottom. Apparently the low redox potential (40–80 mV) is responsible for the dissolution of the oxides and hydroxides of these elements. Related to the dissolution of iron and manganese oxides and hydroxides, a re-liberation of arsenic and phosphorous species can be observed, which are known to adsorb strongly on these oxides/hydroxides. Correlated to increase in Fe, Mn, As, and P the EC increases remarkably below 8 m water depth at the stations B (from around 300 to 400 µS/cm) and C (from around 300 to 370 µS/cm).

Compared with the concentration of some heavy metals in the rivers Sarandi and Ressaca measured by Rietzler et al. (2001), the values measured in the lake water are diluted strongly, generally with decreasing concentrations from stations A to C (e.g. for Cr from max. 850 µg/L in the river Sarandi to 1.14 µg/L in the surface water at station A, 0.94 µg/L at station B, and 0.28 µg/L at station C). Similar dilution effects are detected for Cu (380 µg/L to 12.4, 1.24, 0.75 µg/L), Cd (180 µg/L to 0.22, 0.17, 0.06 µg/L), and Pb (800 µg/L to 2.34, 0.94, 0.51 µg/L). For Fe and Mn this dilution effect is overcompensated by the upward diffusion of reduced Fe^{2+} and Mn^{2+} species leading to 1.14 and 0.56 mg/L for Fe and Mn, respectively, in the surface water at station C (compared to 0.23 and 0.02 mg/L for Fe and Mn, respectively at station A and 0.12 and 0.03 mg/L, respectively, at station B). According to Rietzler et al. (2001) maximal values are 80 mg/L for Fe and 19 mg/L for Mn in the river Ressaca.

S is given as total sulfur (measured by ICP-OES), though it is essentially present as sulfate. This is important to be addressed because there is some sulfide precipitation taking place in the bottom of the reservoir, which must be the result of sulfate-reduction bacterial activity. The depth profiles of S at points B and C indicate an evident and progressive decrease towards the bottom. Because there are also much more reducing conditions in B and C than in point A (Eh values are 200 mV lower, see Table 1), this may indicate that sulfate is being reduced by sulfate-reducing bacteria and precipitated as Fe and/or Cu sulfides (see chapter below).

Sediment mineralogy and geochemistry

Fig. 2 shows the grain size distribution of the six sediment samples which had been split up into grain size fractions. The
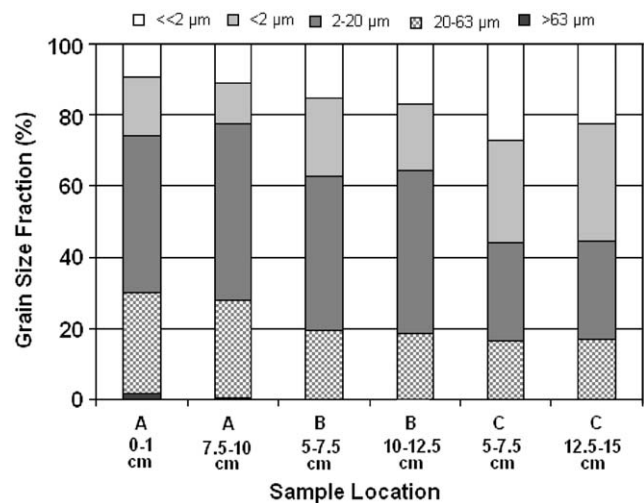
Fig. 2. Grain size distribution in the sediment samples of the Pampulha reservoir.

cores were without any visible structure and dark-gray to black in color. The sediment material was found to be very fine-grained, consisting of fine silt and clay. The clay fraction rises from roughly 25% at point A to over 50% at point C, while the silt fraction shows the opposite trend. Point B shows an intermediate composition. The main differences in grain sizes occur between the cores, not within the core. This fact was verified by using different depth intervals for the grain size analysis. The obvious reason for increase in clay content from station A to C is the increasing distance of the points from the main tributaries, which bring the main sediment load into the lake.

X-ray diffraction showed that the mineral composition of the sediment appears to be uniform throughout the whole reservoir. The main identified components are kaolinite (dominant), illite, and gibbsite. Goethite and hematite were also detected. A clear distinction can be made between minerals which are clearly detritic (allochtonous), such as the clay minerals kaolinite and illite, and those which could be partly the result of in situ precipitation (thus, autochtonous), such as Al (gibbsite) and/or Fe oxides (goethite, less likely hematite). A very rapid calculation of saturation indices for diverse minerals with some common geochemical modeling software (such as PHREEQC or MINTQA2) indicates that, at the surface, the water of the reservoir is clearly oversaturated with respect to several Fe phases such as ferrihydrite, goethite, or lepidocrocite. Therefore it might be possible that some of these phases could be precipitating.

Tables 2 and 3 display the results from the chemical analysis of the sediments for both campaigns. The depth profiles of selected element concentrations (Fig. 3) provide insights into the geo-chemical context of sedimentation. The dominant component, Al, shows an even distribution with a slight decrease in the top layer, where total carbon (TC) is more abundant than below. The distribution of S, Zn, and Cr concentrations consist of a strong enrichment in the top layer and almost constant values in lower depths. The same distribution is also found for TC, P, Mn, Cu, and Sb. A similar but less clear pattern is found for Fe, Pb, Ni, Sn, and Cd. The distinct enrichment in the upper layers of the depth profiles clearly indicates the presence of anthropogenic sources, whereas the deeper layers represent something close to the geogenic background. The mean concentration in the top 5 cm and the corresponding enrichment factors (divided by the minimum concentrations averaged from all sampling points) are

Table 2
Physico-chemical parameters, dry mass (DM), main and trace element concentrations in sediments of the Pampulha reservoir (1st sampling campaign May 2001).

Station	Depth (cm)	T (°C)	pH	Eh (mV)	DM (%)	TC (mg/g)	P (mg/g)	S (mg/g)	Al (mg/g)	Ca (mg/g)	Fe (mg/g)	K (mg/g)	Mg (mg/g)	Mn (mg/kg)	Na (mg/kg)	Ti (mg/g)	Ba (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Sr (mg/kg)	V (mg/kg)	Zn (mg/kg)	Zr (mg/kg)	As (mg/kg)	Cd (mg/kg)	Sn (mg/kg)	Sb (mg/kg)	Pb (mg/kg)
A	0–1	23.6	6.75	30	20.3	34.3	1.47	2.18	144	4.27	42.4	11.9	2.23	433	1042	3.03	377	11.8	119	49.5	34.7	41.3	60.9	522	74.1	10.0	1.13	10.1	1.03	42.9
	1–2	23.9	6.72	*	37.1	20.3	1.09	1.29	196	3.81	41.9	13.5	2.44	341	498	3.08	395	14.2	82.9	30.1	32.3	41.5	63.7	281	73.0	10.0	0.97	9.06	0.83	43.9
	2–3	22.7	6.69	50	34.7	18.7	1.05	1.19	191	3.38	40.7	12.8	2.18	321	455	3.02	373	19.3	82.3	28.9	30.7	38.0	62.6	267	70.4	9.71	0.90	8.75	0.79	41.2
	3–4	22.8	6.65	60	44.2	18.1	1.05	1.69	183	3.22	41.7	13.4	2.29	356	422	3.12	374	19.6	83.4	29.9	34.0	35.1	62.7	257	70.2	10.2	0.96	8.61	0.88	44.8
	4–5	21.7	6.69	−20	47.8	14.8	0.87	1.36	176	3.08	40.6	13.4	2.25	314	440	3.05	381	18.8	72.1	26.4	31.3	34.5	60.8	205	66.7	9.64	1.15	7.70	0.94	41.3
	5–7.5	23.3	6.73	−20	51.9	14.3	0.80	0.87	184	2.77	39.4	14.1	2.32	315	473	2.99	381	18.7	67.2	24.3	30.9	35.7	59.4	196	74.7	8.29	0.70	6.50	0.60	36.9
	7.5–10	23.6	6.74	90	58.0	12.6	0.58	0.46	186	4.20	38.0	15.5	2.60	340	695	2.78	424	23.1	53.3	21.9	27.4	47.7	51.2	173	95.7	7.75	0.66	6.52	0.55	37.1
	10–12.5	23.4	6.85	*	58.8	15.5	0.64	0.46	172	4.51	33.3	15.1	2.62	368	595	2.75	423	25.2	57.5	24.1	28.7	48.1	50.9	199	90.7	8.38	0.74	7.11	0.60	38.9
	12.5–15	23.2	6.78	10	49.4	16.3	0.84	0.84	179	4.30	39.6	14.6	2.64	361	528	2.84	404	20.1	63.7	25.1	31.6	44.6	55.6	224	77.0	8.55	0.77	7.21	0.70	38.5
	15–20	22.8	6.68	10	48.0	24.9	1.35	1.20	186	5.81	42.2	13.9	2.53	419	530	2.85	413	18.9	83.8	32.4	36.1	51.7	56.8	355	74.8	8.83	0.86	8.42	0.87	40.7
B	0–1	24.1	6.63	20	19.8	30.2	1.59	3.60	187	1.50	42.9	11.1	1.66	375	296	3.14	354	17.7	99.1	33.2	38.6	27.2	68.4	341	63.9	10.7	0.82	7.65	0.87	39.8
	1–2	23.8	6.60	80	6.5	72.3	2.72	7.05	153	2.76	43.0	10.5	1.74	709	360	2.88	396	15.8	132	55.8	42.3	33.8	64.0	564	59.3	5.68	0.47	4.22	0.59	21.7
	2–3	23.2	6.50	160	23.4	24.1	1.44	4.14	188	1.63	44.1	11.9	1.76	426	322	3.27	362	15.5	88.0	30.3	39.0	28.9	66.7	250	65.0	10.7	0.81	7.11	0.82	39.6
	3–4	22.4	6.50	70	25.6	18.7	1.25	3.89	190	1.98	45.4	10.8	1.60	331	266	3.61	283	16.3	82.7	28.3	40.0	25.9	67.2	201	61.2	9.83	0.75	6.77	0.78	38.8
	4–5	23.0	6.55	50	31.2	15.0	1.10	1.91	2030	1.03	43.3	10.5	1.49	293	246	3.73	269	16.8	68.7	24.9	35.8	23.5	67.9	180	62.8	11.1	0.71	6.49	0.72	39.1
	5–7.5	22.7	6.55	50	38.8	15.5	1.08	1.40	188	2.86	35.6	14.8	2.05	308	432	3.19	394	17.1	64.9	24.2	33.0	32.1	56.5	208	63.2	8.92	0.73	6.73	0.69	37.0
	7.5–10	23.7	6.53	50	24.6	31.2	2.43	4.80	172	2.60	50.0	10.7	1.59	551	330	3.18	345	20.0	92.3	32.1	47.3	30.6	62.3	325	57.4	7.65	0.60	5.37	0.72	28.5
	10–12.5	23.1	6.64	60	45.7	11.4	0.85	1.15	199	0.88	35.5	14.1	1.79	232	357	3.22	355	17.4	57.2	21.6	32.0	24.4	59.1	149	61.4	9.62	0.68	6.18	0.68	36.0
	12.5–15	22.8	6.55	50	40.1	16.8	1.11	1.96	180	1.02	35.7	13.3	1.95	229	337	3.25	357	19.4	67.5	25.1	35.4	26.0	60.8	171	55.0	10.0	0.73	6.68	0.77	36.9
	15–20	23.4	6.58	−20	37.4	22.7	1.54	2.27	175	1.24	33.8	13.7	1.87	281	329	3.00	309	16.2	89.0	27.2	41.3	26.2	55.7	297	56.1	6.72	0.57	5.19	0.60	28.9
C	0–1		6.66	50	14.7	32.7	1.74	5.72	173	6.60	47.6	9.07	1.56	364	269	3.66	271	20.8	81.9	30.2	43.1	38.7	77.2	246	59.9	11.5	0.85	7.36	1.01	41.0
	1–2		6.58	50	14.5	47.8	2.42	7.94	182	7.71	52.5	8.98	1.66	582	260	3.45	278	20.0	88.3	32.8	53.0	44.5	75.0	310	59.6	13.0	0.93	7.71	1.33	41.4
	2–3		6.59	50	16.7	46.2	2.41	7.81	180	6.55	51.1	8.43	1.44	537	248	3.33	266	20.2	85.5	33.3	54.0	41.0	74.2	299	61.3	12.7	0.95	7.47	1.31	42.0
	3–4		6.56	50	11.8	59.0	3.95	12.3	160	5.60	59.0	6.72	1.31	1013	244	3.02	237	22.1	117	55.5	70.6	37.2	73.2	473	60.1	14.0	1.13	8.26	1.76	44.9
	4–5		6.50	60	14.5	38.1	2.20	9.21	175	3.00	49.6	7.26	1.24	515	241	3.22	236	23.2	96.5	34.2	54.2	27.4	75.4	321	65.4	13.3	1.01	7.69	1.52	44.4
	5–7.5		6.64	30	25.6	26.2	1.35	6.15	170	1.56	46.5	8.05	1.23	272	216	3.39	230	21.3	86.3	32.7	51.9	23.6	78.2	256	66.1	10.5	0.95	8.17	1.37	44.4
	7.5–10		6.51	60	24.1	29.0	1.44	6.19	206	1.97	49.7	7.83	1.34	277	201	3.72	218	21.4	96.7	34.7	51.3	24.2	79.6	317	65.6	10.3	1.13	8.68	1.28	48.1
	10–12.5		6.65	40	25.5	23.1	1.50	5.42	205	3.02	46.0	7.41	1.31	259	199	3.62	220	20.3	92.4	32.4	49.7	27.2	81.9	277	68.2	11.0	1.04	8.63	1.05	46.8
	12.5–15		6.60	50	29.5	22.6	1.33	5.64	204	2.50	46.7	7.07	1.18	251	202	3.64	213	17.9	90.0	31.3	54.9	25.1	81.6	239	64.8	11.2	1.09	8.77	1.02	45.1
	15–20		6.58	50	32.8	18.6	1.29	4.31	186	1.14	43.2	7.34	1.12	218	205	3.64	203	21.5	76.2	27.7	45.9	19.8	81.9	183	65.4	10.1	0.92	8.21	0.81	43.1

* Not reliable values.

Table 3
Physico-chemical parameters, dry mass (DM), main and trace element concentrations in sediments of the Pampulha reservoir (2nd sampling campaign August 2001).

| Station	Depth (cm)	T (°C)	pH	Eh (mV)	DM (%)	TC (mg/kg)	P (mg/kg)	S (mg/kg)	Al (mg/kg)	Ca (mg/kg)	Fe (mg/kg)	K (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Na (mg/kg)	Ti (mg/kg)	Ba (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Sr (mg/kg)	V (mg/kg)	Zn (mg/kg)	Zr (mg/kg)	As (mg/kg)	Cd (mg/kg)	Sn (mg/kg)	Sb (mg/kg)	Pb (mg/kg)
A	0–1		6.67	70	11.3	85.8	5.60	3.88	129	6.10	52.6	11.7	2.44	1177	1038	3.54	504	17.1	210	71.0	43.6	61.3	60.4	1252	81.9	8.89	1.47	12.6	1.38	46.8
	1–2		6.70	80	23.2	40.1	2.68	2.21	161	4.67	50.2	14.6	2.61	543	930	4.26	468	12.1	133	43.8	37.1	48.1	63.7	631	71.3	8.86	1.17	10.4	1.13	44.9
	2–3		6.70	70	34.3	24.2	1.35	1.25	163	3.48	44.4	15.2	2.50	260	906	4.33	421	15.7	105	35.8	37.9	41.1	69.1	432	76.2	8.89	0.97	8.71	0.88	41.9
	3–4		6.73	70	43.1	18.8	1.04	0.71	166	3.14	42.5	15.8	2.62	202	950	4.30	433	13.1	7606	27.7	33.0	40.7	66.9	256	77.7	8.19	0.82	7.30	0.70	39.2
	4–5		6.73	40	42.0	20.4	1.09	0.86	155	3.08	40.2	15.2	2.46	211	880	4.00	438	14.8	80.9	313.3	34.4	42.2	66.4	273	74.6	8.05	0.82	7.61	0.73	40.0
	5–7.5		6.77	50	45.6	19.0	0.94	0.66	155	4.18	41.9	16.0	2.76	228	1047	4.006	457	16.0	78.4	31.6	35.0	48.6	65.4	246	82.2	5.36	0.50	4.85	0.45	26.5
	7.5–10		6.80	60	46.3	15.0	0.83	0.67	166	2.80	43.4	16.5	2.52	218	1035	4.31	442	13.4	67.6	24.0	31.7	39.6	63.1	205	85.6	5.76	0.52	4.66	0.42	28.3
	10–12.5		6.81	80	51.6	14.5	0.66	0.45	159	3.72	40.2	17.6	2.80	237	1566	3.87	487	12.8	58.0	24.1	28.9	51.0	56.6	185	106	7.84	0.73	6.59	0.59	38.2
	12.5–15		6.84	60	49.0	15.8	0.78	0.54	158	4.17	41.0	17.0	2.71	246	1330	3.90	481	15.1	64.2	26.2	32.3	52.1	59.8	219	105	7.63	0.73	6.55	0.61	37.6
	15–20		6.87	40	47.6	18.7	0.89	0.61	161	3.96	42.7	16.7	2.71	245	1117	4.09	469	17.4	73.1	29.6	33.5	48.6	63.4	254	82.7	8.56	0.86	7.63	0.81	40.7
B	0–1	21.0	6.86	80	2.44	14.1	12.3	21.5	123	7.09	89.2	9.95	1.99	1878	1656	3.41	720	24.6	224	65.3	66.0	71.9	66.7	1292	493.7	11.6	1.60	11.6	2.49	46.3
	1–2	20.1	6.81	60	14.4	58.9	2.97	5.00	154	2.59	54.6	10.7	1.76	542	524	4.27	464	18.9	144	48.6	43.6	35.7	73.0	662	65.3	10.9	1.26	10.0	1.54	47.3
	2–3	19.8	6.80	70	23.5	26.5	1.64	2.63	168	1.77	47.8	12.1	1.82	289	527	4.46	407	17.0	101	35.1	38.8	30.6	74.4	311	62.9	10.1	0.91	7.87	0.93	42.7
	3–4	19.8	6.80	70	28.2	20.5	1.40	1.95	178	1.69	49.4	12.1	1.75	220	415	5.00	378	19.5	85.4	29.2	38.4	27.8	74.8	222	63.1	10.0	0.89	7.11	0.90	41.1
	4–5	19.9	6.83	70	38.9	14.7	1.19	0.74	165	1.41	40.3	15.3	2.31	199	747	4.30	429	14.7	65.0	24.9	33.0	26.7	66.6	187	62.5	8.84	0.78	6.69	0.66	38.7
	5–7.5	20.2	6.83	50	24.4	41.2	2.91	3.69	152	4.06	49.2	12.1	1.85	456	568	3.87	403	14.7	105	37.6	51.0	37.4	68.8	395	60.9	11.3	1.08	8.59	1.18	43.2
	7.5–10	20.8	6.82	40	35.2	15.2	1.02	1.05	179	1.11	43.2	14.9	2.17	165	683	4.46	407	18.3	68.2	26.2	37.7	27.5	68.7	175	63.8	10.4	0.83	6.89	0.75	42.0
	10–12.5	20.5	6.85	80	40.8	13.7	0.88	0.85	168	1.14	39.8	14.4	2.06	150	574	4.20	400	16.0	64.7	23.3	35.3	27.9	66.7	160	63.6	7.49	0.65	5.15	1.44	31.3
	12.5–15	20.7	6.83	60	47.9	17.3	0.72	0.49	162	2.89	41.5	16.4	2.70	327	749	3.93	437	17.3	62.9	25.0	33.1	35.9	62.6	194	62.8	9.29	0.84	7.27	0.68	40.1
	15–20	21.3	6.85	30	33.6	26.9	1.83	2.77	159	2.38	41.7	14.6	2.29	251	627	3.76	413	17.1	110	32.7	50.0	35.1	61.4	394	61.2	9.24	1.00	7.91	1.00	41.6
C	0–1	19.7	6.80	90	12.8	46.5	2.05	8.13	185	3.50	62.4	8.46	1.63	383	519	4.81	303	20.8	102	35.1	51.0	35.2	73.4	382	58.9	14.0	1.18	8.79	1.37	46.2
	1–2	20.4	6.78	90	17.4	32.6	1.76	5.28	194	3.72	58.0	9.87	1.80	365	556	5.09	319	20.9	84.4	28.7	41.1	36.2	73.5	254	61.9	13.6	0.99	7.66	1.09	44.8
	2–3	19.0	6.84	90	17.4	45.1	2.00	6.26	192	6.50	61.4	10.6	1.88	406	614	4.99	361	19.2	81.0	28.7	47.2	47.7	69.3	276	64.3	12.8	0.96	7.01	1.21	41.1
	3–4	19.1	6.87	40	16.3	49.7	2.29	7.17	181	7.17	61.4	10.4	1.87	533	615	4.59	373	19.9	84.2	32.1	52.5	52.5	70.1	311	59.8	14.0	1.04	7.41	1.38	44.1
	4–5	19.1	6.85	60	18.1	37.5	2.00	6.74	193	3.98	59.4	9.71	1.77	412	571	4.81	314	17.5	82.7	30.7	46.7	38.8	72.2	279	65.2	14.3	1.08	7.57	1.35	46.3
	5–7.5	20.0	6.78	70	17.8	37.4	2.33	7.18	194	2.04	60.3	10.2	1.77	401	569	4.88	300	21.6	95.8	33.1	56.8	30.5	72.6	320	64.9	14.5	1.18	8.10	1.52	47.7
	7.5–10	19.8	6.77	60	19.6	25.6	1.42	6.75	161	2.58	45.3	8.97	1.71	246	454	4.29	289	19.9	82.8	31.0	51.3	27.4	72.2	239	64.5	13.6	1.08	7.79	1.44	48.7
	10–12.5	20.4	6.80	80	18.2	28.2	1.51	8.07	159	2.67	48.0	7.82	1.57	228	399	4.17	281	18.0	100	36.7	58.9	30.7	74.4	371	66.2	9.08	0.75	5.76	0.89	32.6
	12.5–15	20.3	6.80	40	22.4	26.6	1.54	4.98	173	6.18	48.2	8.08	1.62	232	371	4.61	272	23.0	94.8	32.4	55.1	34.8	77.1	303	66.6	14.1	1.11	8.70	1.14	47.3
	15–20	20.9	6.83	60																										

∗No reliable values.
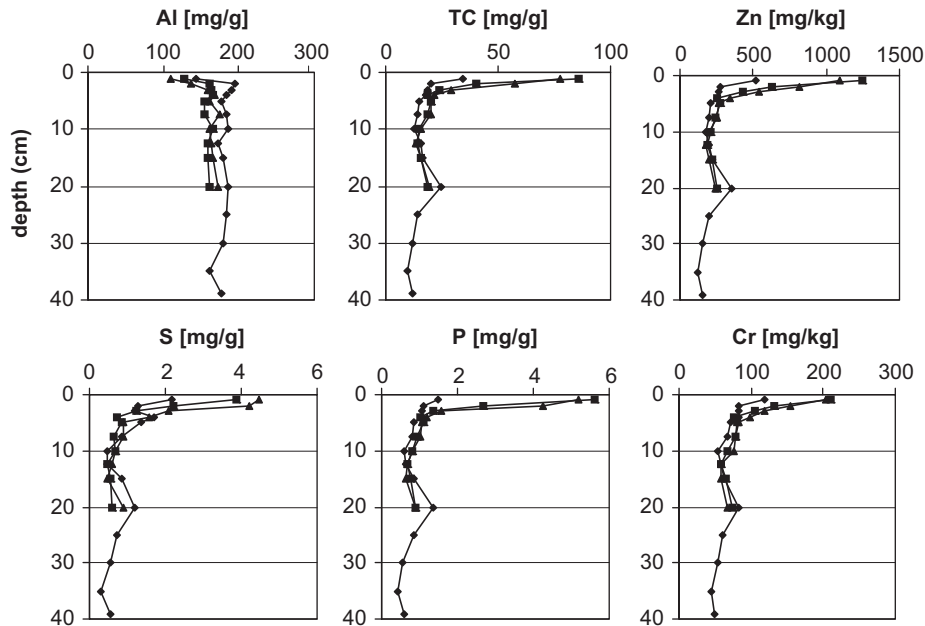
Fig. 3. Depth profiles of selected element concentrations in three different sediment cores from sampling point A (2nd sampling campaign August 2001).

Table 4
Mean concentration c [mg/kg] in top layer (5 cm) and relative enrichment factors EF (by dividing by the minimum concentration averaged from all sampling points) of selected elements in the sediment.

Element	S	P	TC	Zn	Sb	Cd	Cu	Cr	Sn	Pb	Ni
c	4780	2170	37,640	383	1.07	1.09	36.8	102	8.0	43.5	42.6
EF	11	4.1	3.5	3.1	2.5	2.4	2.1	2.0	1.9	1.8	1.4

listed in Table 4. The concentrations of C, S, and P are a clear indication of organic pollution as a consequence of urban wastewater discharge. Previous studies have shown that the reservoir is a sink for large amounts of nutrients introduced from the tributaries (Barbosa et al., 1998). The high sulfur contents are especially evident in the top sediment layer through a strong H_2S smell and black color.

Another point of interest that should be addressed here is the possible nature of the sulfides which seem to be forming near the sediment top layer. Some preliminary PHREEQC calculations using the data of Table 3 offer no possibility for the formation of pyrite or any other FeS phase; it allows, however, the possible formation of an amorphous CuS. But if only some HS^- or H_2S is allowed to exist in the system (in the order of μg/L), the water becomes saturated with respect to most common Fe and Cu sulfides.

Two-element correlations (Fig. 4) reveal some more striking differences between specific elements. C and P show a clear unique correlation with no differences between the sampling points. C and S, in contrast, are correlated differently for each sampling point. Obviously, organic substances in the sediment have higher S contents at point C than at point A, with point B possessing intermediate amounts. The same is true for the correlation of C and Ni, indicating that Ni is uniquely correlated with S (Fig. 4). Cr shows a different behavior. Plotted against C, the steepest correlation line is found at point A and the flattest one at point C. This trend is even more pronounced in the correlation against S. Zn and Cu display the same pattern as Cr (not shown here). The different correlation patterns indicate that S is deposited not only in organic material with C and P, but also occurs as sulfide mineralization of Cu and Zn, more notably in the deeper water regions at sampling point C. This

observation is in close agreement with the lack of oxygen and the low redox potential at this station as well as with decrease in S in the deep water. The correlations also reflect the supply of heavy metals to the lake sediments by the main tributaries, the Sarandi and the Ressaca (Fig. 1). Ni is obviously closely linked to S, whereas Zn, Cr, and Cu seem more related to C, with a tendency to precipitate closer to the main tributaries than S and Ni. None of these elements shows any clear correlation to Fe or Mn concentrations.

A principal component analysis (PCA, Table 5) was done as a statistical summary of all the analyzed total concentrations (Boruvka et al., 2005). The results vary somewhat depending on the data set for which the PCA was calculated. In all cases three principal components were found to be of significance. Factor loadings >0.6 or <-0.6 are printed in bold letters, since they are taken as an indication that the specific element can be assigned to the corresponding component. The following observations can be made:

- Component 1 predominates by the very high communalities and factor loadings. The third component is obviously less significant.
- The elements C, S, Fe, Cr, Ni, and Sb are unambiguously assigned to component 1, irrespective of the data set used for the PCA. The factor loadings are positive in all cases.
- The elements P, Cd, Cu, Sn, and Zn are also assigned to component 1 with positive factor loadings in most cases. Depending on the data set, other elevated positive factor loadings occur. This applies especially to the data set from the first sampling campaign.
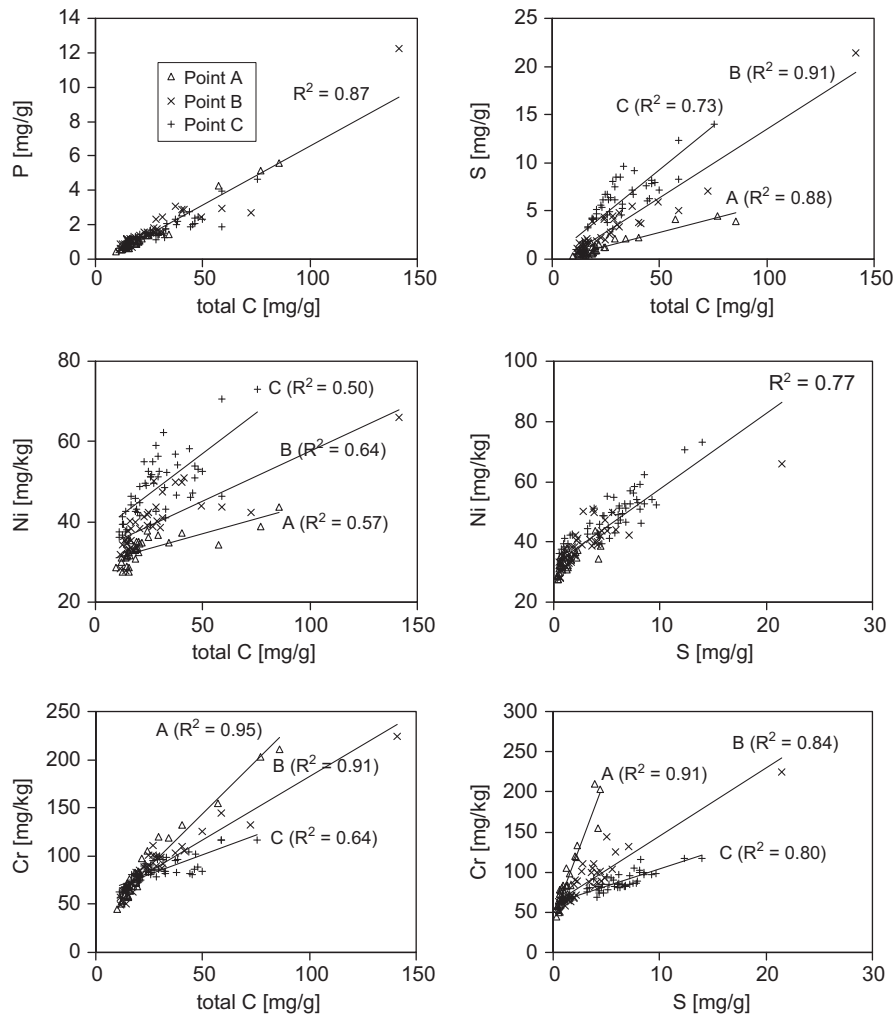
Fig. 4. Correlations of selected pairs of total element concentrations in sediment samples from the three sampling points.

- The allocation of Mn and Pb to component 1 is even more ambiguous. While it is valid in most cases, also with positive factor loadings, there are some elevated positive or negative correlations to other components too, depending on the data set. An influence of the sampling point cannot be detected.
- The elements Al, K, Mg, Na, and Ba show either high positive factor loadings in component 2 or negative ones in component 1. The only exception is a high positive factor loading for Ba in the data set of point B.
- The elements Ca, Ti, As, Co, Sr, V, and Zr cannot be allocated to any component.

Comparing these results with the depth profiles (Fig. 3) reveals that the elements assigned to component 1 are mainly the ones that show enrichment in the top sediment layers. Some of the clear correlations among these elements have already been presented above. The elements are typical components one would expect from pollution sources. According to Rietzler et al. (2001) the main pollution sources are iron and steel industries, which probably are responsible for Fe, Cr, and Ni contamination and the land-fill dump of Belo Horizonte which might be the source for organic pollution. The concentration values of elements within the 2nd component show trends which are contrary to those of component 1. This is most evident in the depth profiles of Al and K, which are less concentrated in the top

layers. The assumption can be made that the elements within component 2 represent the components of the unpolluted sediment material, which is basically the soil eroded within the catchment. This interpretation fits well with the intensive weathering of the granitic sources in the catchment yielding a large and deep soil cover consisting mainly of easily eroded iron and aluminum oxides.

Pore water and fractionation analysis

Some samples with exceptionally high elemental concentrations in the sediment also show high elemental concentrations in the pore water. Zn is the most easily soluble of the trace elements, reaching up to $> 100 \, \mu g/L$, followed by Ni with up to $20 \, \mu g/L$.

For estimation about the behavior of the elements in case of a remediation measure of the lake which will bring oxygen down to the bottom of the lake, selected samples were measured originally and after oxidation in the lab. Differences of elemental concentrations in pore water between originally anoxic and oxidized samples are summarized in Fig. 5. The distribution coefficient K_d is calculated by dividing the mean concentration in the sediment by the mean concentration in the corresponding pore water samples. Most elements become more soluble (lower K_d) after oxidation; exceptions are Zn, Cu, and Cr. S shows the most significant difference, as can be expected from the conversion of

Table 5
Factor loadings resultant from the Principal Component Analysis of the chemical data of the sediment in the Pampulha reservoir.

Component→	All data			First sampling campaign			Second sampling campaign			Data for station A			Data for station B			Data for station C		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Communalities →	40.86	27.40	8.15	43.68	24.51	12.50	45.18	31.27	5.95	49.01	24.90	11.22	52.21	16.35	12.58	48.66	21.72	7.92
C	**0.91**	0.25	−0.25	**0.64**	**0.69**	−0.29	**0.97**	−0.03	−0.11	**0.97**	0.12	0.06	**0.93**	−0.28	−0.13	**0.95**	0.11	−0.14
P	**0.91**	0.22	−0.26	**0.70**	0.58	−0.29	**0.96**	0.02	−0.16	**0.97**	0.07	−0.04	**0.95**	−0.25	0.00	**0.95**	−0.02	−0.13
S	**0.90**	−0.26	−0.18	**0.92**	0.25	−0.20	**0.81**	−0.47	−0.10	**0.92**	−0.28	−0.16	**0.82**	−0.50	0.17	**0.93**	−0.21	0.00
Al	−0.34	**−0.74**	0.24	0.20	**−0.76**	0.26	−0.54	**−0.65**	0.22	−0.52	−0.58	−0.04	**−0.85**	−0.09	0.36	**−0.61**	−0.15	−0.08
Ca	0.43	**0.63**	0.16	−0.09	**0.78**	0.30	**0.67**	0.33	0.09	0.58	0.26	**0.68**	**0.66**	0.16	−0.48	**0.82**	0.21	−0.10
Fe	**0.85**	−0.07	−0.09	**0.88**	0.12	−0.01	**0.81**	−0.23	−0.12	**0.83**	0.26	−0.24	**0.92**	0.02	0.20	**0.75**	0.16	−0.38
K	−0.52	**0.78**	0.08	**−0.90**	0.28	0.03	−0.23	**0.88**	0.21	−0.59	**0.70**	−0.07	**−0.60**	**0.60**	−0.45	0.16	**0.84**	0.21
Mg	−0.37	**0.86**	0.13	**−0.86**	0.39	0.15	−0.09	**0.95**	0.14	−0.14	**0.84**	0.29	−0.09	**0.70**	−0.65	0.24	**0.86**	−0.05
Mn	0.46	−0.04	−0.27	0.32	0.08	−0.28	**0.64**	−0.07	−0.38	**0.62**	−0.35	0.51	**0.80**	−0.28	−0.28	−0.07	−0.10	**−0.92**
Na	−.1	**0.86**	0.04	**−0.77**	0.57	0.14	0.24	**0.89**	0.01	0.28	**0.90**	−0.04	0.61	0.58	−0.41	0.43	**0.83**	0.10
Ti	0.24	−0.24	0.003	**0.71**	−0.59	0.00	−0.36	**−0.68**	0.28	0.29	**0.75**	−0.54	0.22	0.49	0.50	−0.07	**0.82**	0.32
As	**0.63**	−0.48	0.45	**0.71**	−0.16	0.45	0.47	**−0.76**	0.39	0.43	**−0.72**	0.11	0.33	0.55	**0.63**	**0.64**	0.15	−0.07
Ba	−0.04	**0.94**	−0.03	**−0.75**	0.58	−0.02	0.37	**0.86**	0.02	0.32	**0.88**	0.20	**0.75**	0.37	−0.35	**0.67**	**0.71**	0.12
Cd	0.83	0.18	0.47	0.57	0.34	**0.68**	**0.92**	−0.03	0.37	**0.87**	−0.32	0.05	**0.74**	0.58	0.25	**0.88**	−0.28	0.13
Co	0.39	−0.41	0.16	0.32	−0.12	0.23	0.42	**−0.68**	−0.09	−0.32	−0.46	0.51	0.54	0.07	0.01	0.41	−0.41	−0.23
Cr	**0.86**	0.25	−0.28	**0.70**	0.54	−0.26	**0.91**	0.11	−0.21	**0.98**	0.07	−0.11	**0.93**	−0.27	0.05	**0.91**	−0.16	0.06
Cu	**0.83**	0.36	−0.27	**0.63**	**0.69**	−0.21	**0.90**	0.25	−0.18	**0.97**	0.12	−0.02	**0.91**	−0.28	−0.06	**0.87**	−0.27	−0.11
Ni	**0.85**	−0.35	−0.17	**0.94**	0.08	−0.16	**0.72**	−0.54	−0.15	**0.88**	0.17	−0.19	**0.87**	−0.23	0.12	**0.87**	−0.25	0.00
Pb	**0.62**	−0.09	**0.75**	0.49	−0.06	**0.85**	**0.69**	−0.23	**0.63**	**0.68**	−0.42	0.18	0.33	**0.76**	0.45	**0.64**	−0.39	0.19
Sb	**0.89**	0.15	0.20	**0.72**	0.54	0.31	**0.88**	−0.09	0.21	**0.92**	−0.26	0.05	**0.82**	0.27	0.15	**0.96**	−0.18	0.03
Sn	**0.67**	0.21	0.56	0.42	0.21	**0.80**	**0.83**	0.11	0.40	**0.89**	−0.31	0.15	**0.62**	0.59	0.27	**0.66**	−0.51	0.23
Sr	0.23	**0.90**	0.09	−0.46	**0.80**	0.22	0.59	**0.70**	0.06	0.41	**0.66**	**0.61**	**0.78**	0.26	−0.51	**0.86**	0.36	−0.05
V	0.54	**−0.66**	−0.03	**0.91**	−0.29	0.02	0.10	**−0.89**	0.02	0.50	0.24	**−0.76**	0.50	0.02	**0.63**	−0.11	**−0.90**	0.15
Zn	**0.76**	0.57	−0.16	0.32	**0.89**	−0.15	**0.91**	0.34	−0.05	**0.98**	0.10	0.02	**0.94**	−0.22	−0.13	**0.96**	−0.10	0.08
Zr	−0.37	0.54	0.31	−0.53	0.25	0.49	−0.27	**0.70**	0.28	−0.25	**0.70**	0.49	−0.53	0.30	0.05	0.18	−0.39	**0.74**

Fig. 5. Distribution of selected element concentrations between sediment and pore water. The distribution coefficient K_d is calculated by dividing the mean concentration in the sediment by the mean concentration in the corresponding pore water samples.

sulfide to sulfate. The pH in the pore water of most samples was found to decrease from 7 to values between 4 and 5 within 60 days of air exposure, which can be mainly attributed to sulfide oxidation.

The pH of the sediment is in the range of 7. In contrast to the pore water, the sediment samples show no change in pH even after several weeks of oxidation. The logical conclusion is that the sediment provides strong Eh and pH buffering. This observation is in good agreement with the high mass concentration of carbon (Tables 2 and 3) in the uppermost part of the sediment (0–5 cm) at all three stations (around 35–70 mg/g; highest enrichment factor 3.5, see Table 4) which probably act as organic or inorganic carbon buffer against acidification.

The elemental concentrations in the sequential extraction fractions are shown in relation to the total concentrations. Fig. 6 displays the averaged results from six well-preserved (anoxic) and four oxidized samples for the elements Fe, Zn, Cr, and Ni.

With Fe we observe a remarkably high share of the residual fraction, which increases in the oxidized samples. Increase in this

share is attributed to an increased presence of highly crystalline Fe oxide phases. Zn is mainly found in the 3rd, 4th, and 6th extraction steps. Zn found in steps 3 and 4 is bound to Fe oxides. It is not detectable in step 5, which was unexpected because the close correlations between the total concentrations of C, S, and Zn. These findings suggest a dominating organic speciation. Since the chemicals used for step 5 in the sequential extraction scheme are not appropriate for all kinds of sulfides (hypogene sulfide minerals like pyrite, chalcopyrite, or molybdenite might partly survive this leach) the residual fraction might contain some sulfidic residue not extracted in the 5th step. Zn fractionation shows no differences between anoxic and oxidized samples. Cr dominates in the 4th and 6th extraction steps, with a slight increase in the residual fraction for the oxidized samples. This is in good agreement with the well-known association of Cr and Fe oxides. Ni is partly soluble in the first four extraction steps, but the major part remains insoluble (residual phase). Part of the carbonate fraction is apparently dissolved during oxidation and incorporated into newly-formed oxides. From the very clear Ni/S correlations mentioned above, one would expect to find a
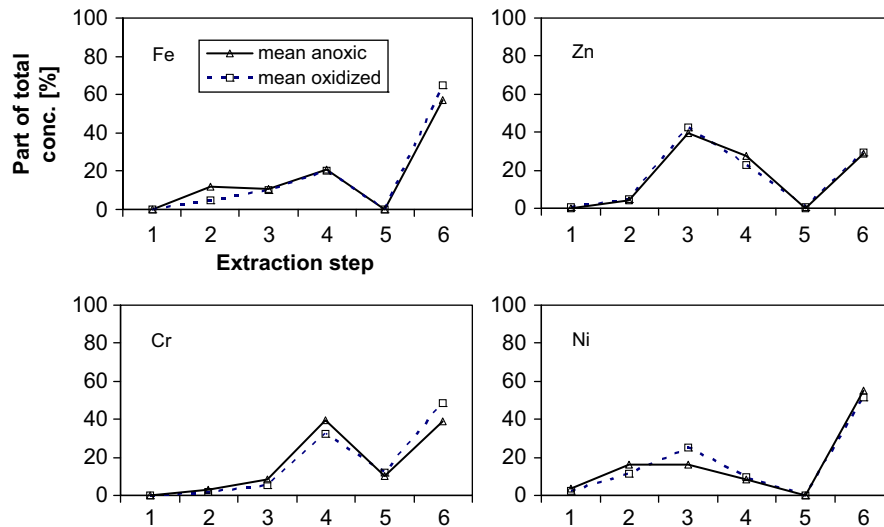
Fig. 6. Mean parts of concentrations found in the fractions of the sequential extraction 1=exchangeable, 2=carbonatic, 3=easily reducible, 4=less easily reducible, 5=organic/sulfidic, 6=residual fraction.

substantial amount in step 5, which is not the case. Again, we assume that the extraction was ineffective and Ni compounds remained insoluble up to step 6. The small differences between the anoxic and the oxidized samples and the missing evidence of a sulfidic fraction by sequential extraction indicate strong Eh and pH buffering of the sediment.

Conclusions

The work allows an insight into the physico-chemical properties of the lake. The lake water is permanently stratified, very poor in oxygen with a high nutrient concentration. In its bottom it was not possible to detect oxygen. The sediment also shows low redox potential values (between 30 and 90 mV). The pH value is in the neutral range both in the water and in the sediment. These results emphasize the strong eutrophication and the ecological degradation of the lake. The measured values, as well as the dark color and the strong smell, suggest the presence of sulfide compounds in the sediment.

The sediment is composed of very fine grains (sand part is < 1%). As one moves away from the main channel of the stream, one can observe an increasing dominance of finer grain sizes. Quartz was not found; instead the clay minerals kaolinite and illite dominate. Also traces of montmorillonite as well as Fe and Al oxides were identified. The clay mineral composition probably corresponds to the mean properties of the eroded soil in the catchment area whereas part of the Fe and Al oxides could be a result of autochthonous *in situ* precipitation. The mineral composition of the sediment is very similar (nearly identical) for the three sampling stations in the first 5 cm, which leads to the conclusion that the source of the sediment input does not change in the course of time.

The sediment also shows a high content of aluminum. Its regular distribution and the correlations with K, Mg, and Ba suggest a geogenic origin. With the exception of the top layer the concentration of the majority of the heavy metals is in the range of the geogenic background values, with only one exception of Zn. P and S, probably dominant as nutrients, show a strong enrichment in the uppermost layer. Almost all heavy metals are enriched in the top layers of the sediment. It is possible to detect clear differences among the sampling stations for S, Ni, Cr, Cu, and Zn, although with different tendencies. While S and Ni concentra-

tions in the sediment from station C are higher compared to station A, the opposite behavior is observed for Cr, Cu, and Zn. This can be attributed to the high content of sulfur in the bottom sediment as well as to the high mobility of Cr, Cu, and Zn compared to the high affinity of Ni for S. The spatial distribution of the concentration in the lake as well as in the profile suggests the presence of an anthropogenic influence for these elements. The results of the PCA give support to the classification of the heavy metals in the lake as enriched due to anthropogenic influence from the iron and steel industries and the solvent and paint industries (Fe, Cr, Ni, Sb, Cd, Cu, Sn, and Zn) and the ones having geogenic origin (Al, K, Mg, Na, Ti, Ba, V, and Zr). For As, Cd, Co, and Pb, a slight anthropogenic contribution may be supposed by the same pollution sources.

Like the upper sediment layers, the pore water of Lagoa da Pampulha is contaminated by P, S, and heavy elements (especially Cr, Cu, Ni, and Zn). The higher concentrations of heavy metals found in the pore water give evidence for the availability of contaminants under oxidizing conditions.

The results of the sequential extraction indicate the presence of a redox buffer in the sediment (most likely organic C), which prevents (i) fast oxidation of sulfides, (ii) buildup of acid conditions, (iii) fast release of heavy metals, and causes (iv) increase in accumulation of heavy elements in the sediment.

The water and sediment of the Pampulha Lake shows no alarming enrichment of heavy metals. However, it shows clear signs of domestic pollution as well as industrial influence. The distribution of elemental concentrations in the sediment points to the main tributaries as the most significant supply of contaminants which leads to the assumption that the main tributaries may be quite severely affected. Therefore we propose that the remediation programs should not only focus on reducing eutrophication but also on identifying and eliminating the sources of metal pollution. Care should be taken with dredged material, from which increasing amounts of metals may be released after oxidation.

References

Bachmann, T.M., Zachmann, D.W., Friese, K., 2001. Redox and pH conditions in the water column and in the sediments of an acid mining lake. J. Geochem. Explor. 73, 75–86.

Backhaus, K., Erichson, B., Plinke, W., Weiber, R., 1996. In: Multivariate Analysenmethoden. Springer, Berlin.

Barbosa, F., Garcia, F., Marques, M., Nascimiento, F., 1998. Nitrogen and phosphorus balance in a eutrophic reservoir in Minas Gerais: a first approach. Rev. Brasil. Biol. 58, 233–239.

Boruvka, L., Vacek, O., Jehlicka, J., 2005. Principal component analysis as a tool to indicate the origin of potentially toxic elements in soils. Geoderma 128, 289–300.

Calmano, W., 1989. Schwermetalle in kontaminierten Feststoffen. Chemische Reaktion, Bewertung der Umweltverträglichkeit, Behandlungsmethoden am Beispiel von Baggerschlämmen. Verlag TÜV Rheinland, Köln.

Charlesworth, S.M., Lees, J.A., 1999. Particulate-associated heavy metals in the urban environment: their transport from source to deposit, Coventry, UK. Chemosphere 39, 833–848.

Cena, T., 2001. R$ 215 milhões são jogados pelo ralo. Estado de Minas 02.08.2001: 25.

CPRM, 2001. Estudo Geológico da Bacia da Lagoa da Pampulha. CPRM/SUREG-BH., Belo Horizonte.

DEV, 2001. Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung. Wiley-VCH, Weinheim.

Giani, A., 1994. Limnology in Pampulha reservoir: some general observations with emphasis on the phytoplankton community. In: Pinto-Coelho, R., Giani, A., von Sperling, E. (Eds.), Ecology and Human Impact on Lakes and Reservoirs in Minas Gerais with Special Reference to Future Development and Management Strategies. SEGRAC, Belo Horizonte, pp. 151–163.

Greenberg, A.E., Cleresci, L.S., Eaton, A.D., 1992. In: Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, DC.

Jakob, G., Dunemann, L., Zachmann, D.W., Brasser, T., 1990. Untersuchungen zur Bindungsform von Schwermetallen in ausgewählten Abfällen. Abfall-wirtschafts Journal 2, 451–457.

JCPDS, 1967. In: Powder Diffraction File. Joint Committee on Powder Diffraction Standards, Philadelphia.

Kelly, J., Thornton, I., Simpson, P.R., 1996. Urban geochemistry: a study of the influence of anthropogenic activity on the heavy metal content of soils in traditionally industrial and non-industrial areas of Britain. App. Geochem. 11, 363–370.

Krischner, H., 1990. In: Einführung in die Röntgenfeinstrukturanalyse. Vieweg, Braunschweig.

Lindström, M., 2001. Urban land use influences on heavy metal fluxes and surface sediment concentrations of small lakes. Water Air Soil Pollut. 126, 363–383.

Mudroch, A., Azcue, J., 1995. In: Manual of Aquatic Sediment Sampling. Lewis Publishers, London.

Pinto Coelho, R., 1998. Effects of eutrophication on seasonal patterns of mesozooplankton in a tropical reservoir: a four year study in Pampulha Lake, Brazil. Freshw. Biol. 40, 159–174.

Rietzler, A.C., Fonseca, A.L., Lopes, G.P., 2001. Heavy metals in the tributaries of Pampulha reservoir, Minas Gerais. Braz. J. Biol. 61, 363–370.

Rose, F., 2001. Verbas podem salvar a Pampulha. Estado de Minas 06.08.2001.

Salomons, W., Förstner, U., 1984. In: Metals in the Hydrocycle. Springer, Berlin.

Tessier, A., Campbell, P., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–850.

Vester, B.P., Zachmann, D.W., 2003. Schwermetallgehalte und Schwermetallspeziationen in Ilsesedimenten und deren potentielle Auswirkung auf die Grundwasserqualität. Zentralbl. Geol. Paläontol. I 1–2, 171–194.

Virkanen, J., 1998. Effect of urbanization on metal deposition in the bay of Töölönlahti, Southern Finland. Mar. Pollut. Bull. 36, 729–738.

Zachmann, D.W., 1994. Tonmineralogie für den Dichtungsbau. In: Rodaz, W. (Ed.), Geotechnische Probleme im Deponie- und Dichtwandbau, 43. Mitteilungen des Institutes für Grundbau und Bodenmechanik, TU Braunschweig, pp. 253–276.

Zachmann, D.W., Mohanti, M., Treutler, H.C., Scharf, B., 2009. Assessment of element distribution and heavy metal contamination in Chilika Lake sediments (India). Lakes Reservoirs: Res. Manage. 14, 105–125, doi:10.1111/j.1440-1770.2009.00399.x.