Azores volcanic lakes: factors affecting water quality

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Abstract Azorean lakes represent strategic sources of freshwater and some supply water for human consumption. Several samples were collected from 13 volcanic lakes on four different islands. The lakes are cold, pH values ranged between 4.2 and 9.9 and demonstrated low levels of mineralization, except for Furnas do Enxofre, due to the input of volcanic gases that are responsible for the highest CO_2 and acidification of the lake. The lake waters were generally fresh and of Na-Cl and Na-HCO₃ types. The highest decline in lake water quality is related to anthropogenic pressure. Although the São Miguel lakes demonstrate a volcanic signature, the effect of the volcano is not a significant contributor to water quality decline, except in the case of Furnas, for which ion charge increased due to the thermal water input and volatile degasification. However, for Furna do Enxofre, the lake is highly contaminated by volcanic fluids. Global warming will destroy the normal balance of water supply. During winter, the greater frequency of precipitation events will increase the input of fertilizers and sediments, causing an increase in water quality degradation. Temperature increases are expected to combine with water shortages due to increased evaporation to decrease lake water volume. Eutrophication is expected to worsen. Consequently, it is hypothesized that climate change will generally lead to an increased water quality degradation of these strategic water reservoirs.

Key words volcanic lakes; eutrophication; volcanic fluids contamination; climate change; Azores

INTRODUCTION

Throughout history, the quantity and quality of water has always been fundamental to the wellbeing of civilizations. The rapid increase in world population and improved living standards has recently contributed to a growing demand for freshwater resources, not only to satisfy people's basic needs, but also to satisfy the demands for agricultural irrigation and industry with the subsequent deterioration of freshwater quality worldwide.

The Intergovernmental Panel on Climate Change (2007) report that average air temperature has increased because of human activity. Improved climate change models have predicted global weather changes, namely, increasing the frequency and magnitude of extreme meteorological weather events. In the Azores, it is expected that an anticyclonic displacement will lead to more frequent episodes of frontal instability (Azevedo & Gonçalves, 2001). Local climate change scenarios predict a moderate air temperature increase (Santos & Miranda, 2006). Winter-time precipitation events are predicted to increase, and as a result, the leaching of soil nutrients will increase and with the accompanying atmospheric temperature increases, water quality degradation is expected to increase (Rodrigues, 2006; Novo, 2007).

Lakes are generally thought of as strategic sources of freshwater. In the Azores archipelago, three lakes are utilized to supply water for human consumption because saltwater intrusion has affected groundwater and few springs are available for water supply in those locations. The islands' geomorphology and climate have provided the Azores with significant quantities of interior surface water. However, eutrophication has been increasing because of agricultural and livestock activities.

The Azores archipelago is located in the North Atlantic Ocean (Fig. 1), between the latitudes 37°N and 40°N and the longitudes 25°W and 31°W. The islands of the Azores represent the emerged portion of the Azores Plateau, limited by the bathymetric line of –2000 m. The archipelago is located near the junction of the North American, Eurasian and African Plates. The location is a complex geodynamic setting and is reflected by several tectonic structures, which explain the high level of seismicity and volcanic activity.

Numerous lakes occur on most islands, each one with its unique physical characteristics conditioned by its specific geological setting. However, these lakes are predominantly located inside explosion craters (Table 1).



Fig. 1 Location map of the Azores Archipelago and sampled lakes on the islands of São Miguel, Terceira, Graciosa and Flores.

Table 1 Physical characteristics of volcanic lakes.

il ator
quality ^b
Moderate
Poor
High
Bad
Bad
High
Bad
High
Good
-

(a: data from PRA; b: data from Gonçalves et al., 2006; c: data from Nunes, 1999; d: data from Morriseau, 1987).

A total of 88 lakes (Porteiro, 2000) are distributed throughout the islands of São Miguel, Terceira, Faial, Flores and Corvo, as well as two small cave lakes on Graciosa and Terceira. The total volume of water stored in the crater lakes is about 90×10^6 m³, 93% of which on São Miguel. Flores lakes contribute 5% of the total water and the remaining 2% correspond to lakes located on the islands of Terceira, Faial and Corvo.

Livestock production is the basis of the local economy and has increased significantly during the second part of the 20th century. Milk and meat production exerts serious pressure on water resources, with the transformation of land use, destruction of habitats, soil erosion, and excess use of fertilizers and pesticides resulting in water contamination (chemical and microbiological), and in particular, lake eutrophication. Lake water quality in the Azores has degraded rapidly during the past few decades due to the input of nutrients and organic matter, leading to a proliferation of macrophytes (Cruz *et al.*, 2008). To monitor this problem, we sampled the 13 largest lakes on São Miguel and Flores and two cave lakes on Graciosa and Terceira (Fig. 1). The objective of this paper is to evaluate the hydrogeo-chemical characteristics of water quality and determine the influence of volcanic fluid inputs on these water systems. The volcanic fluids are a source of natural pollution. However, fertilizer use and the effects of climate change may exacerbate the deleterious effects of the volcanic fluids on water quality.

METHODOLOGY

Several water column samples were taken at the same location in each lake during several campaigns. During the sample campaigns, pH, temperature, electrical conductivity and dissolved oxygen (DO) concentration were recorded with portable digital recorders, e.g. WTW 340i/Set and a thermometer (Hanna, model HI93531). In the field, dissolved CO₂ and alkalinity were determined by titration, and samples were double filtered with 0.45 and 0.2 μ m Millipore membrane filters (cellulose acetate) and stored in double-capped HDPE bottles. The sample for cation analyses was acidified with Suprapur nitric acid (65%). In the laboratory, major cation concentrations were determined by atomic-absorption spectrometry, anion concentrations were determined by ion chromatography, and Si, Fe and Al were analysed by ICP-MS at Activation Laboratories, Canada (<u>http://www.actlabs.com/</u>).

RESULTS

The lake waters are cold. The minimum water temperature (5.2°C) was at the surface of Lake Fogo, the uppermost (587 m) on 1 January (Table 2). However, only the lakes on São Miguel, Terceira and Graciosa were sampled during winter. In contrast, the maximum summer water temperature was obtained at Furnas, registering 23°C.

For all of the sampled lakes, pH ranged between 4.2 and 9.8. The highest pH (9.8) was recorded at the water surface (epilimnion), due to the eutrophication, while slightly acid pH occurred at the bottom (hypolimnion) of the deepest lakes.

Lake waters demonstrated low levels of mineralization, except at Furnas do Enxofre due to the input of volcanic gases, responsible for the highest values of CO_2 and the acidification of this water. Rock hydrolysis is responsible for the highest concentration of ions in this system (Antunes, 2008). Carbon dioxide concentrations were lower in other lakes.

The lake waters were generally fresh of the Na-Cl and Na-HCO₃ types, except that at Furna do Enxofre which was a Mg-HCO₃ type.

During spring the deep lakes (>12 m) thermally stratified; the thermocline was perfectly formed during summer (Fig. 2A). Furnas does not stratify, probably because it is a shallow lake. However, summer hypolimnion temperatures were slightly lower than those in the epilimnion. Lava cave lakes are naturally protected from the sun and the interiors of these caves experience insignificant changes in atmospheric temperature, i.e. they have a relatively constant temperature profile temporally.

The pH profile pattern is very similar to that of temperature. Summer hypolimnion pH was high due to eutrophication. Above the thermocline, pH decreases significantly to more acid/neutral values. At Furnas, pH profiles did not change significantly and pH in the cave lakes was similar throughout the water column (Fig. 2B).

All stratified lakes had anoxic hypolimnia. At Furnas, DO decreased markedly between the depths of -6 and -8 m (Fig. 3C). DO at Furna do Enxofre was lower than at Algar do Carvão. During winter, water circulation mixed the CO₂ concentrations throughout the water column and deep water had a CO₂ enrichment during summer (Fig. 3D). Furnas had the highest hypolimnion CO₂ concentrations compared with Congro and Furna do Enxofre, which had the highest total CO₂ concentrations, i.e. through the entire water column.

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 Table 2 Results from the sampled lakes.

Lake	Value	pН	Temp.	Cond	O ₂	Total CO ₂	Na	K	Mg	Ca	HCO ₃	Cl	SO_4	SiO ₂	Al	Fe
			(°C)	(uS/cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Verde	Max	9.6	23	159	11	73	25	3.3	1.4	3.6	55	19	4.7	4.7	0.2	0.6
	Min	6.5	13	121	1.4	27	16	1.9	0.8	1.4	8.5	14	2.7	0.0	0.0	0.0
Azul	Max	9.4	22	111	10	27	22	3.8	1.7	3.4	25	18	4.1	4.7	0.5	0.4
	Min	6.6	13	90	2.9	12	13	2.1	0.9	0.8	6.7	15	3.1	0.0	0.0	0.0
Santiago	Max	9.8	22	132	9.8	64	23	2.7	1.1	4.2	39	18	4.7	7.8	0.3	2.5
	Min	4.2	12	60	1.5	21	5.1	2.0	0.5	1.0	18	14	2.8	0.0	0.0	0.0
Fogo	Max	9.1	21	49	10	24	8.9	1.9	1.1	5.4	16	13	4.6	7.9	0.1	0.5
	Min	5.9	5.2	14	3.2	1.9	5.7	1.0	0.2	0.3	1.8	7.8	1.7	0.0	0.0	0.0
Congro	Max	9.8	23	135	11	80	13	15	2.3	4.6	49	23	6.0	14	0.5	2.7
	Min	6.2	12	80	1.5	7.6	9.2	4.6	1.1	1.7	3.7	12	1.7	0.2	0.0	0.0
Furnas	Max	9.5	23	152	12	77	21	17	2.6	6.6	59	16	6.0	24	0.4	0.6
	Min	6.5	13	101	2.3	30	16	6.6	1.4	2.2	33	13	3.5	0.4	0.0	0.0
Negra	Max	8.4	15	143	10	41	14	1.7	5.2	7.8	18	16	3.1	14	0.2	0.1
	Min	7.5	13	140	8.1	24	14	1.5	4.7	6.8	12	14	2.6	11	0.0	0.0
Comprida	Max	7.7	20	92	9.2	16	16	1.4	3.1	5.3	18	16	3.1	6.1	0.5	0.1
	Min	6.8	15	76	8.5	10	9.8	0.9	1.8	1.8	12	14	2.6	3.0	0.0	0.0
Funda	Max	9.9	23	148	9.6	38	14	1.9	4.6	8.0	45	19	3.8	8.0	0.3	1.2
	Min	6.7	13	123	3.3	25	13	1.5	3.4	4.0	33	11	2.3	4.8	0.0	0.0
Rasa	Max	7.4	22	71	7.0	7.0	9.5	0.6	1.4	0.7	6.1	18	3.1	3.0	0.2	0.1
	Min	5.4	15	66	3.5	2.1	8.7	0.4	1.3	0.4	1.2	16	2.8	1.1	0.0	0.0
Lomba	Max	8.6	21	60	8.8	11	7.3	0.5	1.8	2.0	12	14	3.9	4.3	0.5	1.7
	Min	6.3	15	55	8.1	4.1	6.5	0.4	1.4	0.7	5.5	11	2.6	1.0	0.0	0.0
Enxofre	Max	6.1	15	611	7.5	474	51	5.7	41	30	268	57	33	52	0.3	0.5
	Min	5.4	14	6	6.0	224	44	1.2	35	26	200	55	31	47	0.0	0.0
Carvão	Max	8.9	12	179	9.8	44	36	2.6	0.1	0.9	62	19	5.0	53	0.2	0.2
	Min	7.7	11	82	8.0	34	14	2.5	0.0	0.5	43	14	4.6	46	0.0	0.2



Fig. 2 Profiles of temperature (A) and pH (B) of Congro, Furnas, Enxofre and Carvão lakes.

Bicarbonate concentration was highly variable through the water column at Congro and generally increased slightly in the hypolimnion (Fig. 4E). Chloride and sulfate concentrations were very low and relatively constant temporally. The highest bicarbonate, chloride and sulfate concentrations



Fig. 3 Profiles of DO (C) and total carbon dioxide (D) of Congro, Furnas, Enxofre and Carvão lakes.

were at Furna do Enxofre measuring >200, >50 and >30 mg L^{-1} , respectively. At Congro, conductivity increased where the water stratifies, i.e. at the hypolimnion. This pattern was less obvious at Furnas. The highest conductivity of any lake was throughout the water profile at Furna do Enxofre (Table 2).



Fig. 4 Anion profiles on Congro, Enxofre and Carvão lakes (E) and conductivity profiles on Congro, and Furnas lakes (F).

DISCUSSION AND CONCLUSION

Temperature affects the chemical equilibrium of aquatic systems. Thermal loading is responsible for stratification during summer. The temperature stratification, called the thermocline, is typically located at between 3 and 14 m below the lake surface, and it stops water from circulating between the epilimnion and the hypolimnion.

Eutrophication makes Azorean lakes highly productive systems (INOVA, 1999; Gonçalves, 1997; Gonçalves *et al.*, 2005, Aguiar *et al.*, 2008; Gonçalves, 2008). Biological production by photosynthesis produces high pH (alkaline) in the epilimnion. The hypolimnion, on the other hand, is more acid as a result carbonic acid from high CO_2 concentrations. The high CO_2 concentrations in the São Miguel hypolimnion (i.e. active volcanic systems) cannot be explained solely by decomposition of organic matter. Due to the anoxic environment, the production of CO_2 by anaerobiosis is inefficient and the Verde, Congro, Furnas and Furna do Enxofre lakes show a significant total CO_2 concentration compared with the Flores lakes at the same depth. Congro, Furnas and Furna do Enxofre lakes receive volcanic fluids (Antunes *et al.*, 2005; Cruz *et al.*, 2006; Antunes, 2008). Water/rock interactions neutralize acidity generating high concentrations of solutes including carbonate/bicarbonate. The excess CO_2 and low pH indicate that the hypolimnion exceeds the ability of the volcanic fluids to buffer the system enough to neutralize the acidity, resulting in the higher conductivity and low pH.

Furnas does not stratify. However, the absence of high winds and lack of rainfall during summer allow the deeper lakes to stratify and because circulation of epiliminion and hypoliminion ceases, DO in the hypolimnion decreased while CO_2 and conductivity increased at depth during this period. The stratified lakes overturn occurs during winter due to temperature decrease.

Cave lakes are different than those exposed to the sun. These aquatic systems are naturally protected, not only from the effects of solar warming/cooling, but from large short-term changes in the weather (wind and rain). Air temperatures remain relatively constant in these caves throughout the year, and most solutes did not vary markedly temporally or through the water column, particularly for Furnas do Enxofre. The CO_2 enrichment was explained by volcanic fluid input in bottom water (Antunes, 2008), whilst the buffer system inhibits extremely low pH. Rock hydrolysis explains the highest mineralisation by the water/rock input in this lake.

The lake water quality degradation is related to anthropogenic pressure. The input of artificial nutrients is the major cause of water quality degradation, causing, as well, the extinction of small lakes such as Lagoa do Ginjal on Terceira and Lagoa dos Nenufares on São Miguel due to eutrophication. Agricultural use of high potassium (K) fertilizers results in eutrophication (Antunes, 2008). In general, the most eutrophic aquatic systems are in basins where the surrounding land is exploited by the livestock industry. In the Regional Water Plan for the Azores, fertilizer application rates for the agricultural area (UAA) were 352 and 707 kg ha⁻¹ for PK and NPK, respectively (DROTRH-INAG, 2001) and excessive use of these compounds, may lead to greater mobility of nutrients into these lakes.

Although the São Miguel lakes demonstrate a volcanic signature, the contamination from the volcanic fluids or weathering is not so significant as to contribute to the water quality degradation, except for Furnas, which shows affects due to thermal water input and volatile degasification by the fumarolic field at the north bank.

It is predicted that global warming will destroy the normal balance of the water supply. During winter, the frequency of precipitation events is predicted to increase, resulting in a larger input of fertilizers and sediments into lakes and contributing to higher rates of water quality degradation.

Summer temperature increases are expected to combine with water shortages due to higher evaporation, which will decrease the lake water volume (with a concentrating effect on solutes). Although seemingly a minor effect, the increase in greenhouse gas concentrations in the atmosphere, mainly CO_2 , will increase CO_2 in the lakes due to surface gas exchange. Increases in the accessibility of nutrients, together with temperature increase, is expected to cause a productivity increase in these aquatic systems with a consequent worsening of eutrophication. Therefore, higher thermal loading will promote stratification, possibly beginning earlier and extending later, which in turn, causes higher pH in the photic zone and the increase of water opacity in the surface water and higher CO_2 from decomposition of organic matter in the hypolimnion. Consequently, it is predicted that climate change will generally lead to greater water quality degradation of these strategic water reservoirs.

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