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Supporting data for Impact of the Macrophyte Nymphaea odorata (Lily Pads) on Dissolved Organic Matter (DOM) in a Lake

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Impact of the Macrophyte *Nymphaea odorata* (Lily Pads) on Dissolved Organic Matter (DOM) in a Lake

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Description of Metadata

The metadata files are the files generated by the Aqualog for the weekly Lake Louise water samples. These are .opj files, readable by commercial graphing software from Origin. The files contain spreadsheets with the absorbance and fluorescence intensity data as a function of wavelength, and the associated spectra. The site description and Aqualog measurement methods are given in the next section.

Methods for Data Acquisition

Site Description The study site is a small freshwater lake located a quarter of a mile west of the larger Lake Whatcom in Whatcom County, Bellingham, in northern Washington State, USA (48°42'40.5"N 122°19'33.0"W) (Figure 1). The land immediately surrounding the lake is largely marsh like, but the watershed is dominated by evergreen forest. The lake itself is contained within a private residential community (Sudden Valley); 30% of the surrounding watershed is developed. It is surrounded by a 1.23 mile walking trail. Six small streams discharge into the lake around the periphery. The open water area of the lake is 93,096 m^2, occupying 11.04% of the total area of the watershed. The physical characteristics of the lake and landscape coverage are given in Table 1. The watershed was delineated in ArcGIS 10.7.1 using 30-m digital elevation models (US Geological Survey, 2020). Here, watershed is defined as the land surface that drains to a specific point (i.e., the lake outlet). Land cover classifications within the watershed were obtained from the 2019 National Land Cover Database (De Witz and US Geological Survey, 2021).

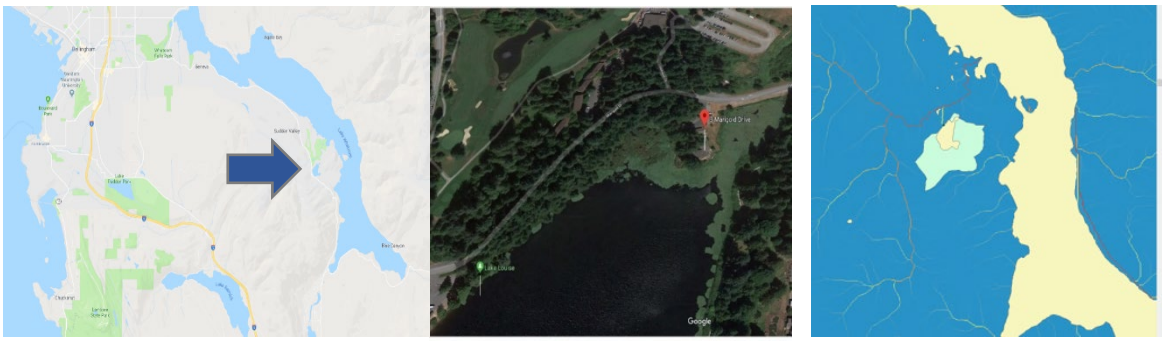

Figure 1. Lake Louise location next to the larger Lake Whatcom in Whatcom County, Washington state, USA is shown on the lefthand side. The sampling site on the shore of Lake Louise is shown in the center figure (red dot). Extensive lily pad growth is visible around the study site (olive green

area). The relative size of the watershed to lake area is shown in the righthand figure. The watershed around Lake Louise is shown in light green and the lake water area in yellow. Lake Whatcom is to the right of the smaller Lake Louise.

Table 1. Lake physical and landscape characteristics

Parameter	Value
Elevation	103 m
Watershed area	0.8425 km^2
Open water	11.05%
Developed, open	19.92%
Developed, low and medium	9.99%
Deciduous and mixed forest	7.17%
Evergreen forest	49.95%
Grassland/herbaceous/pasture	1.06%
Wetlands	0.85%

The sampling site is located on the shore of the lake in a shallower area of the lake with extensive lily pad (*Nymphaea odorata*) growth. The lily pads are prevalent during the summer, die back during the fall and there are no visible lily pad leaves on the lake surface during the winter months. *Nymphaea odorata*, commonly known as the fragrant or white water lily, is an aquatic bottom rooted flowering perennial plant that is native to the eastern half of North America (Woods et al., 2005). It is a floating leaved and rooted plant arising from dense, fleshy rhizomes. Lily pads grow in silty sediments in shallow water in water bodies with limited circulation (Richards et al., 2011). It is an invasive species in the Pacific Northwest region of the United States that can form dense stands that restrict lake-front access, eliminate recreational swimming opportunities and out compete native aquatic vegetation.

Water quality measurements are made on the lake annually in the summer months by the Institute for Watershed Studies (IWS) at Western Washington University. In 2018, the year of the study reported here, the lake was sampled by the IWS on 11 July. Water quality parameters measured at this time are given in Table 2. Also shown in Table 2 are the minimum, maximum and median values measured over the IWS study period from 2006 to 2020; annual data are available on the Institute's web-site (https://www.wwu.edu/iws/). The 2018 values are generally consistent with the median over the study period, with the exception of Total Phosphorus which had the highest value measured over the 14-year timeframe. Rainfall data was obtained from the National Center for Environmental Information of the National Oceanic and Atmospheric Administration (NOAA; https://www.ncdc.noaa.gov/). Results are from Station US1WAWC0073 located in Bellingham, Washington, USA near the study site (48.7221 N; 122.354 W) at an elevation of 160 m.

Table 2. Water quality parameters measured in the summer in Lake Louise

Parameter	**2018 value**	**Range 2006-2020**	**Median 2006-2020**
Dissolved oxygen (mg/L)	8.6	7.1 - 12.3	9.2
Temperature (°C)	21.6	10 - 25.7	21.4
pH	7.1	6.7 – 8.5	7.4
Conductivity (mS cm^{-1})	64.0	43.9 – 71.4	65.2
Chlorophyll *a* (mg L^{-1})	2.9	1.1 – 10.9	3.3
Alkalinity (mg L^{-1})	21.2	17.4 – 24.3	21.2
Turbidity (NTU)	1.30	0.77 – 1.86	1.11
NH_3 (µg L^{-1})	<10	<10 - 65	<10
Total Nitrogen (mg L^{-1})	238.0	234.7 – 756.6	289.8
NO_3 (µg L^{-1})	<10	<10 - 518	<10
Total Phosphorus (mg L^{-1})	14.8	5.6 – 14.8	10.4

SRP	<3	<3 – 14.8	<3

Sample Collection Surface water (<5cm) was sampled in the morning from January 17 to November 29, 2018, on a ~weekly time scale. Samples were collected in amber 150 mL glass sampling bottles and immediately transported to the laboratory for processing and analysis. On arrival in the laboratory, samples were filtered through 0.2 μm Durapore filters to remove microorganisms and stored at 4 ºC until analysis. Optical measurements on the filtrates were conducted the same day and DOC concentrations were measured within 30 days.

Fluorescence Excitation-emission matrices (EEMs) were acquired using a HORIBA Aqualog spectrofluorometer. Samples were analyzed in uncapped quartz fluorescence cells with a path length of 1 cm. The instrument has a wavelength accuracy of ± 1 nm and an effective analysis range from 230-800 nm (HORIBA). The light source is a 150W ozone-free xenon arc lamp. The Aqualog uses a TE-cooled CCD fluorescence emission detector which allows for ultrafast and simultaneous measurement of both absorbance and fluorescence. Instrument software corrects for inner filter effects (Ohno, 2002) and 1st order Rayleigh scattering. EEMs were collected with a resolution of <2 nm with stray light < 0.03% over an excitation range of 240-450 nm for January through March and from 250-450 nm for the remaining samples. An emission range of 260-800 nm was used. Nanopure water was used as a blank for all measurements. The majority of samples were analyzed with an integration time of 1 second. This is to ensure accuracy of optical indices as signals exceeding 50,000 counts are outside the linear range of the detector. All samples were measured with the high gain setting (2.25 e^-/cts) on the CCD detector. Integrated Raman peak areas for water were obtained from Nanopure water blanks and used to convert the microvolt output of the instrument into Raman units (RU; Lawaetz and Stedmon 2009).

Peaks A and C (humic-like peaks from terrestrial material) were identified in the EEM spectra using the classification and wavelength ranges from Coble (1996). The maximum fluorescence intensity in the excitation-emission wavelength range associated with each peak was recorded. The fluorescence index (FIX; ratio of emission at 450 nm to emission at 500 nm for excitation at 370 nm), humification index (HIX; ratio of the integrated peak emission intensities from 435-480 nm and from 300-345 nm at an excitation wavelength of 254 nm), and the index of recent autochthonous contribution (BIX; ratio of the emission intensities at 380 nm and 430 nm for excitation at 310 nm) were calculated using values from the processed EEMs.

Absorbance The Aqualog spectrometer measures absorbance at the same time as fluorescence and uses the same wavelength range. Napierian absorption coefficients were calculated from the absorbance data using equation 1 below (Hu et al., 2002):

$$\alpha = \frac{2.303}{L} \cdot A(\lambda) \qquad (1)$$

where A(λ) is the measured absorbance at the specified wavelength, α is the Napierian absorption coefficient, and L is the path length of the quartz cell in meters. Additionally, the specific ultra-violet absorbance (SUVA) was calculated from the Napierian absorption coefficient at 254 nm and the DOC concentration using equation 2.

$$SUVA = \frac{\alpha_{254\ nm}}{DOC} \qquad (2)$$

Spectral slopes (S) were calculated by fitting data for S_1 (300-400 nm), S_2 (275-295 nm), and S_3 (350-450 nm) to equation 3 below:

$$-S = \frac{\ln\left(\frac{A}{A_0}\right)}{(\lambda - \lambda_0)} \qquad (3)$$

A is the absorbance at wavelength λ and A_o is the absorbance at reference wavelength λ_o which is the highest wavelength in the relevant wavelength range. The slope ratio (S_R) is calculated as the ratio of S_2 to S_3 (Helms et al. 2008).

The fluorescence/absorbance (Flu/Abs) ratio, another useful indicator of CDOM compositional changes, was calculated from the fluorescence intensity at an excitation of 350 nm and emission of 450 nm divided by the absorption coefficient at 350 nm.