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Spatiotemporal drivers of dissolved organic matter in high alpine lakes: Role of Saharan dust inputs and bacterial activity

Natalie Mladenov,¹ Elvira Pulido-Villena,² Rafael Morales-Baquero,¹
Eva Ortega-Retuerta,¹ Ruben Sommaruga,³ and Isabel Reche¹

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[1] The effects of many environmental stressors such as UV radiation are mediated by dissolved organic matter (DOM) properties. Therefore, determining the factors shaping spatial and temporal patterns is particularly essential in the most susceptible, low dissolved organic carbon (DOC) lakes. We analyzed spatiotemporal variations in dissolved organic carbon concentration and dissolved organic matter optical properties (absorption and fluorescence) in 11 transparent lakes located above tree line in the Sierra Nevada Mountains (Spain), and we assessed potential external (evaporation and atmospheric deposition) and internal (bacterial abundance, bacterial production, chlorophyll a, and catchment vegetation) drivers of DOM patterns. At spatial and temporal scales, bacteria were related to chromophoric DOM (CDOM). At the temporal scale, water soluble organic carbon (WSOC) in dust deposition and evaporation were found to have a significant influence on DOC and CDOM in two Sierra Nevada lakes studied during the ice-free periods of 2000–2002. DOC concentrations and absorption coefficients at 320 nm were strongly correlated over the spatial scale ($n = 11$, $R^2 = 0.86$; $p < 0.01$), but inconsistently correlated over time, indicating seasonal and interannual variability in external factors and a differential response of DOC concentration and CDOM to these factors. At the continental scale, higher mean DOC concentrations and more CDOM in lakes of the Sierra Nevada than in lakes of the Pyrenees and Alps may be due to a combination of more extreme evaporation, and greater atmospheric dust deposition.

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1. Introduction

[2] In most aquatic ecosystems, dissolved organic matter (DOM) is derived from plant/soil or microbial material, such as bacteria and algae, or a combination of these two end-members. As the largest pool of organic carbon in surface waters [Thurman, 1985], DOM is an essential part of the microbial loop, serving as an energy source for heterotrophic microorganisms. In addition, chromophoric DOM (CDOM) absorbs strongly in the ultraviolet (UV) and visible spectrum and regulates the amount of light penetrating the water column. Attenuation of UV radiation (UVR) by CDOM and phytoplankton is especially important in alpine lakes, which have some of the highest rates of UVR penetration reported for lake environments [Morris et al., 1995; Sommaruga and Psenner, 1997].

[3] Across-system studies have identified significant relationships between DOC concentration and UV absorbance due to the presence of CDOM, mostly derived from organic matter (OM) exported from the watershed [Kortelainen, 1993; Morris et al., 1995; Xenopoulos et al., 2003; Yacobi et al., 2003]. In high DOC natural waters, CDOM is generally thought to be dominated by more refractory OM, such as humic and fulvic acids [Molot and Dillon, 1997; Xenopoulos et al., 2003]. At a global scale, DOC concentrations in alpine lakes were highly correlated with proportion of wetlands in the catchment, followed by lake elevation [Xenopoulos et al., 2003]. In a study of 26 lakes in the Alps and Pyrenees, Laurion et al. [2000] found that phytoplankton contributed strongly to the attenuation of UVR and contained high concentrations of UV-absorbing compounds. More recent studies have found that bacteria can generate CDOM directly [Nelson et al., 2004] or indirectly throughout the processing of phytoplankton exudates [Rochelle-Newall and Fisher, 2002].

[4] The reported relationships between DOC and CDOM appear to be weaker across temporal than spatial scales [Tipping et al., 1988; Molot and Dillon, 1997; Pace and Cole, 2002; Reche and Pace, 2002], and their variability may be attributed to both external factors, such as climatic

¹Departamento de Ecología, Facultad de Ciencias, Universidad de Granada, Granada, Spain.

²Laboratoire d'Océanographie de Villefranche, UMR7093, CNRS, Villefranche-sur-Mer, France.

³Laboratory of Aquatic Photobiology and Plankton Ecology, Institute of Ecology, University of Innsbruck, Innsbruck, Austria.



Figure 1. Satellite image of an African dust storm reaching southern Spain where the Sierra Nevada is located. Credit provided by the SeaWiFS project, NASA Goddard Space Flight Center, and ORBIMAGE (http://veimages.gsfc.nasa.gov/1236/S1999082124653_md.jpg).

forcing (solar irradiation or rainfall) and internal (biological and chemical) factors. For example, in systems with low terrestrial inputs of DOM, autochthonous bacterial and algal contributions to the CDOM pool may produce a seasonal overprinting effect on background CDOM levels due to the seasonal nature of microbial production and photobleaching [Nelson *et al.*, 2004; Sommaruga and Augustin, 2006]. In terms of external factors, high alpine environments cope with extreme conditions, such as intense wind and solar radiation [Blumthaler *et al.*, 1992]. These conditions can result in high evaporative losses, and DOM in such settings is particularly vulnerable to photobleaching by UVR, especially in lakes located on rocky terrain [Reche *et al.*, 2001]. In addition, the effects of solar radiation are not equally pronounced in terms of DOC and CDOM dynamics because photomineralization (the loss of DOC) is a slower process than photobleaching (the loss of CDOM) [Reche and Pace, 2002].

[5] High alpine lakes are known to be very responsive to the atmospheric deposition of dust in terms of inorganic nutrient and base cation loadings [Psenner, 1999; Pulido-Villena *et al.*, 2006], but the contribution from atmospheric dust deposition to lake DOM and its optical properties have yet to be examined. Although the organic carbon component of dust deposition can be substantial (20–60% of C in fine particulate matter is due to WSOC) [Aumont *et al.*, 2000], atmospheric deposition of OM has not been widely considered as an important source of DOM to high alpine lakes [Psenner, 1999]. Further, the potentially high aromaticity of WSOC [Duarte *et al.*, 2005] can influence lake CDOM, especially in the most transparent alpine lakes.

[6] The alpine lakes of Sierra Nevada (Spain) are a system of oligotrophic, low DOC lakes (<0.5 mM) located within 1000 km of the Sahara Desert, which is the source of more than 50% of global dust transport [Schütz *et al.*, 1981]. In addition to being located within the main zone of dust deposition (70% of dust export is deposited within the first 2,000 km [Jaenicke and Schütz, 1978]), the high elevation of these lakes places them in the mainstream of Saharan dust transport (between 1,500 and 4,000 m a.s.l. [Talbot *et*

al., 1986]) (Figure 1). In fact, previous research on these remote lakes has revealed a significant influence of Saharan dust inputs on lake biogeochemistry [Morales-Baquero *et al.*, 2006; Pulido-Villena *et al.*, 2006] and a fertilizing effect on phytoplankton [Morales-Baquero *et al.*, 2006; Pulido-Villena *et al.*, 2008] and bacteria [Reche *et al.*, 2008].

[7] To better understand the spatial and temporal drivers of DOM patterns in low DOC alpine lakes, we evaluate the influence of internal and external factors, including the influence of atmospheric dust deposition in lakes of the Sierra Nevada Mountains. We also compare DOM properties of the Sierra Nevada lakes to those reported for other alpine lakes across Europe.

2. Site Description

[8] During the ice-free period of 2000, 11 lakes were sampled in the Sierra Nevada Mountains, Spain (Table 1). Physical characteristics of these lakes are reported by Morales-Baquero *et al.* [1999]. Two of the lakes in this series, La Caldera and Río Seco, are among the highest elevation lakes in the Iberian Peninsula (at 3,050 and 3,020 m a.s.l., respectively; Table 1). La Caldera is a seepage lake and is located in a rocky, unvegetated watershed with no surface water inlets. In contrast, Río Seco is located in a moderately vegetated watershed (~15%) and receives seasonal inputs from two inlets draining alpine meadows [Pulido-Villena *et al.*, 2005].

[9] Mean annual precipitation for the study area is 640 mm [Pulido-Villena, 2004]. Precipitation data (Table 2) show average conditions in 2002, but above average precipitation in 2000 and 2001.

3. Methods

3.1. Sample Collection

[10] To obtain a spatial range, each of the 11 lakes was sampled once during August 2000 (Table 1). To obtain a temporal range, La Caldera and Río Seco lakes were sampled weekly during the ice-free periods (from July to

Table 1. Summary of Characteristics, Dissolved Organic Carbon Concentration, and Optical Properties of 11 Lakes in the Sierra Nevada Mountains^a

Lakes	Elevation ^b (m a.s.l.)	BP ^c (pmol leu L ⁻¹ h ⁻¹)	Chl <i>a</i> ^d (μg L ⁻¹)	DOC ^d (mM)	<i>a</i> ₂₅₀ (m ⁻¹)	<i>a</i> ₃₂₀ ^d (m ⁻¹)	ϵ_{250} (m ² mol ⁻¹)	ϵ_{320} (m ² mol ⁻¹)	FI ^e	S _{uv} (× 10 ⁻³ nm ⁻¹)
La Caldera (CA)	3050	24.8	0.5	0.113	2.25	1.08	19	10	1.89	11.9
Rio Seco (RS)	3020	10.7	0.2	0.119	4.67	1.65	38	14	1.86	14.8
Aguas Verdes	3050	83.2	0.6	0.102	5.90	2.90	56	28	1.88	10.9
Yeguas	2880	3.3	2.2	0.078	2.43	0.92	30	12	1.72	12.0
Virgen Superior	2950	392.5	0.4	0.047	2.37	1.09	48	23	R	11.1
Virgen Inferior	2940	373.3	2.2	0.223	14.79	5.68	64	25	1.69	13.9
Siete Lagunas 2	3020	687.4	0.5	0.300	15.71	8.45	50	28	1.73	11.7
Siete Lagunas 4	2970	115.8	0.7	0.075	4.68	2.24	60	30	1.67	12.7
Siete Lagunas 5	2980	98.3	1.7	0.091	5.56	2.65	59	29	1.79	12.5
Siete Lagunas 7	2890	162.7	0.8	0.047	3.74	1.67	77	36	1.66	13.1
Peñón Negro	2820	391.4	4.1	0.106	7.30	3.27	67	31	R	12.9

^aDOC, dissolved organic carbon.^bSource: *Morales-Baquero et al.* [1999].^cSource: *Pulido-Villena et al.* [2003].^dSource: *Reche et al.* [2005].^eFI values reported only for spectra with emission peaks between 440 and 460 nm. 'R' indicates values removed for this reason.

October) of 2000, 2001, and 2002. Water samples were collected from the center of La Caldera (maximum depth ~10 m) by pumping water from depths of 9, 7, 5, 3, and 1 m and mixing them in equal parts to produce a single integrated sample. In Río Seco (maximum depth ~3 m) samples were collected between 0 and 1 m depth using a column sampler. More details on water sample collection can be found elsewhere [*Morales-Baquero et al.*, 2006]. All DOC samples were transported chilled (at approximately 4°C) to the laboratory, where they were filtered through precombusted (2 h at 500°C) Whatman GF/F filters and stored in precombusted amber glass bottles at approximately 4°C in the dark until analysis. Separate samples of dry and wet deposition were collected weekly (to coincide with lake water sample collection) during the ice-free periods of 2000, 2001, and 2002 using a MTX1 ARS 1010 automatic deposition sampler located at 2,900 m a.s.l. (37.03N, 3.23W) near the study lakes. More details on atmospheric sample collection can be found elsewhere [*Morales-Baquero et al.*, 2006]. We took aliquots from atmospheric deposition samples to determine water soluble organic carbon (WSOC) and its optical properties.

3.2. Laboratory and Data Analyses

[11] DOC and WSOC concentrations were measured with a Shimadzu TOC-5000 equipped with a Shimadzu platinumized-quartz catalyst for high sensitivity analysis. For lake and

atmospheric samples, absorbance scans from 250 to 700 nm were measured in 10-cm quartz cuvettes using a Perkin Elmer Lambda 40 spectrophotometer connected to a computer equipped with UV-Winlab software. Absorbance at 250 nm (*A*₂₅₀) and 320 nm (*A*₃₂₀) wavelengths were expressed as Napierian absorption coefficients (*a*₂₅₀ and *a*₃₂₀) in m⁻¹ and were calculated as follows:

$$a_{250,320}(m^{-1}) = \frac{2.303A_{250,320}}{l}$$

where *l* is the optical path length in meters and 2.303 is the conversion to natural logarithms (ln10). Molar UV absorption coefficient at wavelengths between 250 to 280 nm is often used to evaluate the contributions of vascular plant sources and organic soil to the DOM pool [*Stewart and Wetzel*, 1981; *Chin et al.*, 1994; *Weishaar*, 2003]. We calculated molar absorption coefficients (ϵ) at 250 nm and 320 nm as follows:

$$\epsilon_{250,320}(m^2 mol^{-1}) = \frac{a_{250,320}}{C}$$

where *C* is the DOC concentration in mM. The spectral slope (S_{uv}) was calculated from the regression line between ln absorption coefficients versus wavelengths from 290 nm to 400 nm (*Green and Blough*, 1994). Fluorescence

Table 2. Summary of External Factors From Years 2000–2002

Sampling Periods	2000 18 July to 20 October	2001 24 July to 25 September	2002 9 July to 24 September
Cumulative precipitation ^a (mm)	1079	1175	780.7
Cumulative WSOC in dry deposition (mM m ⁻²)	0.72	1.17	1.41
Mean <i>a</i> ₃₂₀ in dry deposition (m ⁻¹)	0.72	-	0.45
Mean ϵ_{320} in dry deposition (m ⁻¹ mM ⁻¹)	36.4	-	27.4
Cumulative WSOC in wet deposition (mM m ⁻²)	1.38	1.34	1.68
Mean <i>a</i> ₃₂₀ in wet deposition (m ⁻¹)	0.83	-	0.90
Mean ϵ_{320} in wet deposition (m ⁻¹ mM ⁻¹)	33.3	-	20.4

^aFrom November of previous year to October of current year. Source: *Pulido-Villena* [2004].

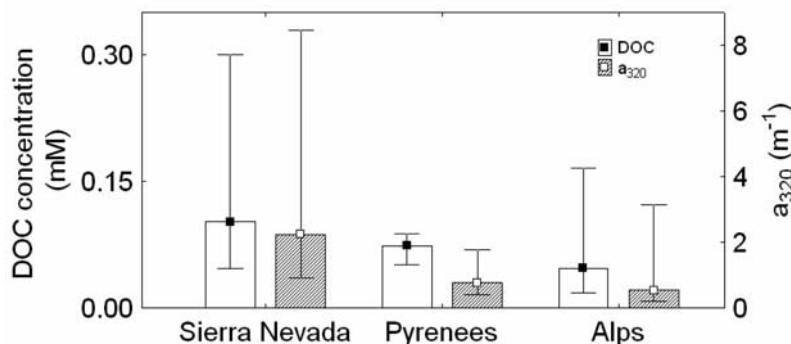


Figure 2. Mean and range (maximum and minimum values shown with error bars) of DOC concentration (empty bar) and absorption coefficient at 320 nm (a_{320}) (filled bar) for alpine lakes in catchments in the Sierra Nevada, Spain ($n = 11$; this study) and in the Spanish Pyrenees ($n = 6$ [Laurion *et al.*, 2000]) and Tyrolian Alps ($n = 16$ [Laurion *et al.*, 2000]).

emission spectra from 370 to 650 nm (excitation at 370 nm, slit width of 0.5 nm) were measured in a Perkin Elmer LS50B spectrofluorometer using a 1-cm quartz cuvette (rinsed twice with the sample). All scans were blank-subtracted and location of emission peak positions was verified. Scans in which the emission peak positions fell outside of the range reported for microbial and terrestrial end-member fulvic acids (approximately between 440 and 460 [McKnight *et al.*, 2001]) were not used. The fluorescence index (FI [McKnight *et al.*, 2001]) was calculated as the ratio of intensities measured at 450 and 500 nm emission wavelengths at an excitation of 370 nm. FI measurements were not corrected for lamp spectral properties.

[12] Oxygen isotopic signature ($\delta^{18}O$) was used as a surrogate for evaporation and was determined in waters of La Caldera and Río Seco during the three ice-free periods studied. A Finnigan-MAT 251 mass spectrometer was used and isotopic values have been previously reported [Pulido-Villena *et al.*, 2006].

[13] Bacterial abundance (BA) was determined by epifluorescence microscopy after staining subsamples of 2 or 4 mL with DAPI [Porter and Feig, 1980]. At least 400 cells were counted per filter in 30 random fields. Bacterial production (BP) was measured as (3H -leucine) protein synthesis following the centrifugation technique proposed by Smith and Azam [1992]. More details on BA and BP methods can be found elsewhere [Pulido-Villena *et al.*, 2003]. Chlorophyll *a* was measured spectrophotometrically after pigment extraction with methanol [American Public Health Association (APHA), 1992].

[14] To test for significant relationships between parameters, linear regressions and bivariate correlations were performed using *Statistica* software. Multiple regressions used a forward stepwise regression. Fisher tests were performed to test for significance in the difference of regression line slopes [Sokal and Rohlf, 1995].

4. Results

4.1. Spatial Patterns

[15] DOC concentrations of the Sierra Nevada lakes ranged from 0.047 mM to 0.300 mM and a_{320} values ranged from 0.92 to 8.54 m^{-1} (Figure 2). In comparison to

similarly positioned lakes in the Alps and Pyrenees, mean DOC concentrations and a_{320} values were highest in Sierra Nevada, followed by Pyrenees and Alps (Figure 2). In all these alpine systems there were significant relationships between DOC and a_{320} . However, the slope of the regression line for the Sierra Nevada data set (27.8) was more than twice that of the slope of the regression line for lake samples from the Alps (12.8), with the slope of Pyrenees lakes regression (24.4) falling between these two sites (Figure 3).

[16] Values of ε_{250} ranged from 19 to 77 $m^2 mol^{-1}$, with lowest values observed in La Caldera (Table 1). S_{UV} values were similar in the 11 lake data set, ranging from 10×10^{-3} to $14 \times 10^{-3} nm^{-1}$ (Table 1). The values of FI ranged from 1.66 to 1.89 and are representative of greater microbial DOM contributions compared to plant/soil DOM inputs (McKnight *et al.*, 2001). FI values were significantly and positively related to lake elevation (Figure 4a).

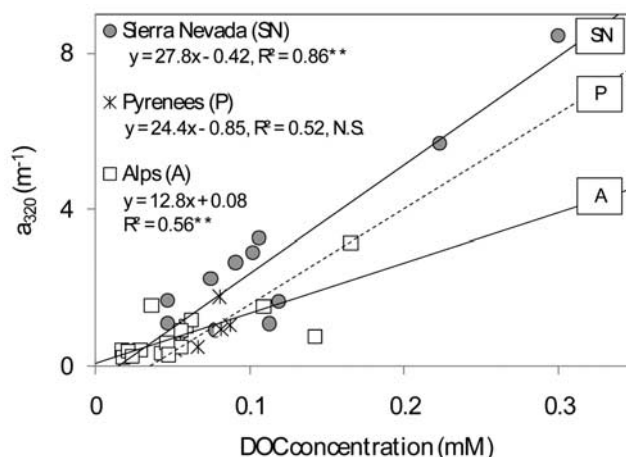


Figure 3. Relationships between DOC concentration and absorption coefficient at 320 nm (a_{320}) for lakes in catchments above tree line in Sierra Nevada, Spain (this study) and in the Spanish Pyrenees and Tyrolian Alps [Laurion *et al.*, 2000]. Regression lines, equations and level of significance are shown. The dashed regression line indicates a no significant relationship. ** $p < 0.01$; N.S., not significant.

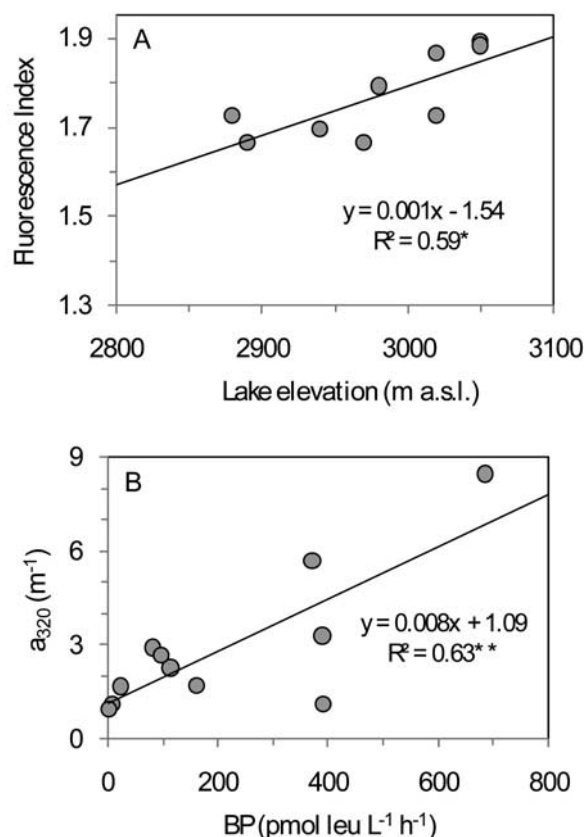


Figure 4. Relationships between (a) fluorescence index (FI) and lake elevation ($n = 9$) and between (b) absorption coefficient at 320 nm (a_{320}) and bacterial production (BP) ($n = 11$) in Sierra Nevada lakes. Regression lines, equations and level of significance are shown. * $p < 0.05$; ** $p < 0.01$.

[17] Lake DOC concentration was not correlated with chlorophyll a or BA, but it was significantly related to BP ($n = 11$, $R^2 = 0.43$, $p < 0.05$). Similarly, a_{320} values were not correlated with chlorophyll a , but they were significantly and positively related with BP ($n = 11$, $R^2 = 0.63$, $p < 0.01$, Figure 4b).

4.2. Temporal Patterns

[18] DOC concentration and optical properties were contrasting in lakes La Caldera and Río Seco and among the ice-free periods of 2000, 2001, and 2002 (Table 3). In all ice free periods, mean DOC concentrations and absorption

coefficients were higher in Río Seco than in La Caldera (Figure 5a). DOC concentrations ranged from 0.02 to 0.23 mM in La Caldera and from 0.06 to 0.28 mM in Río Seco. In both lakes, mean DOC concentrations were highest in 2002, followed by 2000, and lowest in 2001. During the three study years, there was a trend of increasing absorption coefficients in both lakes over the ice-free period and this increase was more pronounced in Río Seco, where a_{250} ranged from 2.38 m^{-1} to 8.35 m^{-1} , than in La Caldera, where the range was from 0.13 m^{-1} to 2.25 m^{-1} (Figure 5b). Among years, the most noticeable differences were in 2002, which had the lowest mean ϵ_{250} values and most dynamic S_{uv} values in both lakes (Figure 5d). Although DOC concentration patterns were not synchronous in both lakes, synchrony was found for the values of a_{250} , ϵ_{250} , and S_{uv} time series and displayed significant correlations when all three data sets were grouped (Figures 5b–5d).

[19] To test the robustness of the positive relationship between DOC and absorption coefficients at the temporal scale, we performed correlations for each year and lake. In La Caldera, we found significant relationships in two of the three study years, although with significantly different slopes (using Fisher test, $p < 0.05$) (Figure 6). In Río Seco, the only significant relationship occurred in 2000, and the slope of this relationship was not significantly different than the slope found in La Caldera the same year (Figure 6).

[20] To assess external drivers on lake DOC, we analyzed WSOC in atmospheric deposition samples and $\delta^{18}\text{O}$ as a surrogate for evaporation. Atmospheric WSOC loadings ranged from $0.04 \text{ mmol m}^{-2} \text{ d}^{-1}$ to $0.57 \text{ mmol m}^{-2} \text{ d}^{-1}$ in dry deposition and from $0.10 \text{ mmol m}^{-2} \text{ d}^{-1}$ to $0.69 \text{ mmol m}^{-2} \text{ d}^{-1}$ in wet deposition. Total WSOC loadings were highest in 2002 and lowest in 2000 (Table 2). In La Caldera in 2001, the regression between DOC and dry collector WSOC loading was significant ($n = 9$, $R^2 = 0.574$, $p < 0.05$, Figure 7). In 2001, DOC concentration in Río Seco was significantly related with $\delta^{18}\text{O}$ ($n = 10$, $R^2 = 0.396$, $p < 0.05$, Figure 7).

[21] The a_{320} values of WSOC ranged from 0.10 m^{-1} to 1.97 m^{-1} in dry deposition and from 0.52 m^{-1} to 1.02 m^{-1} in wet deposition. Mean a_{320} values of WSOC were lower in the dry collector in 2002 than in 2000 and similar in the wet collector in both years (2001 data were not available; Table 2). Considering all study years, the values of a_{320} in La Caldera displayed a significant and positive relationship with the value of a_{320} of WSOC of total deposition (Figure 8a). This relationship was also highly significant considering exclusively the data set of 2000 ($R^2 = 0.930$, $p < 0.01$,

Table 3. Mean Values and Range (in Parentheses) for DOC Concentration, Absorption Coefficient (a_{250} , a_{320}), Molar Absorption Coefficient (ϵ_{250} , ϵ_{320}), and Spectral Slope (S_{uv}) During Each Ice-Free Season in La Caldera and Río Seco

Parameter	La Caldera			Río Seco		
	2000	2001	2002	2000	2001	2002
DOC (μM)	63.8 (33.9–116)	46.4 (23.3–89.7)	80.4 (37.8–231)	145 (77.5–224)	114 (62.1–205)	164 (125–284)
a_{250} (m^{-1})	1.51 (1.01–2.25)	0.85 (0.67–1.38)	1.06 (0.13–1.59)	5.78 (4.44–7.42)	4.58 (2.37–6.62)	5.36 (3.66–8.24)
a_{320} (m^{-1})	0.56 (0.33–1.08)	0.32 (0.12–0.80)	0.38 (0.21–0.62)	2.13 (1.65–3.16)	1.73 (1.02–2.64)	1.74 (0.81–3.39)
ϵ_{250} ($\text{m}^{-1} \text{ mM}^{-1}$)	24.6 (18.6–37.9)	21.1 (10.4–29.4)	16.2 (3.42–27.8)	41.6 (30.4–60.2)	44.3 (24.9–68.7)	34.1 (12.9–56.6)
ϵ_{320} ($\text{m}^{-1} \text{ mM}^{-1}$)	8.96 (5.52–14.1)	7.05 (2.45–18.0)	5.22 (2.70–8.19)	15.2 (11.1–21.5)	16.8 (9.11–27.1)	11.1 (4.42–23.3)
S_{uv} ($\times 10^{-3} \mu\text{m}^{-1}$)	12.3 (10.9–13.9)	13.1 (9.29–21.3)	24.3 (15.2–40.9)	13.9 (12.7–14.8)	14.5 (12.5–17.6)	17.2 (10.5–30.5)

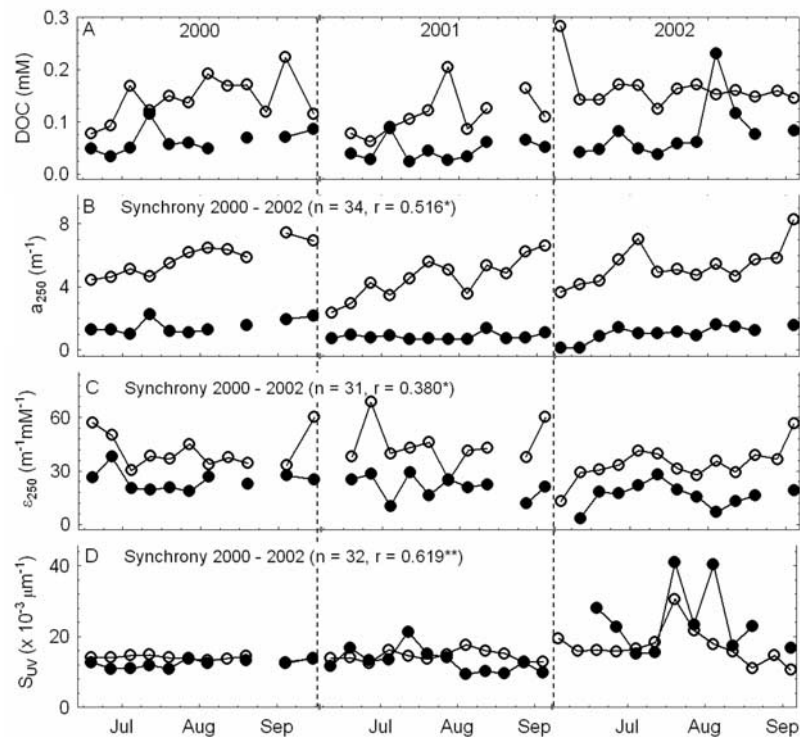


Figure 5. Temporal patterns of (a) DOC concentration (mM), (b) absorption coefficient at 250 nm (a_{250}), (c) molar absorption coefficient at 250 nm (ϵ_{250}), and (d) spectral slope (S_{uv}) in Río Seco (empty circles) and La Caldera (filled circles) during the ice-free periods of 2000–2002. Levels of significance are shown. * $p < 0.05$; ** $p < 0.01$.

$n = 11$). However, we did not find significant relationships for Río Seco (Figure 8b).

[22] Internal (within-lake) drivers on lake DOM were evaluated by determining whether bacterial abundance and/or chlorophyll *a* concentration were significantly related with DOC concentration or DOM optical properties during the ice-free period. Neither BA nor chlorophyll *a* had a significant relationship with DOC concentration or a_{250} values in either lake. Multiple regression analyses indicated that these internal factors did not serve as secondary controls of lake DOC concentration or a_{250} values. However, in 2002 BA was significantly related with a_{320} in Río Seco (Figure 9) but not in La Caldera or in Río Seco during other years.

5. Discussion

5.1. Spatial Patterns of DOM in Sierra Nevada Lakes

[23] In general, the spatial analyses of DOM optical properties in Sierra Nevada lakes indicate that the DOM in this high alpine system is dominated by microbial sources. The low ϵ_{320} and high FI values of the 11 Sierra Nevada lakes studied here are consistent with values observed in similar European alpine lakes in which the dominant DOM sources were found to be microbially derived [Laurion *et al.*, 2000; Sommaruga and Augustin, 2006]. The high FI values measured in the Sierra Nevada lakes are in the range typically reported for surface waters dominated

by microbial inputs of DOM [McKnight *et al.*, 2001]. Further, the significant relationship between FI and lake elevation reflects lower inputs of soil DOM and vascular plant material and greater microbial DOM sources at higher elevations. This result is consistent with a recently reported inverse relationship between DOC and lake elevation at the global scale [Xenopoulos *et al.*, 2003].

[24] Unexpectedly we found a significant relationship between the values of a_{320} and BP at the spatial scale. This relationship suggests that bacterial activity could be an important source of CDOM in these alpine lakes. Previous studies have also shown the direct influence of bacterial activity on the generation of CDOM [Nelson *et al.*, 2004] or fluorescent DOM [Cammack *et al.*, 2004], a process closely linked to nutrient availability [Nelson *et al.*, 2004]. Another, nonexclusive, explanation could be that terrestrial DOC export is usually associated to phosphorus (P) export. In fact, Kopáček *et al.* [2000] found that mountain lakes with higher DOC and P concentrations usually have higher bacterial numbers. In the study lakes, we did not find significant relationships between chlorophyll *a* or bacterial abundance and a_{320} or DOC, but Pulido-Villena *et al.* [2003] found a significant relationship between BP and total phosphorus (TP). Therefore, the stronger relationship between BP and a_{320} than BP versus DOC and a similar relationship between BP versus TP suggest that bacterial activity, extremely constrained by P availability, could generate CDOM.

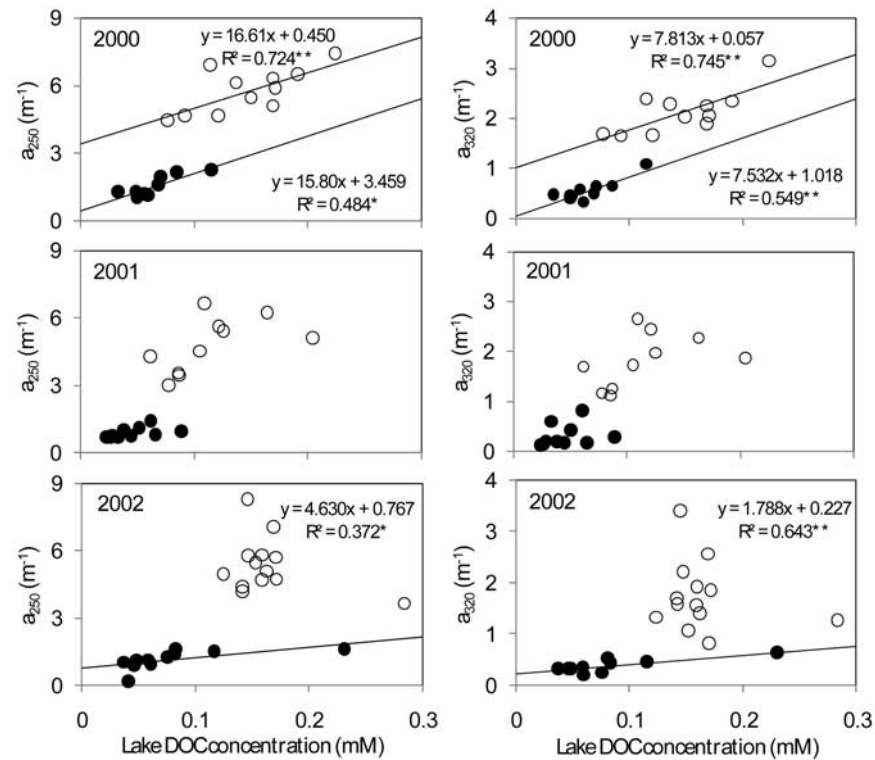


Figure 6. Scatterplots between absorption coefficient at (left) 250 nm (a_{250}) and (right) 320 nm (a_{320}) in La Caldera (filled circles) and Río Seco (empty circles) and lake DOC concentration during the ice-free period of 2000 ($n = 10$), 2001 ($n = 10$), and 2002 ($n = 11$). Regression lines, equations and level of significance are shown. * $p < 0.05$; ** $p < 0.01$.

[25] A low input of allochthonous DOM from catchments appears to be a shared feature of transparent alpine lakes at the global scale [Baron *et al.*, 1991; McKnight *et al.*, 1997; Sommaruga *et al.*, 1999; Laurion *et al.*, 2000; Kamenik *et al.*, 2001; Reche *et al.*, 2001; Sommaruga and Augustin, 2006]. However, the current study highlights important differences between the Sierra Nevada and other alpine systems across Europe, primarily that Sierra Nevada lakes have more and greater ranges of DOC and CDOM than their counterparts in the Pyrenees and Alps [Laurion *et al.*, 2000]. We hypothesize that it is possible that the higher absorption coefficients associated with DOM in the Sierra Nevada lakes compared to lakes of the Alps and Pyrenees could be to some extent due to the proximity of Sierra Nevada to the persistent Saharan dust source, given the higher absorption coefficients associated with WSOC in atmospheric deposition. In addition, presumably higher mean temperatures in Sierra Nevada lakes than in the other European alpine lakes may stimulate bacterial activity and consequently contribute to CDOM biogeneration. The CDOM inputs via dust deposition and CDOM generated by bacteria may be essential for mediating the effects of UV radiation in this and other extreme high mountain environments.

5.2. Temporal Patterns in La Caldera and Río Seco

[26] Significant relationships between the optical properties of lake DOM and WSOC from atmospheric collectors

reveal that atmospheric deposition exerted a measurable influence on DOM optical properties in an alpine lake (La Caldera) of the Sierra Nevada Mountains, Spain. Previous studies [Pulido-Villena *et al.*, 2006; Morales-Baquero *et al.*, 2006] had demonstrated the importance of Saharan dust deposition for concentration of inorganic substances in this particular lake.

[27] Previous studies [Morales-Baquero *et al.*, 2006; Pulido-Villena *et al.*, 2006], showed a higher sensitivity to atmospheric deposition in La Caldera than in Río Seco, where evaporation exerted a greater influence on in-lake concentrations of cations. Similarly, our study shows that La Caldera reflected the effects of atmospheric deposition of WSOC, while the temporal variation in DOC concentration in Río Seco was controlled mainly by evaporation. Lake-specific differences, such as the absence of vegetation in the catchment of La Caldera and its larger lake volume can explain its higher susceptibility to atmospheric WSOC deposition. By contrast, in Río Seco, the influence of meadows export on DOC concentration may represent an overprinting effect of vegetation-derived DOM atop the potential atmospheric DOM signals. Also, on a molar basis, the optical quality of WSOC in both dry and wet samples has relatively more absorption (higher ϵ_{320}) than DOM in La Caldera, but less absorption than DOM in Río Seco, supporting that atmospheric fingerprinting could be observed in La Caldera but masked in Río Seco. The effect of DOC evapoconcentration over time, observed in Río

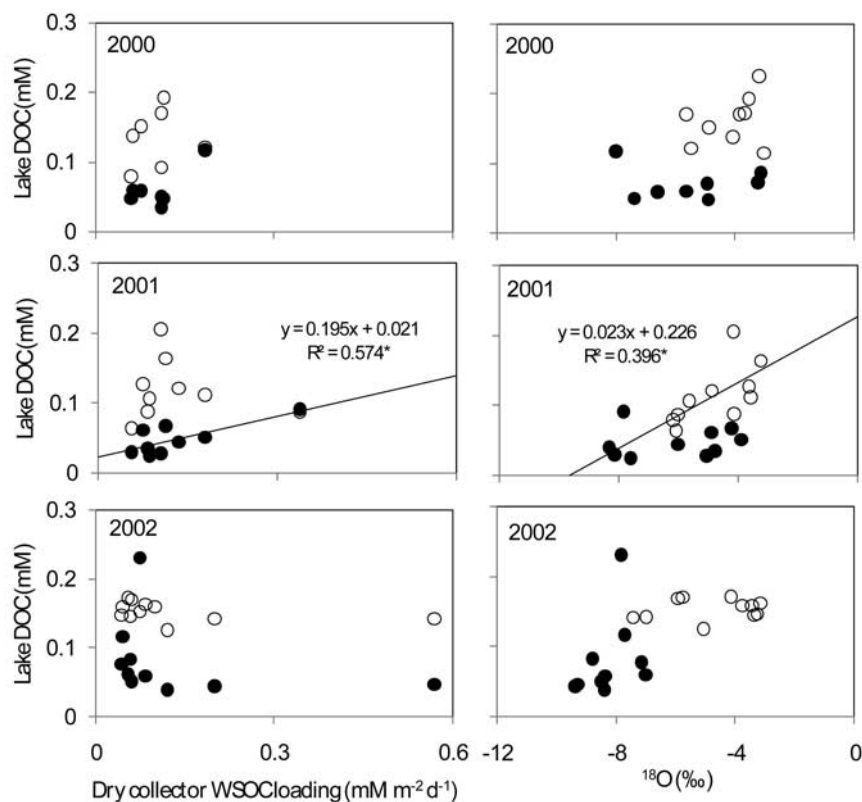


Figure 7. Scatterplots between DOC concentration in La Caldera (filled circles) and Río Seco (empty circles) and (left) WSOC loading of dry deposition and (right) ¹⁸O in 2000 (n = 10), 2001 (n = 9), and 2002 (n = 10). Regression lines, equations and level of significance are shown. * p < 0.05.

Seco and not in La Caldera, may be due in part to the greater ratio of surface area to lake volume of Río Seco ($\sim 1.5 \text{ m}^{-1}$) compared to that of La Caldera ($\sim 0.43 \text{ m}^{-1}$) [Pulido-Villena *et al.*, 2006]).

[28] The synchrony observed in DOM optical properties but not in DOC in the two lakes suggests that the drivers of DOC concentration and CDOM optical properties are different and that CDOM is relatively more affected by external drivers than DOC concentration. Previous studies [Tipping *et al.*, 1988; Molot and Dillon, 1997; Pace and Cole, 2002] indicated that common external drivers of DOC

and optical properties are climatic conditions, such as precipitation and ice-out, and photodegradation. However, Reche and Pace [2002] showed that despite both DOC concentration and absorption coefficients being influenced by rainfall, solar radiation had a more accentuated influence on the dynamics of absorption coefficients because photobleaching is a faster process than photomineralization. Given that only DOM optical properties were synchronous in the current study, a scenario in which photobleaching is a more effective driver of absorption coefficients than photomineralization of DOC is probable. This divergence in the

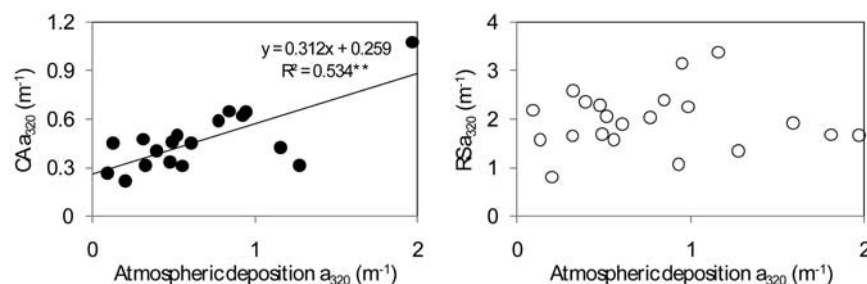


Figure 8. Scatterplots between absorption coefficient at 320 nm (a_{320}) in (left) La Caldera (filled circles) and (right) Río Seco (empty circles) and the values of a_{320} of atmospheric deposition of water soluble organic carbon during 2000 and 2002 (n = 18). Regression lines, equations and level of significance are shown. ** p < 0.01.

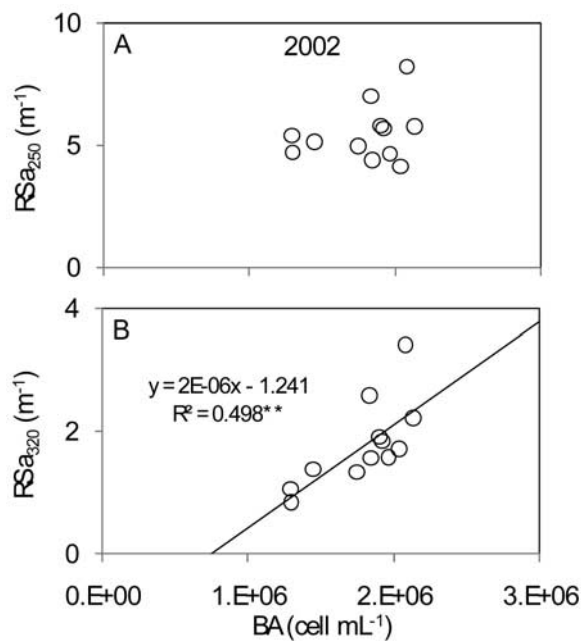


Figure 9. Scatterplots between bacterial abundance (BA) and absorption coefficient at (a) 250 nm (a_{250}) and (b) 320 nm (a_{320}) in Río Seco in 2002 ($n = 11$). Regression lines, equations and level of significance are shown. ** $p < 0.01$.

drivers for DOC and CDOM could explain, to some extent, the low consistency in both lakes of the relationships between these two parameters at the temporal scale.

[29] Indeed, consistent with previous studies that report relationships between DOC concentrations and absorption coefficients at spatial scales [Kortelainen, 1993; Molot and Dillon, 1997; Morris *et al.*, 1995; Xenopoulos *et al.*, 2003] and temporal scales [Tipping *et al.*, 1988; Pace and Cole, 2002; Reche and Pace, 2002], we found that DOC concentration was a good predictor of absorption coefficients over a spatial scale (explained variance of 85% at 250 nm and 86% at 320 nm), but a moderate to poor predictor at the temporal scale (explained variance of 75%, at best). This interannual variability in DOC-absorption relationships of this study is more pronounced than in other multiyear temporal studies of lakes in forested catchments [Pace and Cole, 2002; Reche and Pace, 2002]. In any case, these large differences preclude the predictive use of DOC-absorption relationships universally, at least in temporal studies [Sommaruga and Augustin, 2006].

[30] The surprising result of a relationship between a_{320} and BA in Río Seco in 2002 suggests that bacteria may also have an important effect on optical properties over time. The presence of this relationship in 2002 and not in the other years corresponds to lower mean annual precipitation and mean specific absorption coefficients in 2002 than in 2000 or 2001. These results suggest that catchment DOM sources, mobilized by runoff, may have been low enough in 2002 to allow for the influence of bacteria on CDOM to be discerned. However, the lack of a relationship between a_{250} and BA suggests that the effects of bacterial activity are more pronounced at higher wavelengths, where larger molecular weight, more chromophoric compounds are known to absorb.

[31] In summary, the temporal effects of atmospheric deposition in La Caldera and bacterial abundance in Río Seco highlight the ability of high elevation, low DOC systems to respond to phenomena that are linked to global change, such as temperature and dust increases. The synchrony in DOM optical properties, but not in DOC concentration, in La Caldera and Río Seco suggests that DOM optical properties are more sensitive to climatic or other external factors than DOC concentrations.

6. Conclusion and Implications

[32] This study has shown that at the spatial scale bacterial activity appears to be an important source of CDOM. At the temporal scale, bacteria also exerted an important influence on CDOM in Río Seco, whereas atmospheric deposition of WSOC produced a measurable effect on DOC and CDOM in La Caldera, a lake located on unvegetated, rocky terrain. At the continental scale, we observed that alpine lakes in the Sierra Nevada have more DOC and CDOM than their counterparts in the Pyrenees and Alps, likely due to greater influences by evaporation as a concentrating factor, temperature as a driver for bacterial activity, and atmospheric inputs of WSOC. Depending on distance from desert dust sources, other transparent, high mountain lakes devoid of allochthonous plant/soil DOM sources, may be similarly affected by long-range dust transport and may, thereby, serve as sensors of global change.

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References

- American Public Health Association (APHA) (1992), *Standard Methods for the Examination of Water and Wastewater*, 18th ed., Washington, D. C.
- Aumont, B., S. Madronich, I. Bey, and G. S. Tyndall (2000), Contribution of secondary VOC to the composition of aqueous atmospheric particles: A modeling approach, *J. Atmos. Chem.*, 35, 59–75, doi:10.1023/A:1006243509840.
- Baron, J., D. McKnight, and A. S. Denning (1991), Sources of dissolved and particulate organic material in Loch Vale Watershed, Rocky-Mountain-National-Park, Colorado, USA, *Biogeochemistry*, 15(2), 89–110, doi:10.1007/BF00003219.
- Blumthaler, M., W. Ambach, and W. Rehwald (1992), Solar UV-A and UV-B radiation fluxes at 2 alpine stations at different altitudes, *Theor. Appl. Climatol.*, 46(1), 39–44, doi:10.1007/BF00866446.
- Cammack, W. K. L., J. Kalff, Y. T. Prairie, and E. M. Smith (2004), Fluorescent dissolved organic matter in lakes: Relationships with heterotrophic metabolism, *Limnol. Oceanogr.*, 49(6), 2034–2045.
- Chin, Y., G. Aiken, and E. O'Loughlin (1994), Molecular weight, polydispersity and spectroscopic properties of aquatic humic substances, *Environ. Sci. Technol.*, 28, 1853–1858, doi:10.1021/es00060a015.
- Duarte, R. M. B. O., C. A. Pio, and A. C. Duarte (2005), Spectroscopic study of the water-soluble organic matter isolated from atmospheric aerosols collected under different atmospheric conditions, *Anal. Chim. Acta*, 530, 7–14, doi:10.1016/j.aca.2004.08.049.
- Jaenicke, R., and L. Schütz (1978), Comprehensive study of physical and chemical properties of the surface aerosols in the Cape Verde Islands Region, *J. Geophys. Res.*, 83, 3585–3599, doi:10.1029/JC083iC07p03585.
- Kamenik, C., R. Schmidt, G. Kum, and R. Psenner (2001), The influence of catchment characteristics on the water chemistry of mountain lakes, *Arct. Antarct. Alp. Res.*, 33(4), 404–409, doi:10.2307/1552549.
- Kopáček, J., E. Stuchlík, V. Straškrabová, and P. Pšenáková (2000), Factors governing nutrient status of mountain lakes in the Tatra Mountains, *Freshwater Biol.*, 43, 369–383, doi:10.1046/j.1365-2427.2000.00569.x.

- Kortelainen, P. (1993), Content of total organic carbon in Finnish lakes and its relationship to catchment characteristics, *Can. J. Fish. Aquat. Sci.*, 50(7), 1477–1483.
- Laurion, I., M. Ventura, J. Catalan, R. Psenner, and R. Sommaruga (2000), Attenuation of ultraviolet radiation in mountain lakes: Factors controlling the among- and within-lake variability, *Limnol. Oceanogr.*, 45(6), 1274–1288.
- McKnight, D. M., R. Hamish, R. L. Wershaw, J. S. Baron, and S. Schiff (1997), Chemical characteristics of particulate, colloidal, and dissolved organic material in Loch Vale Watershed, Rocky Mountain National Park, *Biogeochemistry*, 36(1), 99–124, doi:10.1023/A:1005783812730.
- McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Andersen (2001), Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, *Limnol. Oceanogr.*, 46, 38–48.
- Molot, L. A., and P. J. Dillon (1997), Colour–mass balances and colour–dissolved organic carbon relationships in lakes and streams in central Ontario, *Can. J. Fish. Aquat. Sci.*, 54, 2789–2795, doi:10.1139/cjfas-54-12-2789.
- Morales-Baquero, R., P. Carillo, I. Reche, and P. Sanchez-Castillo (1999), Nitrogen–phosphorus relationship in high mountain lakes: Effects of the size of catchment basins, *Can. J. Fish. Aquat. Sci.*, 56, 1809–1817, doi:10.1139/cjfas-56-10-1809.
- Morales-Baquero, R., E. Pulido-Villena, and I. Reche (2006), Atmospheric inputs of phosphorus and nitrogen to the southwest Mediterranean region: Biogeochemical responses of high mountain lakes, *Limnol. Oceanogr.*, 51(2), 830–837.
- Morris, D. P., H. Zagarese, C. E. Williamson, E. G. Balseiro, B. R. Hargreaves, B. Modenutti, and C. Queimaliños (1995), The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon, *Limnol. Oceanogr.*, 40, 1381–1391.
- Nelson, N. B., C. A. Carlson, and D. K. Steinberg (2004), Production of chromophoric dissolved organic matter by Sargasso Sea microbes, *Mar. Chem.*, 89, 273–287, doi:10.1016/j.marchem.2004.02.017.
- Pace, M. L., and J. J. Cole (2002), Synchronous variation of dissolved organic carbon and color in lakes, *Limnol. Oceanogr.*, 47, 333–342.
- Porter, K. G., and Y. S. Feig (1980), The use of DAPI for identifying and counting aquatic microflora, *Limnol. Oceanogr.*, 25, 943–948.
- Psenner, R. (1999), Living in a dusty world: Airborne dust as a key factor for alpine lakes, *Water Air Soil Pollut.*, 112, 217–227, doi:10.1023/A:1005082832499.
- Pulido-Villena, E. (2004), The role of atmospheric deposition in the biogeochemistry of high mountain lakes (Sierra Nevada, Spain), Ph.D. dissertation, 324 pp., Dep. de Ecol., Univ. de Granada, Granada, Spain.
- Pulido-Villena, E., E. Ortega-Retuerta, R. Morales-Baquero, and I. Reche (2003), The role of scale in bacterioplankton patterns in high mountain lakes, *Limnetica*, 22, 183–193.
- Pulido-Villena, E., I. Reche, and R. Morales-Baquero (2005), Food web reliance on allochthonous carbon in two high mountain lakes with contrasting catchments: A stable isotope approach, *Can. J. Fish. Aquat. Sci.*, 62, 2640–2648, doi:10.1139/f05-169.
- Pulido-Villena, E., I. Reche, and R. Morales-Baquero (2006), Significance of atmospheric inputs of calcium over the southwestern Mediterranean region: High mountain lakes as tools for detection, *Global Biogeochem. Cycles*, 20, GB2012, doi:10.1029/2005GB002662.
- Pulido-Villena, E., I. Reche, and R. Morales-Baquero (2008), Evidence of an atmospheric forcing on bacterioplankton and phytoplankton dynamics in a high mountain lake, *Aquat. Sci.*, 70, 1–9, doi:10.1007/s00027-007-0944-8.
- Reche, I., and M. L. Pace (2002), Linking dynamic of dissolved organic carbon in a forested lake with environmental factors, *Biogeochemistry*, 61, 21–36, doi:10.1023/A:1020234900383.
- Reche, I., E. Pulido-Villena, J. M. Conde-Porcuna, and P. Carrillo (2001), Photoreactivity of dissolved organic matter from high-mountain lakes of Sierra Nevada, Spain, *Arct. Antarct. Alp. Res.*, 33(4), 426–434, doi:10.2307/1552552.
- Reche, I., E. Pulido-Villena, R. Morales-Baquero, and E. O. Casamayor (2005), Does ecosystem size determine aquatic bacterial richness?, *Ecology*, 86, 1715–1722, doi:10.1890/04-1587.
- Reche, I., E. Ortega-Retuerta, O. Romera, E. Pulido-Villena, R. Morales-Baquero, and E. O. Casamayor (2008), Effect of Saharan dust inputs on bacterial activity and community composition in freshwater ecosystems, *Limnol. Oceanogr.*, in press.
- Rochelle-Newall, E. J., and T. R. Fisher (2002), Production of chromophoric dissolved organic matter fluorescence in marine and estuarine environments: An investigation into the role of phytoplankton, *Mar. Chem.*, 77, 7–21, doi:10.1016/S0304-4203(01)00072-X.
- Schütz, L., R. Jaenicke, and H. Pietrek (1981), Saharan dust transport over the North Atlantic Ocean, in *Desert Dust*, edited by T. L. Péwé, *Spec. Pap. Geol. Soc. Am.*, 186, 87–100.
- Smith, D. C., and F. Azam (1992), A simple, economical method for measuring bacterial protein synthesis rates in seawater using 3H-leucine, *Mar. Microb. Food Webs*, 6, 107–114.
- Sokal, R. R., and F. J. Rohlf (1995), *Biometry*, 3rd ed., 887 pp., Freeman, New York.
- Sommaruga, R., and G. Augustin (2006), Seasonality in UV transparency of an alpine lake is associated to changes in phytoplankton biomass, *Aquat. Sci.*, 68, 129–141, doi:10.1007/s00027-006-0836-3.
- Sommaruga, R., and R. Psenner (1997), Ultraviolet radiation in a high mountain lake of the Austrian Alps: Air and underwater measurements, *Photochem. Photobiol.*, 65, 957–963, doi:10.1111/j.1751-1097.1997.tb07954.x.
- Sommaruga, R., R. Psenner, E. Schaffner, K. A. Koinig, and S. Sommaruga-Wogratz (1999), Dissolved organic carbon concentration and phytoplankton biomass in high-mountain lakes of the Austrian Alps: Potential effect of climatic warming on UV underwater attenuation, *Arct. Antarct. Alp. Res.*, 31(3), 247–253, doi:10.2307/1552253.
- Stewart, A. J., and R. G. Wetzel (1981), Asymmetrical relationships between absorbance, fluorescence, and dissolved organic carbon, *Limnol. Oceanogr.*, 26(3), 590–597.
- Talbot, R. W., R. C. Harriss, E. V. Browell, G. L. Gregory, D. I. Sebacher, and S. M. Beck (1986), Distribution and geochemistry of aerosols in the tropical North Atlantic troposphere: Relationship to Saharan dust, *J. Geophys. Res.*, 91(D4), 5173–5182, doi:10.1029/JD091iD04p05173.
- Thurman, E. M. (1985), Humic substances in groundwater, in *Humic Substances in Soil, Sediment, and Water*, edited by G. R. Aiken, D. M. McKnight, D. L. Wershaw, and P. MacCarthy, pp. 87–103, John Wiley, New York.
- Tipping, E., J. Hilton, and B. James (1988), Dissolved organic matter in Cumbrian lakes and streams, *Freshwater Biol.*, 19, 371–378, doi:10.1111/j.1365-2427.1988.tb00358.x.
- Weishaar, A. (2003), Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, *Environ. Sci. Technol.*, 37, 4702–4708, doi:10.1021/es030360x.
- Xenopoulos, M. A., D. M. Lodge, J. Frentress, T. A. Kreps, S. D. Bridgman, E. Grossman, and C. J. Jackson (2003), Regional comparisons of watershed determinants of dissolved organic carbon in temperate lakes from the Upper Great Lakes region and selected regions globally, *Limnol. Oceanogr.*, 48, 2321–2334.
- Yacobi, Y. Z., J. J. Alberts, M. Takács, and M. McElvaine (2003), Absorption spectroscopy of colored dissolved organic carbon in Georgia (USA) rivers: The impact of molecular size distribution, *J. Limnol.*, 62, 41–46.

N. Mladenov, R. Morales-Baquero, E. Ortega-Retuerta, and I. Reche, Departamento de Ecología, Facultad de Ciencias, Universidad de Granada, Campus Fuentenuueva s/n, E-18071 Granada, Spain. (ireche@ugr.es)

E. Pulido-Villena, Laboratoire d'Océanographie de Villefranche, UMR7093, CNRS, Quai de la Darse, BP 8, F-06238 Villefranche-sur-Mer, France.

R. Sommaruga, Laboratory of Aquatic Photobiology and Plankton Ecology, Institute of Ecology, University of Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria.