

Trends in hydrogen peroxide levels in relation to solar radiation in the Water of Leith

Steven A. Rusak, Luc E. Richard, Barrie M. Peake

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

William J. Cooper

Center for Marine Science, University of North Carolina at Wilmington, 28409, USA

Abstract. Hydrogen peroxide (H_2O_2) is recognized as the most stable of the reactive oxygen species produced by sunlight-driven photochemical reactions in natural waters. To assess the long-term trend in steady-state hydrogen peroxide levels in relation to solar radiation, we have been making daily measurements of hydrogen peroxide in surface water samples from the Water of Leith, in combination with measurements of solar radiation intensities, over the past three years. Our results show that concentrations of hydrogen peroxide in this surface water stream fluctuated roughly concomitant with the intensity of solar UVB radiation. Over seasonal timescales, maximum hydrogen peroxide concentrations were observed in summer, and minimum values in winter.

Introduction

Hydrogen peroxide is an important mediator of redox processes in natural waters (Cooper and Zika 1983). For example, H_2O_2 can affect the fate of organic material and the bioavailability of nutrients (Cooper and Lean 1992; Scully *et al.* 1996). In natural waters, H_2O_2 is predominantly the product of reactions involving sunlight and chromophoric dissolved organic material (CDOM). Previous work has shown that quantum yields for the photochemical formation of H_2O_2 in natural waters are greatest in the high-energy UVB band ($\lambda = 290\text{-}315\text{ nm}$) (Cooper *et al.* 1988). Based on unusually large summertime increases in solar radiation at sea level in southern New Zealand, particularly with regard to the photochemically important UVB band (McKenzie *et al.* 1999), we hypothesized that H_2O_2 concentrations in surface water would be higher in summer than in winter. The objective of this project was to test for a relationship between solar UVB irradiance and hydrogen peroxide concentration in The Water of Leith over seasonal timescales.

Hydrogen Peroxide Measurements

Water samples for 24 hour diel-timescale experiments were collected from a specific site in the Water of Leith at several times throughout the course of a day. Water samples for the seasonal-timescale experiments were collected from the same site in the Water of Leith at 1:00 pm New Zealand Standard Time on most days from September 2003 to March 2006. The time of day (1:00 pm NZST) was chosen both for the sake of consistency, and in order to represent local solar noon, when photochemical activity in the Water of Leith is greatest. H_2O_2 concentrations were measured immediately after collection of the samples using flow injection analysis with a

chemiluminescent acridinium ester reagent (Cooper *et al.* 2000). The acridinium ester reacts specifically with H_2O_2 in the sample to form an intermediate compound. When alkaline solution is added to the water-ester mixture, the intermediate compound decays, emitting a single photon ($\lambda \approx 470\text{ nm}$) for each molecule of H_2O_2 in the sample (Kaltenbach and Arnold 1992). The number of photons emitted was counted using a photomultiplier tube, and was proportional to the amount of H_2O_2 in the original sample.

UV Instrumentation

Solar radiation was measured using Skye High-Output Sensors, models SKU 420 (UVA) and SKU 430 (UVB). Sensors are located on the roof of the University of Otago Physics building ($45^\circ 52'\text{S}$, $170^\circ 31'\text{E}$), which is adjacent to the Water of Leith sampling site.

Results and Discussion

Results from the diel-timescale experiments show that hydrogen peroxide concentrations changed dramatically over the course of a light-dark cycle with the maximum H_2O_2 concentration occurring shortly after solar noon. On 3 August 2005, the maximum H_2O_2 concentration of 140 nM was measured at 2:00 pm NZST. Later in the day, H_2O_2 concentrations decreased as the rate of H_2O_2 decomposition, which is most likely biologically-mediated, exceeded that of photochemically-mediated production (Figure 1).

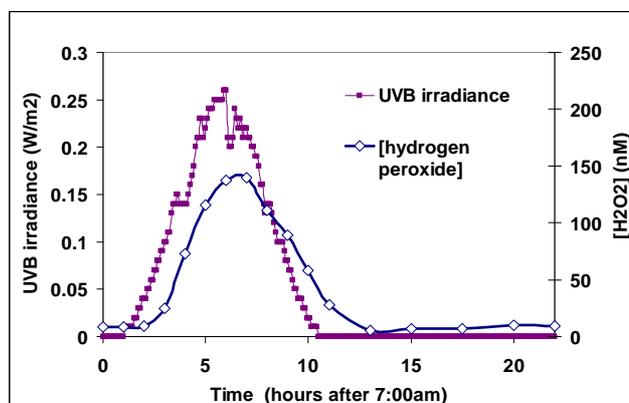


Figure 1. Diel changes in UVB irradiance and the concentration of H_2O_2 in the Water of Leith on 3 August 2005.

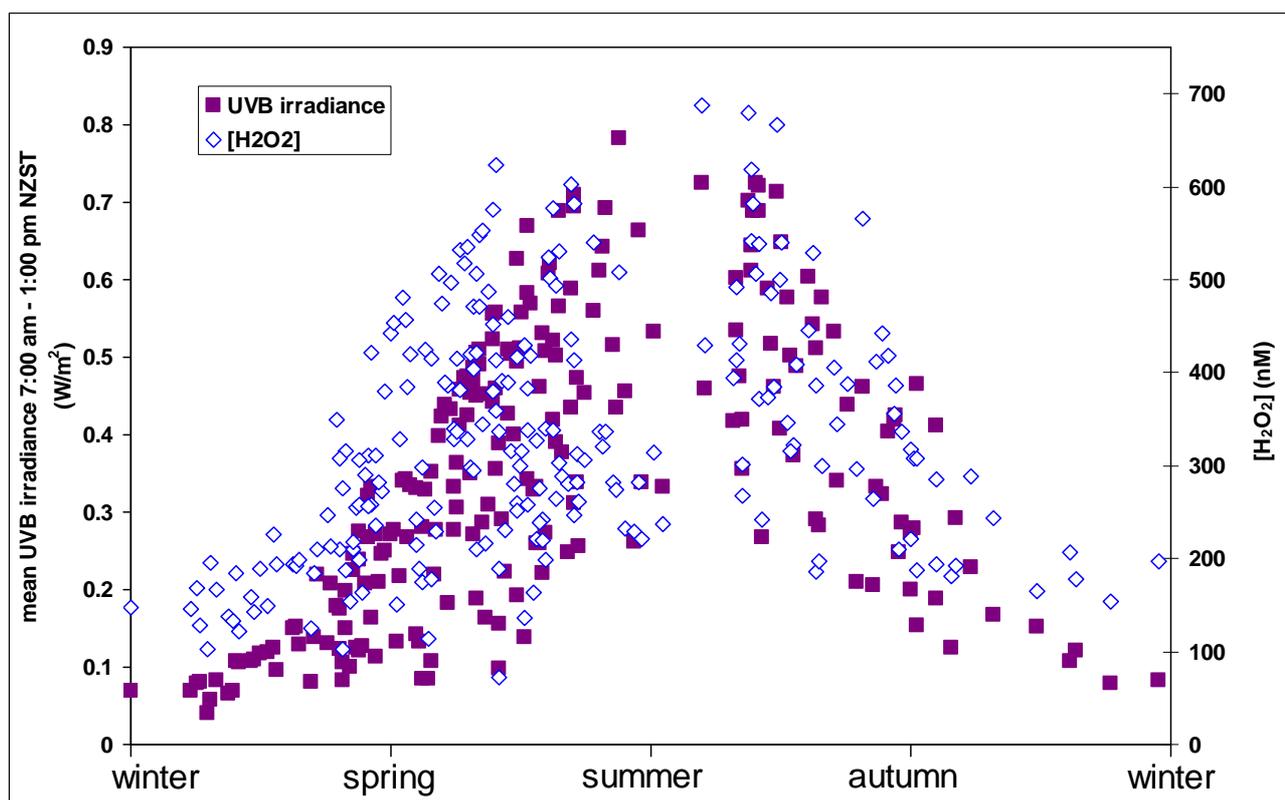


Figure 2. Seasonal changes in the concentration of H_2O_2 in the Water of Leith and UVB irradiance at Dunedin, New Zealand. Each UVB irradiance value represents the mean of 73 instantaneous measurements recorded at 5-minute intervals from 7:00 am to 1:00 pm NZST on the indicated day. The origin of the x-axis is the southern winter solstice (21 June). The graph shows pooled data collected between 29 August 2003 and 30 March 2006.

Results from the seasonal-timescale experiments suggest an annual pattern in H_2O_2 concentrations with maximum levels in the summer when solar radiation is most intense, and minimal values in the late winter. (Figure 2). The maximum concentration of H_2O_2 measured in the Water of Leith was $687.9 \text{ nM} \pm 8.9 \text{ nM}$ on 7 January 2004. The minimum concentration of H_2O_2 measured at 1:00 pm NZST was $72.2 \pm 2.7 \text{ nM}$ on 28 October 2005. The data shows a clear seasonal pattern in concentrations of H_2O_2 in the Water of Leith. Of the parameters that we tested, UVB irradiance was the best predictor of H_2O_2 concentrations. The relationship between steady-state hydrogen peroxide levels and solar UVB intensity is best described using a kinetic-type model, which takes into account both light-dependent formation rates, and light-independent decomposition rates of H_2O_2 .

Conclusions

A multitude of variables affect the formation and decay of hydrogen peroxide in The Water of Leith. Our data confirm that a sunlight-driven photochemical mechanism is primarily responsible for formation of H_2O_2 in this surface water stream, and that concentrations of hydrogen peroxide fluctuate roughly concomitant with the intensity of solar UVB radiation. There is a clear seasonal cycle in hydrogen peroxide concentrations in the Water of Leith. This seasonal trend in H_2O_2 concentrations in the Water of Leith has important implications with regard to temporal patterns in redox cycling and bioavailability of metals, organic material, and nutrients in natural waters.

Acknowledgements

Laimonis Kavalieris in the Department of Mathematics and Statistics, University of Otago, provided statistical advice. The Energy Studies Programme at the Department of Physics, University of Otago, provided solar radiation data.

References

- Cooper, W. J. and Lean, D. R. S. 1992. Hydrogen Peroxide Dynamics in Marine and Fresh Water Systems. *Encyclopedia of Earth System Science, Vol.2*, Academic Press, 527-535.
- Cooper, W. J., Moegling, J. K., Kieber, R. J. and Kiddle, J. J. 2000. A chemiluminescence method for the analysis of H_2O_2 in natural waters. *Marine Chemistry*, 70, 191-200.
- Cooper, W. J. and Zika, R. G. 1983. Photochemical Formation of Hydrogen Peroxide in Surface and Ground Waters Exposed to Sunlight. *Science*, 220, 711-712.
- Cooper, W. J., Zika, R. G., Petasne, R. G. and Plane, J. M. C. 1988. Photochemical Formation of H_2O_2 in Natural Waters Exposed to Sunlight. *Environmental Science and Technology*, 22(10), 1156-1160.
- Kaltenbach, M. S. and Arnold, M. A. 1992. Acridinium Ester Chemiluminescence: pH Dependent Hydrolysis of Reagents and Flow Injection Analysis of Hydrogen Peroxide and Glutamate. *Mikrochimica Acta*, 108, 205-219.
- McKenzie, R., Connor, B. and Bodeker, G. 1999. Increased Summertime UV Radiation in New Zealand in Response to Ozone Loss. *Science*, 285, 1709-1711.
- Scully, N. M., McQueen, D. J., Lean, D. R. S. and Cooper, W. J. 1996. Hydrogen peroxide formation: The interaction of ultraviolet radiation and dissolved organic carbon in lake waters along a 43-75°N gradient. *Limnology and Oceanography*, 41(3), 540-548.