Chemical and isotope monitoring at Lake Albano (central Italy): water-rock interaction and climate change effects

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Abstract

Albano is a typical maar lake showing mainly a bicarbonate-alkali geochemical facies. However, chemical monitoring shows a switch toward an alkaline earth composition in the deeper layers. Water isotope compositions of the lake from this study are compared with lake and groundwater data from the literature and are used to infer meteoric recharge and humidity variations. Enhanced evaporation is inferred, and in conjunction with a reduction in lake volume, is linked to a global relative humidity drop of about 3\% by our model, which agrees with the ground level measurements during the last 20 years.

1 Introduction

Natural isotopic studies may contribute to hydrodynamic characterization of lakes, considered as complex systems. Most frequently, research on lake waters using stable isotopes focuses on hydrodynamic studies for the development of hydrological balance. Moreover other studies using steady-state isotope balance models have often been applied to estimate long-term average water balance conditions for lakes [1]. Such studies have commonly employed values for the kinetic isotope fractionations for oxygen and hydrogen determined from wind tunnel experiments [2], and have assumed isotopic equilibrium between atmospheric moisture and precipitation [3, 4]. The most profound isotope effects in lakes are due to the enrichment produced by evaporation. The fractionation of a evaporating water body typically gives rise to evaporating moisture which is isotopically lighter (depleted in $^{18}$O or D) relative to the remaining liquid, an effect which has been exploited to study evaporation by several approaches, including tracing of heavy isotope buildup which occurs in the residual liquid, i.e., in water bodies (e.g. [2, 1]). Typically the residual waters lie along a slope of 5 on a $\delta$-plot. The precise gradient of the evaporation slope in a particular area is largely a function of local humidity, while the amount of evaporation determines the amount of displacement along the slope [2].

The slope of the evaporation line is strongly dependent on the relative humidity, and the difference between initial meteoric water; the lake’s surface value reflects the rate of vapor separation and isotopic exchange with atmospheric vapor [5]. However, short-term variations of relatively humidity inferable by the isotope composition of evaporating water body [6], has been rarely applied to study climate change.
In this paper we describe the results of several geochemical surveys carried out on Lake Albano during 2003 and 2010. Our goal is to monitor and explain the chemical and isotope composition changes with depth and time. In particular, the isotope composition of water molecule obtained in this study is compared with literature data and to infer humidity variation used for a climate change evaluation.

2 Study area

Lake Albano, located 20 km to the SE of Rome, is hosted within the most recent crater of the quiescent Alban Hills volcanic complex. It is the major lake of the Alban Hills volcano, with a surface area of 5.70 km² and a maximum depth of 175 m. Lake Albano is also located in a high population density area with a high usage of groundwater.

3 Sampling and analysis

Water samples were collected during May and July 2003 and June 2010. Water temperature, electrical conductivity, pH and O₂ values were determined in the field by a multiparametric probe. Bicarbonate was determined by titration. Water samples were filtered through cellulose filters (0.45 μm), and their major and minor constituents were determined with a Dionex DX-120 ion chromatograph (reliability ±2%). Analyses of δ²H/H isotopes used the method of Kendall and Coplen (1985) (reaction with Zn at 450 °C), while δ¹⁸O/δ¹⁶O analyses relied on the CO₂ water equilibration [7, 8]. Mass spectrometry was performed with a Finnigan Delta Plus mass spectrometer.

4 Results

4.1 Geochemical characterization

Albano Lake is constituted by: (i) an oxidized epilimnion from the surface down to 30 m depth, (ii) a thermocline down to 50 m depth and (iii) an anoxic hypolimnion down to the lake bottom. The vertical profile of dissolved oxygen revealed the existence: of ossic epilimnion from the surface to a depth of 30 m; a quite large thermocline (metalimnic zone) from 30 to 50 m depth. The epilimnion measured by T and pH at 10 meters depth changes with the season: 13.5°C and 8.37 during May 2003, 19.7°C and 8.93 during July 2003, 16.1°C and 8.89 during June 2010. T decreases rapidly with depth, but it remains nearly constant at about 8.7-9°C in the hypolimnion. The pH decreases to 6.7, 6.93 and 7.65 in the hypolimnion (respectively May 2003, July 2003 and June 2010).

The main hydrogeochemical facies of the Albano Lake is bicarbonate sodium-potassium. The anion composition is quite stable showing HCO₃ > Cl > SO₄ (in meq/L), while the cation component changes from K = Mg = Na > Ca in 2003 and K > Na > Ca > Mg in 2010 on the surface; Ca> Mg> Na = K in 2003 and K=Na=Ca>Mg in 2010 in the deeper layers. The unusual hydrogeochemical composition of the lake (alkaline and alkaline-earth bicarbonates) can be interpreted as the result of water - rock interaction with volcanic rocks, mainly K-foidites, phonolitic tephrite and tephrites of the Alban Hills volcano [9].

4.2 Stable isotope results

All values of δ¹⁸O and δ D measured during the campaigns in May and July 2003 and June 2010 were correlated with each other and shown in figure 1. In the same plot were also reported the Mediterranean (d = 22), Tyrrenian (d = 15) and Latium meteoric line [10] plus the literature data of other local lakes (Nemi, S. Giovanni), local mean precipitations, springs and wells [10-14]. It may be noted that lake samples and pools are situated below local meteoric lines showing highest isotope enrichment. This is due to open surface evaporation process. In fact, it has been demonstrated [5, 15] that when a basin is subjected to evaporation, its content increases in the heavy isotopes because of the evaporation of light elements. Due to the isotopic disequilibrium that follows and in which evaporation takes place, the
isotopic composition of evaporating basin lies $\delta^{18}$O-D, below the meteoric water line. Well samples below the meteoric line (Fogliano well in [14]; Marmista and Cemetery wells in [13]) have been excluded from the best fit. Their shift may be due to an $^{18}$O-shift related to water-rock interaction at relatively high temperature; however, this interpretation contradicts the position of the deep CA1 borehole (data from [14]) which is positioned to the left of the meteoric line.

Therefore, shift may be caused by water evaporation in the stagnant air level of the soil with a slope of about 2 [6]. The slope of the evaporation line is strongly dependent on the relative humidity, and the difference between initial meteoric and the lake’s surface value reflects the rate of vapor separation and isotopic exchange with atmospheric water vapor [5].

**Figure 1:** values of $\delta^{18}$O and $\delta$ D measured during the campaigns in May 2003, July 2003, June 2010 plus data for other local lakes.

Assuming that the lake is in a steady state (the inflow is balanced by the evaporation flux) and the isotopic equilibrium between local water vapor and the total inflow, a simplified isotope-mass balance equation can be assumed [6]:

$$\Delta \delta = \delta_S - \delta_I = (1-h) \left( \varepsilon_{lv} + \phi^* n^* C_k \right)$$  

where $\delta_S$ stands for isotopic composition of the lake, $\delta_I$ the composition of the total inflow (the lake before evaporation as stated above), $h$ the relative humidity, $\varepsilon_{lv}$ the liquid-vapor enrichment factor calculated as $\varepsilon_{lv} = (\alpha_{lv} -1)10^3$. The parameters pertaining to the kinetic fractionation (Craig-Gordon model) were assumed as $\phi$ (weighting factor) = 1 typical for small lakes, $n$ = 0.5 appropriate for an open water body, $C_k$ (max diffusion depletion) which has the value of $^{18}$C_k = +28.5‰ in the case of the $^{18}$O-labelled water molecule and $^{2}$C_k = +25.1‰ for the $^2$H-water molecule diffusing through air.

The equation has been solved for $h$, with $\varepsilon_{lv}$ for $T = 26{^\circ}C$ [16] in line with the lake surface temperature during the summer season, and using two different values for $\delta_S$: July 1982 [14] and July 2003 (this study). Results obtained from oxygen isotope composition are $h = 74\%$ for 2003 and $h = 77\%$ for 1982, in line with the mean air humidity at the ground level revealed in the area (NOAA dataset). It is noted that the relative humidity decreases by about 3% during the considered period from 1948 to 2010. Furthermore, relative humidity at ground level is rarely considered in climate change studies because local variations contribute to air moisture through transpiration and evaporation, nocturnal-diurnal variations and wind effects. To confirm that isotope variations are due to climate change, we can use a different approach. The isotopic composition of the lake water at the time $t$ could be defined as [4], [17]:

$$\delta_L = \delta_S - \left( \delta_S - \delta_0 \right) \exp \left[ -\frac{E_v}{V} \left( 1 + m \right) \right]$$

where the $m$ parameter, enrichment slope, is assumed as 5.25 in accord with [2]; $\delta_S = (\delta_t + m\delta^*)/(1+m)$ is the steady-state isotopic composition; $\delta^* = (h\delta_A + \varepsilon)/(h - \varepsilon 10^{-3})$ is defined as the limiting isotopic
composition under local meteorological conditions, where $\delta_A = \delta_I - \varepsilon_{I-V}$ is the isotopic composition of atmospheric moisture; $V$ and $E_t$ are the lake and volume evaporated at the time $t$ volume, respectively, assuming a closed lake ($I = E$). Considering the 1984 to 2003 volumetric reduction of $1.6210^6 \text{m}^3$ relatively to the total lake volume of $4.6410^6 \text{m}^3$ ($E/V = 3.510^{-2}$ [10]), the isotope composition of the lake during 1982 as starting composition $\delta_0$ and the relative humidity of $h=0.74$, we obtain an isotope composition of $\delta^{18}O = +0.2 \text{‰}$ and $\delta^2H = -0.6 \text{‰}$, in line with the values measured in this study.

5. Conclusions

The study of the chemical composition of Lake Albano shows mainly bicarbonate-alkaline composition, with some changes in time and depth toward alkaline-earth facies, whereas water isotope composition shows an enrichment caused by enhanced evaporation. Whereas the lake chemistry may be related to water-rock interaction and lake stratification, the isotope effect is related to a global humidity decrease. Our model shows a relative humidity drop of about 3% during the last 20 years that agrees with ground level monitoring. It is concluded that systematic measurements of isotope composition can be used to assess the effect of future climates on lakes and also vice-versa.

References