

## UV Radiation and the Production of Reactive Oxygen Species (ROS) in Aquatic Environments

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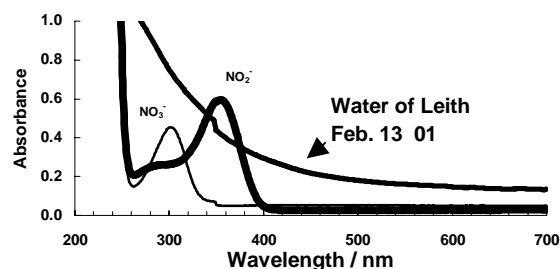
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**Abstract.** Aspects of the UV-induced production and analytical detection of reactive oxygen species (ROS) in aquatic environments are reviewed. Examples are given of net hydrogen peroxide levels observed in the Water of Leith (Dunedin) and Otago Harbour in February and May 1992 and February 1999, and in Doubtful Sound in May 2000.

### Introduction

Many of the effects that have been reported for UV radiation – induced effects in aquatic environments, directly or indirectly involve the production of a number ROS and in particular, singlet oxygen ( $^1\text{O}_2$ ), the hydroxyl radical ( $\cdot\text{OH}$ ), and the superoxide anion ( $\text{O}_2^-$ ). The formation of these ROS species and many of their reactions are summarised in Figure 1. The initial step in their formation in natural aquatic environments is the absorption of UV by the dissolved organic matter (DOM) to form  $^1\text{O}_2$  or  $\text{O}_2^-$ , and either nitrate and/or nitrite anions to form  $\cdot\text{OH}$ . This situation is illustrated in the UV-Vis absorbance spectra shown in Figure 2 which show significant UV absorption for 10 mM aqueous solutions of nitrate, nitrite and a sample of Water of Leith (Dunedin) water where the absorption is dominated by the characteristic featureless spectrum of DOM. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is formed from disproportionation of the superoxide anion and is the most stable ROS observed in natural aquatic environments.

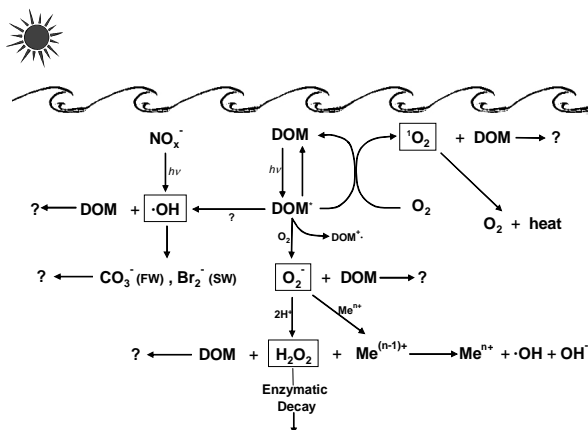


**Figure 2.** UV-Vis absorbance aqueous solution spectra of: (i) Water of Leith (Dunedin); (ii) 10 mM aqueous nitrate ( $\text{NO}_3^-$ ); and (iii) 10 mM aqueous nitrite ( $\text{NO}_2^-$ ). 5 cm quartz cell; Cary 500 Scan UV-Vis-NIR spectrophotometer.

Apart from  $\text{H}_2\text{O}_2$ , these ROS are in either an excited state ( $^1\text{O}_2$ ) or have an unpaired electron ( $\text{O}_2^-$  and  $\cdot\text{OH}$ ) and hence they are very reactive. This means they also have very short lifetimes which is reflected in their relatively low steady state concentrations under average mid-day irradiation conditions (eg.  $^1\text{O}_2$ :  $10^{-12} - 10^{-15}$  M;  $\cdot\text{OH}$ :  $10^{-17} - 10^{-19}$  M). These very low levels also mean that direct detection of these ROS apart from  $\text{H}_2\text{O}_2$ , is virtually impossible and so indirect methods of detection must be used instead. Most of these detection methods involve the reaction of an ROS with a probe to form a stable adduct which can then be detected by conventional analytical techniques particularly HPLC (see Kieber *et al.*, in press; Blough and Zepp, 1995).

The efficiency of production of these ROS species can be described by the apparent quantum yield which can be determined as a function of wavelength. Recent measurements of this parameter for  $\text{H}_2\text{O}_2$  have shown that it is remarkably similar in diverse marine and fresh waters with production in the marine waters being primarily due to absorption of UV by DOM (Yocis *et al.*, 2000). Photochemical production rates have also been measured for both  $\text{H}_2\text{O}_2$  (Yocis *et al.*, 2000) and  $\cdot\text{OH}$  in Antarctic waters (Qian *et al.*, 2000) and clearly showed an increase in the presence of ozone hole atmospheric conditions (151 DU) compared to more normal conditions (336 DU) as observed at Palmer Station.

There would appear to have been only one previous literature report of ROS levels in New Zealand aquatic environments and this involved measurements of the  $\text{H}_2\text{O}_2$  levels in a series of South Island lakes (Herrmann, 1996).

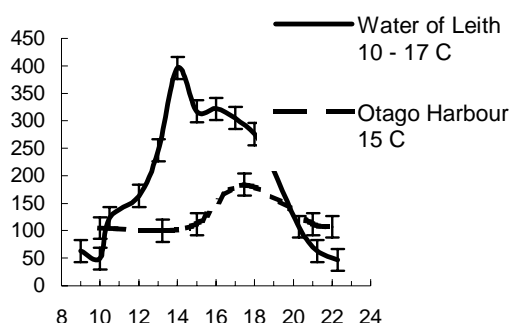


**Figure 1.** Schematic summary of the sources and removal pathways of reactive oxygen species (ROS). The main reactive oxygen species are indicated by squares. Notation: FW, freshwater; SW, seawater;  $\text{Me}^{n+}$  or  $\text{Me}^{(n-1)+}$ , metal in the  $n+$  or  $(n-1)+$  oxidation state;  $\text{NO}_x^-$ , the nitrate or nitrite anion; and ?, unknown pathway (from Kieber *et al.*, in press).

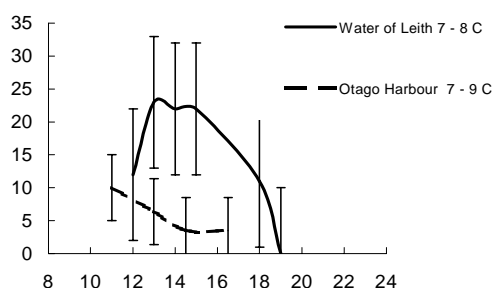
## Some New Zealand Results

We have been making measurements for a number of years of such levels in a range of other southern New Zealand aquatic environments including the fresh water of the Water of Leith in the vicinity of Otago University, Dunedin and the saline surface water of Otago Harbour. Some plots of these levels as a function of the time of day are shown in Figure 3 and these clearly exhibit the well known diel variability with net levels building up to a maximum in the early afternoon. The lower levels measured at the same time in Otago Harbour surface waters reflect lower DOM levels in the harbour. Similarly the lower levels for winter compared to summer are largely due to the decreased overall light intensity in winter and lower water temperatures.

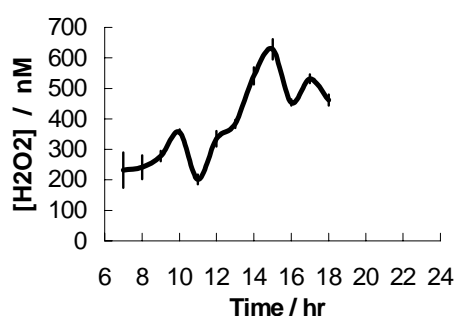
### Dunedin Summer ( 20 Feb. 92)



### Dunedin Winter (May 92)



### Water of Leith (Feb. 10 / 99)

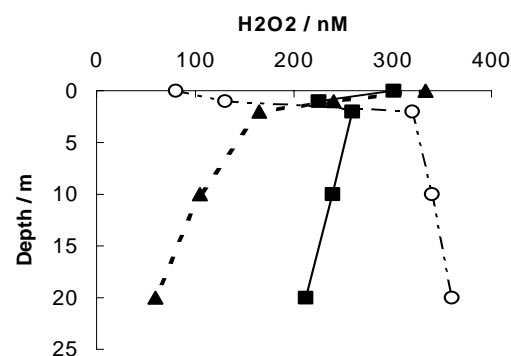


**Figure 3.** Diel, seasonal and temporal variability in net  $\text{H}_2\text{O}_2$  levels in surface waters of Water of Leith (Dunedin) and Otago Harbour.

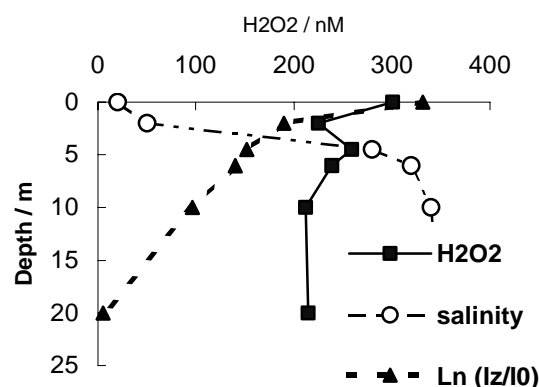
Measurements made in surface samples from the Water of Leith in February 1999 gave significantly higher net  $\text{H}_2\text{O}_2$  levels than in the same month seven years earlier and are comparable to some of the highest levels reported anywhere overseas for fresh waters.

There appear to have been no previous literature reports of the determination of  $\text{H}_2\text{O}_2$  in a fiordic environment where there is typically a unique situation involving a DOM – rich surface layer of fresh water overlying a salt water layer with much lower DOM levels. We have measured the net  $\text{H}_2\text{O}_2$  levels in Doubtful Sound, Fiordland and the depth profiles of net  $\text{H}_2\text{O}_2$  for two sites are shown in Figure 4 along with profiles of salinity and  $\ln I_z / \ln I_0$  where  $I$  is the intensity of PAR light. The  $\text{H}_2\text{O}_2$  profiles show high levels in the upper surface freshwater with high DOM and a characteristic decrease with increasing depth as the light levels decrease. There is also an unusual behaviour occurring in the immediate vicinity of the fresh water-saltwater interface.

### Mid-Thompson Sound May 3 2000



### Lady Alice Falls May 3 2000



**Figure 4.** Depth profiles of net  $\text{H}_2\text{O}_2$  levels, salinity and  $\text{Log} (I_z / I_0)$  for mid-channel sites in the vicinity mid-Thompson Sound and Lady Alice falls in Doubtful Sound.

## Summary

UV radiation of natural waters can lead to the photochemical production of appreciable levels of reactive oxygen species which are enhanced during ozone hole atmospheric conditions. Significant net levels of  $\text{H}_2\text{O}_2$  which is the most stable photoproduct, have been observed

in a range of different types of freshwater and marine waters in southern New Zealand. Further investigations of the production of ROS in these waters could well be undertaken in conjunction with more detailed simultaneous radiation measurements particularly under conditions of diminished ozone levels.

## References

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