



Optical properties and light penetration in a deep, naturally acidic, iron rich lake: Lago Caviahue (Patagonia, Argentina)

Gustavo D. Baffico*

INIBIOMA (UNComahue-CONICET), Quintral 1250, 8400 San Carlos de Bariloche, Río Negro, Argentina

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ABSTRACT

The optical properties and light climate in the deep and extremely acid Lake Caviahue have been studied in order to better understand its characteristics and the possible influence upon the phytoplankton community. The absorption coefficients for the dissolved fraction were maximal in the ultraviolet (UV) region and the water absorption spectra showed a shoulder around 300 nm, which was attributed to the concentration of Fe(III). No radiation was detected in the water column below 360 nm. The depth of the 1% incident radiation was dependent of wavelength, showing its maximum of 13.3 m at 565 nm, compared to 1.7 m and 4.8 m at 400 nm and 700 nm, respectively. Phytoplankton biomass was low and showed an almost constant profile with depth despite the relative darkness of the water column. Optical climate of Lake Caviahue is not typical of high elevation lakes but is more similar to low elevation shallow lakes of the Andean region. The chemical composition of the water, mainly Fe oxidation state and concentration, is the responsible for the high attenuation of the UV radiation (UVR). Living organisms are protected of UVR because Lake Caviahue waters are a shield against UV-B.

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Introduction

The quantity and quality of light within an aquatic ecosystem is a very important physical variable with profound implications on the biological communities. For example, a direct effect of this variable is the depth distribution, abundance and primary production of photoautotrophs in the water column, while an indirect effect is the bacterioplankton enhanced production as a consequence of the photobleaching of dissolved organic matter (DOM) (Lindell et al., 1996; De Lange et al., 2003; Engelhaupt et al., 2003).

The underwater light field is affected by the properties of the incoming irradiance and those of the aquatic medium. The spectral dimension of light in a water body can be studied by examining optical properties of water which can be classified as: inherent properties, that depend on the nature and composition of particles and dissolved substances in the medium (e.g. absorption coefficient, scattering coefficient, etc.) and apparent properties, that depend on the medium and on the geometrical structure of light (e.g. the angular distribution of the underwater radiation) (Maritorena and Guillocheau, 1996; Van Duin et al., 2001; Kirk, 2011).

In order to characterize the radiation within an aquatic system the apparent optical property, diffuse attenuation coefficient (K_d) is calculated based on the measurement of the downward irradiance

flux at different depths (Kirk, 2011). The attenuation coefficient will vary spatially and temporally with the chemical and physical characteristic of the medium. Besides the water itself, dissolved and particulate matter in the water play a role in the attenuation of ultraviolet (UV) and photosynthetically active radiation (PAR) (Morris et al., 1995; Bracchini et al., 2004). Light attenuation in most fresh waters is dominated by organic chromophores or algal biomass. Chromophoric DOM (CDOM) absorption decreases exponentially with decreasing wavelength. Therefore the short wavelength visible and UV radiation (UVR) is most highly attenuated (Kirk, 2011). Understanding the depth profile of solar UVR and its underwater spectral composition is essential, for example, when evaluating exposure to harmful doses of UVR to aquatic organisms in their habitats (Huovinen et al., 2003). Alpine lakes (lentic ecosystems located above tree line) and organisms inhabiting them have been cited to be more sensitive to increased UVR as a consequence of their elevation and their low content of DOM (e.g. Sommaruga, 2001; Vinebrooke and Leavitt, 2005).

Strongly acidic aquatic environments (pH < 4) originate either naturally (volcanic springs, peat bogs, natural acid rock drainage) or through anthropogenic activities (acid mine drainage, acidification of lakes and ponds) (Geller et al., 1998). Both situations can lead to similar results: water with low pH often accompanied by high metal concentrations (particularly iron). Iron-rich lakes of natural origin are few and in consequence less studied than human acidified lakes. Lessmann et al. (2000) reported that the light environment in acidic lakes is different than in normal lakes because attenuation of wavelengths < 600 nm is enhanced due to the Fe(III)

* Tel.: +54 294 4428505; fax: +54 294 4422111.

E-mail addresses: bafficogd@comahue-conicet.gov.ar, gbaffico@gmail.com

in the water. Koschorreck and Tittel (2002) studied benthic photosynthesis in an acid mine lake with high iron content and stated that iron-rich waters create an unusual spectral profile, but did not show the profile. Gómez et al. (2007) found that the presence of high concentrations of soluble ferric iron in Río Tinto river (Spain) protects acidophilic algae from UV radiation in the 200–315 nm range.

In the present study, absorption coefficients (inherent optical properties) of acid Lake Caviahue were investigated, and spectral attenuation coefficients (apparent optical properties) were determined in order to know the underwater optical climate present in the lake. The aim of the study was to arrive at a more detailed understanding of the light climate in a high elevation, deep, naturally acidic, iron-rich lake and its possible effects on the biomass of the phytoplankton community.

Materials and methods

Study area

Lake Caviahue is located at 1600 m a.s.l. in the Copahue-Caviahue Provincial Park (37°53' S; 71°02' W), in the Andean area of Neuquén Province, Patagonia, Argentina. The lake has two arms (North and South), an area of 9.2 km², and a maximum depth of 93 m. It is naturally acidified by the acidic waters of the Upper Agrio River (pH < 2) (Pedrozo et al., 2001; Baffico et al., 2004; Varekamp, 2008), one of the main inflows of the lake, as a consequence of the close location of the river sources to the crater of the active Copahue Volcano (2965 m a.s.l.). The water of the lake has a pH < 3, high concentrations of sulphate (SO₄²⁻), iron (Fe), and aluminium (Al) (Pedrozo et al., 2001; Gammons et al., 2005; Varekamp, 2008), and low dissolved organic carbon (DOC) concentrations (0.2–1.6 mg/l, Beamud et al., 2010). Thermal, chemical, and biological characteristics of the lake have been described previously in detail (Pedrozo et al., 2001, 2002; Beamud et al., 2007, 2010; Varekamp, 2003, 2008). The phytoplankton community has very low diversity and is dominated by *Keratococcus raphidioides* (Hansgirg) Pascher (Chlorophyta) accounting for >90% of the total biomass (Pedrozo et al., 2001; Beamud et al., 2007). The zooplankton community is dominated by the rotifer *Philodina* sp. (Pedrozo et al., 2001).

The vegetation on the basin of the lake is mainly composed of herbaceous steppes with important percentage of naked soil (between 20 and 60%) below 2000 m a.s.l., and light forest of *Araucaria araucana* trees until 1800 m a.s.l. (Martin et al., 1988). Above 2000 m a.s.l. there are no vegetation on the basin of the lake.

Field methods

The lake was sampled during the warm season in different years (2000, 2004, 2005, 2007–2011). Samples were obtained at a central sampling point located at the deepest part of the North Arm (93 m). Water samples were obtained with a Van Dorn bottle at different depths in order to measure optical properties of the water and the phytoplankton biomass. Sampling depths were selected as 0 (first 20 cm of the water column), 2, 5, 10, 20, 30, 50 and 80 m. The samples were transferred to acid-washed polypropylene containers which were kept in darkness and immediately taken to the laboratory. Vertical profiles of downward irradiance for the UV range (290–400 nm, 1 nm resolution) and the visible range (400–750 nm, 1 nm resolution) were measured using a spectroradiometer (USB2000, Ocean Optics; grating #2, UV2/OFLV-4 detector, L2 lens, 25 μm slit) during the 2009 sampling campaign. UV measurements were made at 0, 10, 20, 40, 60 and 100 cm depth, while visible measurements were made at 0, 0.1, 0.2, 0.5, 1, 2, 3

and 4 m depth. The equipment was calibrated against tungsten and mercury reference lamps following the procedure defined by the manufacturer, in order to give measurements in irradiance units. The spectral vertical attenuation coefficient for downward irradiance ($K_{d,\lambda}$) was obtained from the slope of the linear regression of the natural logarithm of measured irradiance versus depth. Since the distance to the depth where the irradiance falls below the detection limit was very short, only a few centimetres at UV, the estimates of K_d at these wavelengths are less precise, or in some cases could not be determined.

Laboratory methods

For the determination of the optical properties, lake water was filtered with a 0.22 μm membrane (GE nylon syringe filters) to remove the particulate fraction. The filters were not tested for potential CDM release. Absorbance (190–1100 nm, every 1 nm) of the dissolved fraction was measured with a UV-visible spectrophotometer (Hewlett Packard 8453) in a 1 cm quartz cuvette, using filtered deionized distilled water as a blank. Absorbance at 750 nm was assumed to be zero and was subtracted from each spectrum to correct for offsets due to instrument baseline drift, temperature, scattering and refractive effects. Absorbance units were converted to absorption coefficients (ad) for the dissolved fraction of lake water as $ad = 2.303A(\lambda)/l$, where A is absorbance, λ is wavelength (nm) and l is the optical path length (m).

Total Fe concentrations were determined in the filtered 0 m depth water sample by total reflection X-ray fluorescence spectroscopy (detection limit of 1 μg/l; 2000, 2004 and 2005 sampling campaigns) or with commercial test kits (detection limit of 0.02 mg/l, FerroVer Method 8008, HACH Company, USA; 2007–2011 sampling campaigns). Samples were diluted with distilled water to provide Fe concentrations within the analytical range of the test.

Phytoplankton biomass was estimated by measurement of chlorophyll *a* concentrations. The water samples from each depth were filtered on glass fibre filters (Whatman GF/F) and kept frozen at –20 °C until extraction in 90% acetone and spectrophotometric measurements (APHA, 1992).

Results

Absorption coefficients for the dissolved fraction of Lake Caviahue water showed high values in the UV region and lower values

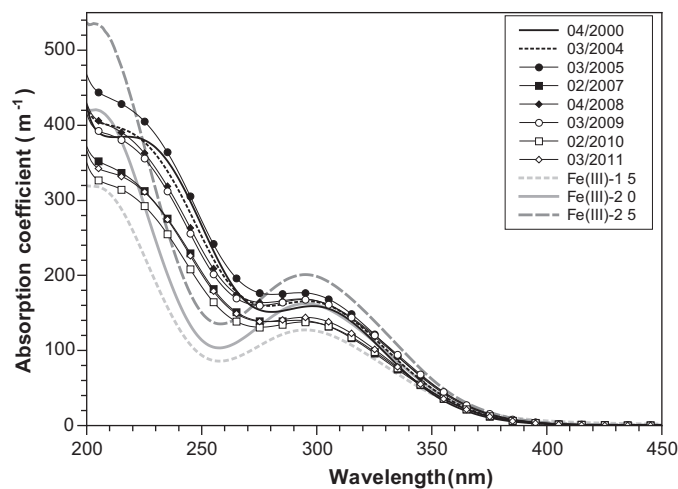


Fig. 1. Absorption coefficients for the dissolved fraction of Lake Caviahue water at 0 m depth in different sampling years. Three different concentrations of FeCl₃ dissolved in distilled water (15, 20 and 25 mg Fe(III)/l) are shown for comparison.

in the visible region of the spectrum (Fig. 1, visible not showed), but did not follow the typical exponential decrease characteristic of CDOM. Despite some minor differences between years the shape of the curves were almost the same, suggesting that similar compounds were responsible for the obtained absorptions. The shape of the curves and the value of absorption were very similar from the surface to the bottom of the lake (Fig. 2a–e). Due to the non exponential behaviour of the obtained absorption

coefficients, it was not realistic to calculate absorption spectral slopes (as defined by several authors, for example, Morris et al., 1995; Osburn et al., 2001; Helms et al., 2008; Loiselle et al., 2009). The absorption spectra showed a higher peak at around 230 nm and a clear shoulder at around 300 nm, while in the visible region, the absorption decreased exponentially with increasing wavelength (data not shown). The 300 nm shoulder was coincident with a similar peak found in FeCl₃ dissolved in distilled water

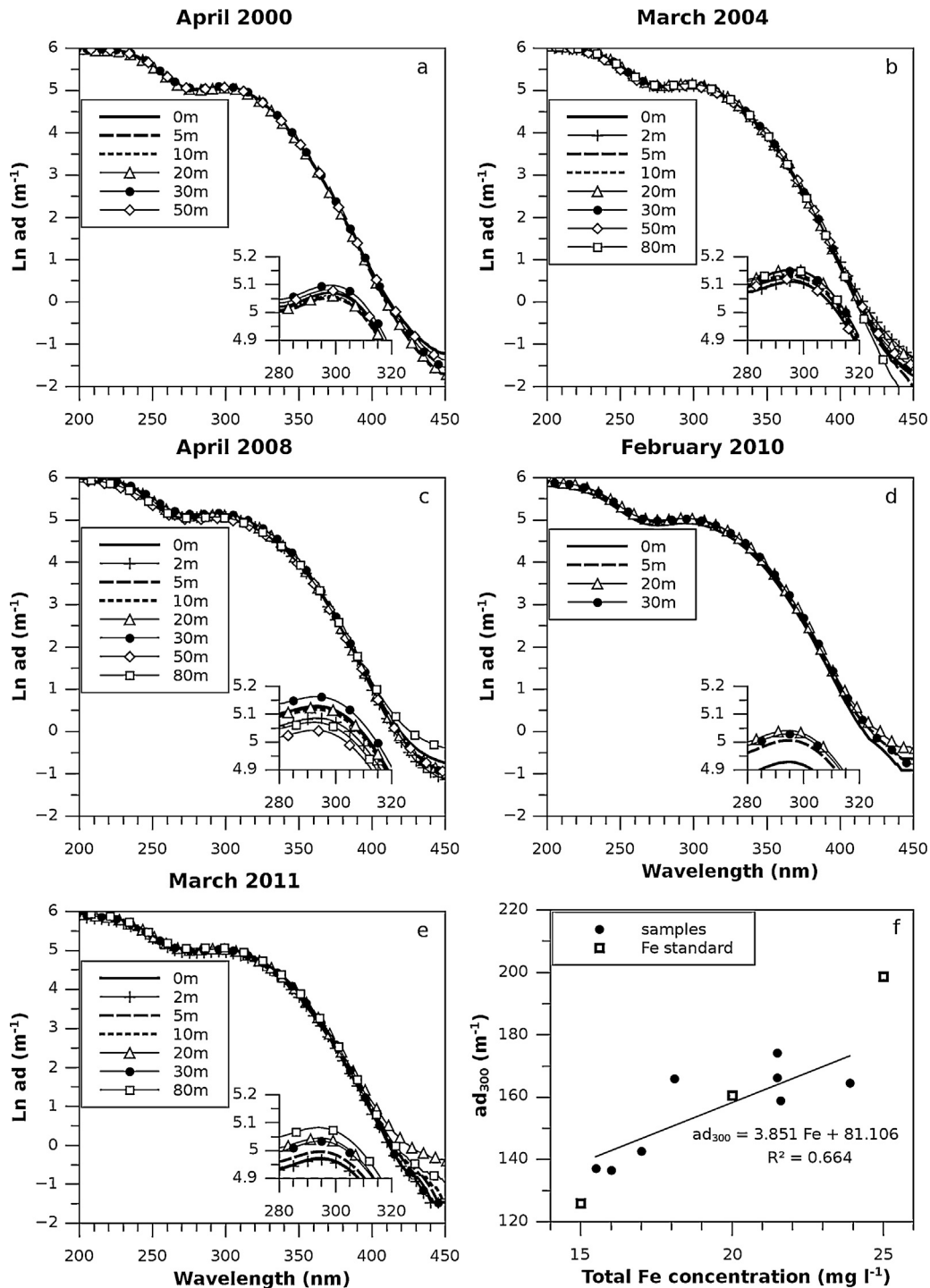


Fig. 2. (a–e) Natural log-transformed absorption spectra of Lake Caviahue water at different depths and in different sampling years. A detailed view around 300 nm is shown in the insets. (f) Absorption coefficient at 300 nm as a function of total Fe concentration in 0 m depth water samples. The equation shows the linear fit for the samples. Fe(III) concentrations of Fig. 1 are shown for reference (standard).

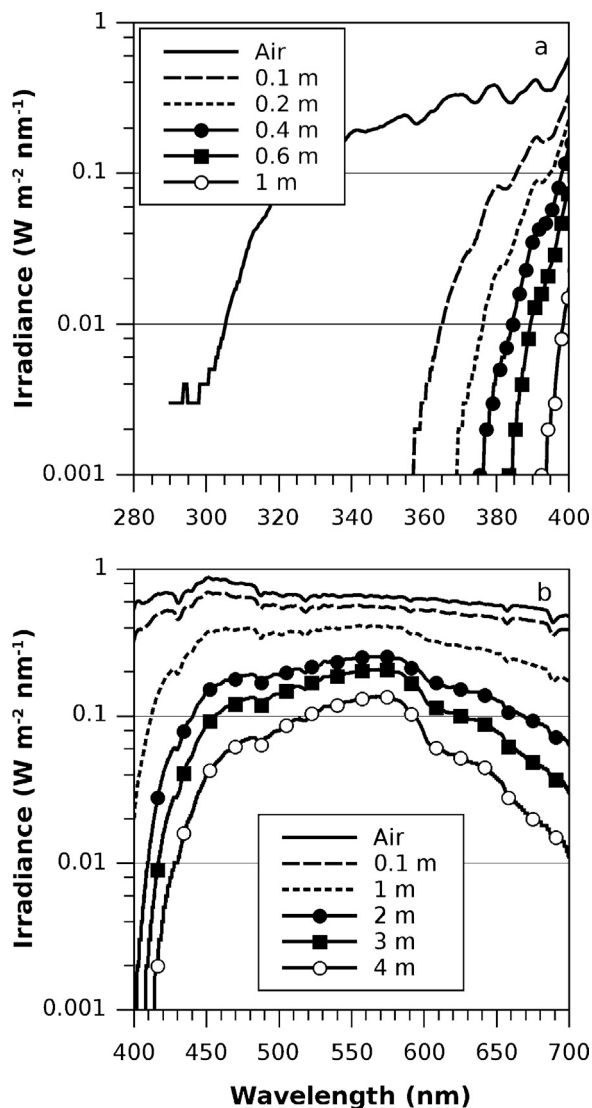


Fig. 3. Spectral irradiance (logarithmic scale) measured in the air (just above water surface) and at several depths in the water column of Lake Caviahue in summer 2009. (a) Spectral UV irradiance and (b) spectral visible irradiance.

(e.g. Fe(III), Fig. 1). Total Fe concentration of the lake water was around 20 mg/l (Table 1) and there was a good linear correlation between these concentrations and $ad_{(300\text{nm})}$ ($R^2 = 0.66$, $p = 0.014$, Fig. 2f).

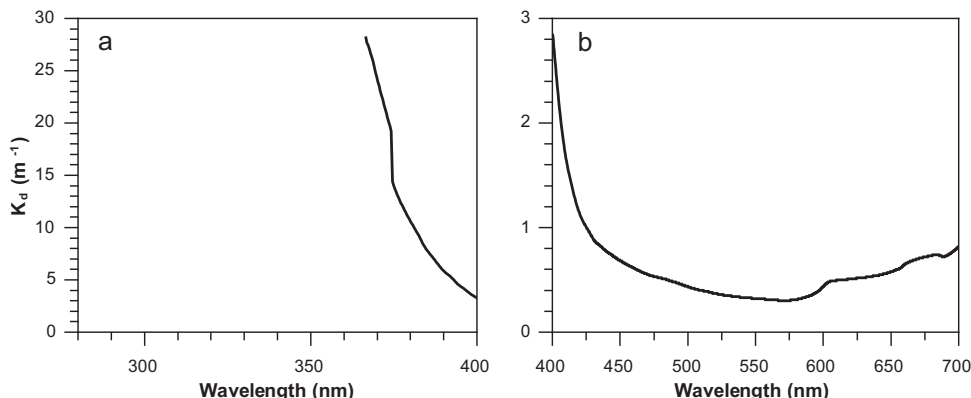


Fig. 4. Spectral vertical attenuation coefficient for downward irradiance ($K_{d,\lambda}$) in Lake Caviahue for the UV (a) and the visible range (b) in the 2009 sampling campaign.

Table 1

Total iron concentration (mg/l) measured in 0 m depth water samples from Caviahue lake in different years.

Date	Total Fe
04/2000	21.6
03/2004	23.9
03/2005	21.5
02/2007	15.5
04/2008	21.5
03/2009	18.1
02/2010	16.0
03/2011	17.0

UV irradiance was attenuated in the first centimetres of the water column (Fig. 3a) implying below 1 m depth there were no UV radiation present in the lake. Shorter (400–450 nm) and longer (>650 nm) wavelengths of visible light were also rapidly absorbed (Fig. 3b). For this reason, K_d value increased sharply below 450 nm and above 650 nm (Fig. 4) but was almost constant for the range 450–650 nm. In the visible region, $K_{d,\lambda}$ was calculated from the profiles recorded at the 8 different depths (minimum $R^2 = 0.923$). In the UV region, as a consequence of the strong attenuation, $K_{d,\lambda}$ was calculated from as many profiles as the data were meaningful (higher than noise), resulting in a different number of points: 366–377 nm, 3 profiles (min $R^2 = 0.969$); 378–391 nm, 4 profiles (min $R^2 = 0.957$); 392–400 nm, 6 profiles (min $R^2 = 0.988$). As a consequence of this approach, $K_{d,\lambda}$ values below 392 nm could have some inconsistency. Based on K_d values the calculated depth of 1% incident radiation was wavelength dependent (Fig. 5) with a maximum of 13.3 m at 565 nm, compared to 1.7 m and 4.8 m at 400 nm and 700 nm, respectively. In the UV region, wavelengths lower than 360 nm were attenuated in the top 10 cm of the water column and the 1% radiation for 380 nm was registered at 0.5 m depth.

Phytoplankton biomass of Lake Caviahue was low for the different years (0.06–0.55 mg chl. $a\ m^{-3}$) and showed an almost constant profile with depth (Fig. 6), despite the relative darkness of the water column.

Discussion

Optical properties and light climate

The present study shows that the light climate in the deep and acidic Lake Caviahue presents some peculiarities that differentiate this aquatic environment from other lakes. In the visible region of the spectrum, measured K_d in Lake Caviahue was similar to the results found in other studies in North Patagonia Andean lakes (Morris et al., 1995; Pérez et al., 2007, 2010). The main difference with those studies was that Lake Caviahue showed K_d values

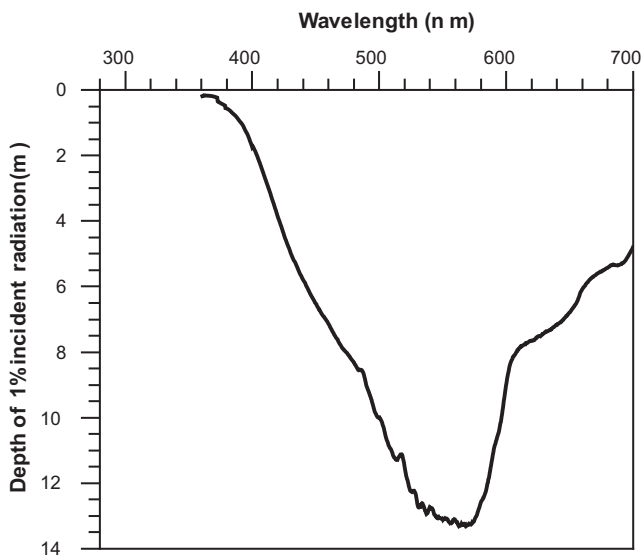


Fig. 5. Depth of 1% incident radiation calculated from K_d values from the 2009 sampling campaign.

comparable to small area shallow lakes (e.g. Lake Escondido and Lake Los Patos in Pérez et al., 2010). Unlike shallow lakes, that in general contain DOM that attenuates the incoming light, Caviahue is a deep lake with low DOC concentration (Beamud et al., 2007, 2010) where the attenuation of the radiation (mainly UV) is controlled by the chemical composition of its water (see more details below). The low DOC content could be attributed to a low organic

matter production in the basin of the lake (herbaceous steppes with small forests and important percentages of naked soil), and a low in situ production in the lake (oligotrophic). Compared with North Patagonia Andean deep lakes, Caviahue shows high attenuation of light resulting in a dark water column. For example, the depth of the 1% incident radiation was a little more than 13 m only for the range 544–577 nm, while for the remaining visible range it varied between 1.7 and 10 m (400 and 500 nm, respectively) or between 9 and 4.8 m (600 and 700 nm, respectively). This means that the potentially photoautotrophic zone is less than 10% of the water column of the lake. However, despite the relative darkness of the water column, phytoplankton distribution was almost constant with depth. Vertical mixing of the whole lake was considered to be minimal during the sampling dates due to thermal stratification in summer months (Varekamp, 2003; Beamud et al., 2007). The apparent contradiction between a dark water column and phytoplankton distribution could be attributed to the possible mixotrophic nutrition (Beamud et al., 2010) of the dominant phytoplanktonic species present in the lake (*K. raphidioides*). Mixotrophy is used in a broad sense to describe an organism that undertakes some combination of both photoautotrophic and heterotrophic nutrition (Jones, 1994).

Generally, high elevation Andean lakes are shallow and their waters contain low DOC concentrations, implying that the penetration of UVR is substantial throughout the water column (Morris et al., 1995). By contrast, Lake Caviahue showed a strong UV attenuation, and only a portion of the UV-A range (360–400 nm) is present in the first centimetres of the water column while the shorter wavelengths are attenuated in the top 10 cm. Measured $K_{d(380)}$ in Lake Caviahue was 10.59 m^{-1} , that means 3 times higher than in Lake Escondido (a shallow Andean lake with high DOC content located at $\sim 770 \text{ m a.s.l.}$), or 53 times higher than in Lake Gutierrez (a deep Andean lake with low DOC content located at $\sim 770 \text{ m a.s.l.}$), or 143 times higher than in Lake Schmoll (a shallow Andean lake with low DOC content located above the tree line, $\sim 1900 \text{ m a.s.l.}$) (Morris et al., 1995). For this reason, the optical climate of Lake Caviahue is not typical of high elevation lakes but is more similar to low elevation shallow lakes of the Andean region, despite its location at 1600 m a.s.l.

Iron as a shield

The chemical composition of the water, mainly Fe, is responsible for the very high attenuation of the UVR. In this sense, Lake Caviahue waters were a shield against UV-B because below the wavelength of 360 nm no light penetrates more than a few mm into the water column. As a result of this strong cut in UVR, living organisms may be protected against its deleterious effects (Sinha and Häder, 2002). The main source of protection could be the Fe(III) concentration of the water because iron in this oxidation state presents a high absorption in the UV range (Feng and Nansheng, 2000; McKnight et al., 2001) as shown in Fig. 1. The height of the observed shoulder in the absorption at 300 nm was correlated to the total Fe concentration probably because Fe(III) represents the major proportion of total Fe in Lake Caviahue (Gammons et al., 2005). Presumably, other compounds (CDOM, iron ligands or other chromophores) also contribute to water absorption and have influenced the spectral shape around 300 nm, giving as a result a slight difference between the spectra of Fe(III) and lake water. Recently, Xiao et al. (2013) showed that Fe associated with humic substances produces not only an important increase in light absorption by CDOM but also a change in the spectral slopes used for the characterization of CDOM.

The results of ferric iron as a protection agent against UV are coincident with the findings of Gómez et al. (2007) in Río Tinto, an extremely acidic river in Spain with very high Fe concentration (27 g/l). These authors showed the absorption of Fe(III) in the UV

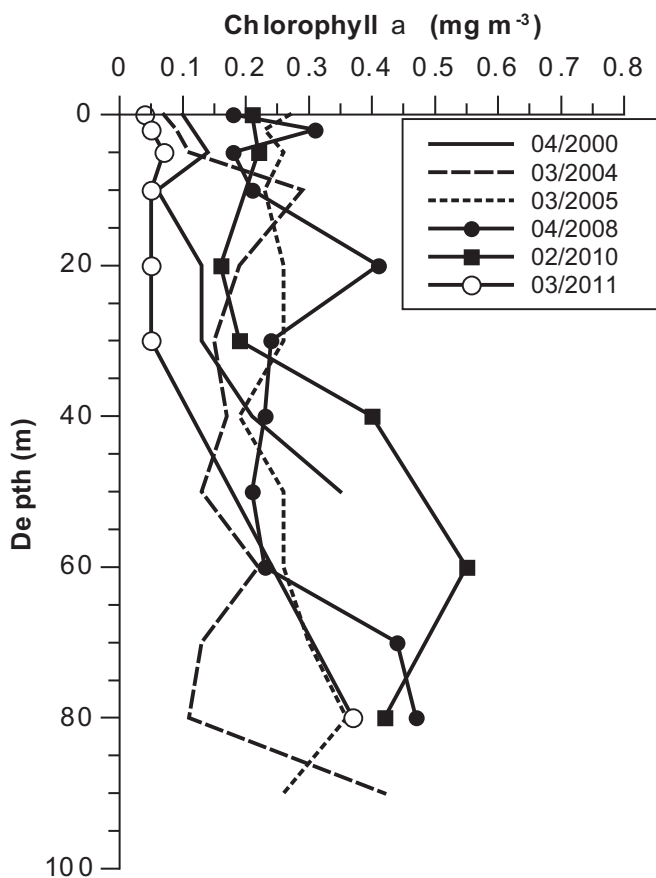


Fig. 6. Chlorophyll *a* concentration (indicator of phytoplankton biomass) at different depths in Lake Caviahue.

range and demonstrated through laboratory experiments the protection of ferric iron against UVR on the growth of algal species obtained from the river. In the present case, the UV protection that Lake Caviahue water represents was derived from measurements of UVR carried out in the lake showing values below the detection limit of the instrument. A difference between both studies is that the Fe concentration in Río Tinto is several orders of magnitude higher than in Lake Caviahue (~20 mg/l), but despite this lower Fe concentration in Caviahue water the shielding effects against UVR still is very important. In neutral water bodies, the CDOM protects organisms from the effects of UVR, while in iron-rich environments protection comes from this element (particularly as Fe(III)) according to the present and other studies (Pierson et al., 1999; Phoenix et al., 2001; Maloney et al., 2005; Gómez et al., 2007), resulting probably in an equally effective protection against this radiation.

Effects on phytoplankton community

The phytoplankton chlorophyll concentrations measured in the lake were very low throughout the measurement periods. According to Pedrozo et al. (2001) Lake Caviahue is ultraoligotrophic if it is classified by the chlorophyll concentration, but mesotrophic based on the values of algal density or fresh weight of phytoplankton. These authors relate the difference between both estimates with the low primary production of algae due to unfavourable water column light climate or nutrient limitation. While nitrogen limitation has been suggested for Lake Caviahue, due to the low recorded concentrations (Pedrozo et al., 2001; Beamud et al., 2007, 2010) and the imbalance in the N:P ratio (Pedrozo et al., 2001; Gammons et al., 2005), the values of phytoplankton biomass that allow to classify the lake as mesotrophic imply that the nutrients necessary to reach that level of biomass were obtained. However, for Lake Caviahue not only nutrient but also light limitation needs to be considered. In this sense, in the wavelengths in which the chlorophyll *a* molecule has its absorption peaks (around 430 and 660 nm) the 1% of the incident radiation is found at 5 and 6 m depth, respectively. Therefore, the photosynthetic zone in the lake is greatly reduced (as is shown in the present study), so maybe the mixotrophic nutrition of algae does serve a twofold purpose: first to offset any nutrient limitation and second to cope with a low amount of light that does not allow the photoautotrophy except in a few metres of the upper water column. Future research on the physiology of *K. raphidioides* will allow a more complete understanding on the nutritional mode of this species.

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References

- APHA, 1992. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington.
- Baffico, G.D., Diaz, M.M., Wenzel, M.T., Koschorreck, M., Schimmele, M., Neu, T.R., Pedrozo, F., 2004. Community structure and photosynthetic activity of epilithon from a highly acidic (pH ≤ 2) mountain stream in Patagonia, Argentina. *Extremophiles* 8, 463–473.
- Beamud, S.G., Diaz, M.M., Pedrozo, F.L., 2007. Summer phytoplankton composition and nitrogen limitation of the deep, naturally-acidic (pH ~2.2) Lake Caviahue, Patagonia, Argentina. *Limnologia* 37, 37–48.
- Beamud, S.G., Diaz, M.M., Pedrozo, F.L., 2010. Nutrient limitation of phytoplankton in a naturally acidic lake (Lake Caviahue, Argentina). *Limnology* 11, 103–113.
- Bracchini, L., Loiseau, S., Dattilo, A.M., Mazzuoli, S., Cózar, A., Rossi, C., 2004. The spatial distribution of optical properties in the ultraviolet and visible in an aquatic ecosystem. *Photochem. Photobiol.* 80, 139–149.
- De Lange, H.J., Morris, D.P., Williamson, C.E., 2003. Solar ultraviolet photodegradation of DOC may stimulate freshwater food webs. *J. Plankton Res.* 25, 111–117.
- Engelhaupt, E., Bianchi, T.S., Wetzel, R.G., Tarr, M.A., 2003. Photochemical transformations and bacterial utilization of high-molecular-weight dissolved organic carbon in a southern Louisiana tidal stream (Bayou Trepagnier). *Biogeochemistry* 62, 39–58.
- Feng, W., Nansheng, D., 2000. Photochemistry of hydrolytic iron (III) species and photoinduced degradation of organic compounds. A minireview. *Chemosphere* 41, 1137–1147.
- Gammons, C.H., Wood, S.A., Pedrozo, F., Varekamp, J.C., Nelson, B.J., Shope, C.L., Baffico, G., 2005. Hydrogeochemistry and rare earth element behaviour in a volcanically acidified watershed in Patagonia, Argentina. *Chem. Geol.* 222, 249–267.
- Geller, W., Klapper, H., Schultze, M., 1998. Natural and anthropogenic sulfuric acidification of lakes. In: Geller, W., Klapper, H., Salomons, W. (Eds.), *Acidic Mining Lakes*. Springer, New York, pp. 3–14.
- Gómez, F., Aguilera, A., Amils, R., 2007. Soluble ferric iron as an effective protective agent against UV radiation: implications for early life. *Icarus* 191, 352–359.
- Helms, J., Stubbins, A., Ritchie, J., Minor, E., Kieber, D., Mopper, K., 2008. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnol. Oceanogr.* 53, 955–969.
- Huovinen, P.S., Penttilä, H., Soimasuo, M.R., 2003. Spectral attenuation of solar ultraviolet radiation in humic lakes in Central Finland. *Chemosphere* 51, 205–214.
- Jones, R.L., 1994. Mixotrophy in planktonic protists as a spectrum of nutritional strategies. *Mar. Microb. Food Webs* 8, 87–96.
- Kirk, J.T.O., 2011. *Light and Photosynthesis in Aquatic Ecosystems*, 3rd edition. Cambridge University Press, Cambridge.
- Koschorreck, M., Tittel, J., 2002. Benthic photosynthesis in an acidic mining lake (pH 2.6). *Limnol. Oceanogr.* 47, 1197–1201.
- Lessmann, D., Fyson, A., Nixdorf, B., 2000. Phytoplankton of the extremely acidic mining lakes of Lusatia (Germany) with pH = 3. *Hydrobiologia* 433, 123–128.
- Lindell, M.J., Granéli, H.W., Tranvik, L.J., 1996. Effects of sunlight on bacterial growth in lakes of different humic content. *Aquat. Microb. Ecol.* 11, 135–141.
- Loiseau, S., Bracchini, L., Dattilo, A., Ricci, M., Tognazzi, A., Cózar, A., Rossi, C., 2009. Optical characterization of chromophoric dissolved organic matter using wavelength distribution of absorption spectral slopes. *Limnol. Oceanogr.* 54, 590–597.
- Maloney, K., Morris, D., Moses, C., Osburn, C., 2005. The role of iron and dissolved organic carbon in the absorption of ultraviolet radiation in humic lake water. *Biogeochemistry* 75, 393–407.
- Maritorea, S., Guillocheau, N., 1996. Optical properties of water and spectral light absorption by living and non-living particles and by yellow substances in coral reef waters of French Polynesia. *Mar. Ecol. Prog. Ser.* 131, 245–255.
- Martin, C., Pires, A., Castro, M., 1988. Plan general de manejo del Parque Provincial Copahue. Áreas Naturales Protegidas, Neuquén, Argentina.
- McKnight, D.M., Kimball, B.A., Runkel, R.L., 2001. pH dependence of iron photoreduction in a rocky mountain stream affected by acid mine drainage. *Hydrol. Process.* 15, 1979–1992.
- Morris, D.P., Zagarese, H., Williamson, C.E., Balseiro, E.G., Hargreaves, B.R., Modenutti, B., Moeller, R., Queimaliños, C., 1995. The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon. *Limnol. Oceanogr.* 40, 1381–1391.
- Osburn, C., Zagarese, H., Morris, D., Hargreaves, B., Cravero, W., 2001. Calculation of spectral weighting functions for the solar photobleaching of chromophoric dissolved organic matter in temperate lakes. *Limnol. Oceanogr.* 46, 1455–1467.
- Pedrozo, F., Geller, W., Beamud, G., Woelfl, S., Diaz, M., Whitton, B.A., Wenzel, M.T., Kringel, R., Schimmele, M., Baffico, G., Temporetti, P., Mages, M., 2002. The acidic waters of the Copahue crater – Agrio River – Lake Caviahue system (Patagonia, Argentina). *Verh. Int. Verein. Limnol.* 28, 112–113.
- Pedrozo, F., Kelly, L., Diaz, M., Temporetti, P., Baffico, G., Kringel, R., Friese, K., Mages, M., Geller, W., Woelfl, S., 2001. First results on water chemistry, algae and trophic status of an Andean acidic lake system of volcanic origin in Patagonia (Lake Caviahue). *Hydrobiologia* 452, 129–137.
- Pérez, G., Queimaliños, C., Balseiro, E., Modenutti, B., 2007. Phytoplankton absorption spectra along the water column in deep North Patagonian Andean lakes (Argentina). *Limnologia* 37, 3–16.
- Pérez, G.L., Torremorell, A., Bustingorry, J., Escaray, R., Pérez, P., Diéguez, M., Zagarese, H., 2010. Optical characteristics of shallow lakes from the Pampa and Patagonia regions of Argentina. *Limnologia* 40, 30–39.
- Phoenix, V.R., Konhauser, K.O., Adams, D.G., Bottrell, S.H., 2001. Role of biomineralization as an ultraviolet shield: implications for Archean life. *Geology* 29, 823–826.
- Pierson, B.K., Parenteau, M.N., Griffin, B.M., 1999. Phototrophs in high-iron-concentration microbial mats: physiological ecology of phototrophs in an iron-depositing hot spring. *Appl. Environ. Microb.* 65, 5474–5483.
- Sinha, R.P., Häder, D.-P., 2002. UV-induced DNA damage and repair: a review. *Photochem. Photobiol. Sci.* 1, 225–236.
- Sommaruga, R., 2001. The role of solar UV radiation in the ecology of alpine lakes. *J. Photochem. Photobiol. B* 62, 35–42.

- Van Duijn, E.H.S., Blom, G., Los, F.J., Maffione, R., Zimmerman, R., Cerco, C.F., Dortch, M., Best, E.P.H., 2001. Modeling underwater light climate in relation to sedimentation, resuspension, water quality and autotrophic growth. *Hydrobiologia* 444, 25–42.
- Varekamp, J.C., 2003. Lake contamination models for evolution towards steady state. *J. Limnol.* 62 (Suppl. 1), 67–72.
- Varekamp, J.C., 2008. The volcanic acidification of glacial Lake Cavihue, Province of Neuquen, Argentina. *J. Volcanol. Geoth. Res.* 178, 184–196.
- Vinebrooke, R.D., Leavitt, P.R., 2005. Mountain lakes as indicators of the cumulative impacts of ultraviolet radiation and other environmental stressors. In: Huber, U., Bugmann, K., Reasoner, M. (Eds.), *Global Change and Mountains Regions – A State of Knowledge Overview*. Springer, Dordrecht, pp. 497–509.
- Xiao, Y.H., Sara-Aho, T., Hartikainen, H., Vähätalo, V., 2013. Contribution of ferric iron to light absorption by chromophoric dissolved organic matter. *Limnol. Oceanogr.* 58, 653–662.