Characterisation of Natural Organic Matter (NOM) in Highly Coloured Surface Waters
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EXECUTIVE SUMMARY

This study was conducted to improve understanding of the behaviour of dissolved organic carbon (DOC) in drinking water source reservoirs in Western Australia. Water treatment to effectively remove organic carbon from these source waters has been problematic, and a better understanding of the fundamental behaviour of the DOC was required. Five of the six sources studied are located in southern WA and have characteristic 'brown' water, with DOC concentrations up to 40 mg/L. The sites are Quickup Dam, Quinninup Dam, Bolganup Dam, Denmark River and Walpole River. The other site, Harding Dam located in the Pilbara in northwestern WA, had much lower DOC concentrations (3-5 mg/L) and the DOC in this source is quite different in character to the DOC in the southern sources. Water from all sites was sampled every month over a two year period (Nov 2005 – Nov 2007) and analysed qualitatively and quantitatively for organic carbon, nutrients, major ions, trace metals and physicochemical characteristics. Information on weather observations, including temperature and rainfall was also collected. Overall observations of the study indicated that stratification occurred in most dams, even in a very shallow dam such as Quickup. The major controls on DOC concentrations were allochthonous input from surface runoff, Fe cycling in stratified systems, preservation of DOC during anoxic events, and autochthonous input from a variety of phytoplankton species. All reservoirs were mesotrophic except Walpole River, which was impacted by agricultural practices within the catchment and was considered eutrophic and Quinninup, which was considered oligotrophic. Phosphorus spikes resulted in increases in phytoplankton numbers, e.g. at Quinninup, although this did not always result in an observable increase in DOC.

A more detailed study on Bolganup Dam, using hydrodynamic modelling showed that during periods of stratification (anoxic bottom waters) DOC release from sediments dominated. The data indicated that this is also likely to be the case for several of the other sites. Sufficient data was collected for hydrodynamic modelling to be performed for all of the study sites and this could be a subject for further study.

An assessment of the impact of source water quality on the quality of distributed water, in terms of disinfection by-products, was conducted at each site (Section 3.8.1). Positive correlations were found between total trihalomethanes (TTHMs) in distributed water and bromide in the raw water in both the Denmark and Harding systems. In both of these systems bromide, rather than DOC, appeared to be the main driver of trihalomethane (THM) formation. However, at Walpole, THM concentrations in treated water appeared to be controlled by DOC, rather than bromide concentrations in the source water. At both Harding and Denmark, water is extensively treated for DOC removal, but not for bromide removal. These observations suggest that chlorine reacts preferentially with DOC in circumstances where DOC is high, leading to incorporation of chlorine rather than bromine to form disinfection by-products (DBPs). However, where DOC was low due to removal by treatment, chlorine reacts with bromide to form reactive bromine, leading to the formation of brominated DBPs. Since brominated DBPs are reported to be more toxic than their chlorinated analogues, steps should be taken to remove bromide as well as DOC from sources that contain appreciable concentrations of this halide. In terms of THM formation, the preferential incorporation of bromide may counter any benefits gained by DOC removal.

The following points summarise more specific key observations.

- DOC inputs varied between sites, and to different degrees each year. Significant increases in DOC concentration were noted for Bolganup, Quickup and Quinninup during stratification periods. This suggests DOC release from the sediments, a hypothesis supported by DYRESM-CAEDYM modelling of the Bolganup site. Denmark had a delayed increase in DOC after rainfall, indicating that inputs from upstream were significant. DOC concentrations in Walpole strongly correlated with rainfall, indicating that allochthonous inputs are an important source of DOC for this site.

- In some cases catchments were impacted by events at the extremities. For example, in Harding and Denmark Rivers, salinity increases were not observed until months after major rainfall events.

- Conditions of anoxia led to increases in concentrations of dissolved metals as well as DOC. Some indicators (e.g. fluorescence measurements) suggested that changes to DOC with decreasing dissolved oxygen (DO) were qualitative as well as quantitative.
- Specific UV Absorbance (SUVA), particularly in samples taken from anoxic bottom waters, is partly comprised of inorganic components, probably reduced sulphur and/or Fe bound to DOC.

- Resin fractionation analysis of organic matter revealed that very hydrophobic acids (VHA) dominated the composition of natural organic matter (NOM) from all sites, particularly those from southern sites. The VHAs in South-Western Australian sites ranged from approximately 70% for Bolganup, up to approximately 80-90% for Quickup and Quinninup. This indicated strong humic character and allochthonous sources. The NOM composition in Harding Dam was significantly different, with percentage of VHAs ranging from 40-70%. Other indicators (e.g. fluorescence spectroscopy, SUVA, C/N ratio) also demonstrated fundamental differences in DOC from Harding with respect to DOC from the southern sources.

- The use of different analytical techniques was advantageous in understanding the character of NOM. For example, high performance size-exclusion chromatography coupled with DOC detection provided extra information on the composition of high molecular weight peaks found in South Western Australian study sites.

- A dissolved oxygen level of >50% saturation was shown to significantly reduce the quantity of iron, manganese and DOC present in raw water, thus reducing the level of treatment required. Careful observation of dissolved oxygen levels in relation to placement of the off-take for a water source may lead to savings in the cost of chemicals for treatment.

A more detailed study on carbon flux was conducted at Bolganup Dam using the hydrodynamic modelling packages CAEDYM and DYRESM (Harris and Antenucci, 2008). The conclusions from this study are listed below and the full report is included as Appendix II in this report.

1. Significant concentrations of DOC (0.11g DOC/m²/day), primarily in a highly refractory form, flux out of the sediments under anoxic conditions between October and May of each year.

2. DOC flux from the sediments can be explained in terms of bacterial production. DOC is transported into the hypolimnion from overlying waters, and depending on the rate of the stepwise degradation processes of particulate organic carbon (POC) and high molecular weight DOC, refractory and labile portions of DOC may accumulate in the sediment and diffuse into the overlying waters.

3. The refractory DOC fluxed from the sediments is predominantly of the VHA component, and is highly aromatic in nature. Associated with this compound, is a high SUVA indicating higher potential for DBP production and thus a larger amount of chlorine is required to treat this water.

4. The DOC in Bolganup reservoir is sourced primarily by that released from the sediments. The DOC in the sediments would have entered the reservoir either in previous inflow events, prior to the study period, or may have been accumulated in the sediments prior to construction of the dam. It is likely that inflow events continue to deliver small concentrations of POC and refractory DOC to the reservoir, although this was not evident during the study period.

5. DYRESM-CAEDYM is capable of predicting stratification, salinity, pH, DO, nitrogen and phosphorus species, carbon compounds and phytoplankton biomass in Bolganup reservoir.
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<th>Description</th>
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<tbody>
<tr>
<td>AHD</td>
<td>Australian Height Datum</td>
</tr>
<tr>
<td>AWQC</td>
<td>Australian Water Quality Centre</td>
</tr>
<tr>
<td>BDOC</td>
<td>Biodegradable Dissolved Organic Carbon</td>
</tr>
<tr>
<td>BoM</td>
<td>Bureau of Meteorology</td>
</tr>
<tr>
<td>CALM</td>
<td>Department of Conservation and Land Management (Western Australia)</td>
</tr>
<tr>
<td>CWQRC</td>
<td>Curtin Water Quality Research Centre</td>
</tr>
<tr>
<td>CWR</td>
<td>Centre for Water Research (University of WA)</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection by-product</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>DoE</td>
<td>Department of Environment (Western Australia)</td>
</tr>
<tr>
<td>DWTP</td>
<td>Denmark Water Treatment Plant</td>
</tr>
<tr>
<td>EEM</td>
<td>Excitation Emission Matrix</td>
</tr>
<tr>
<td>FOC</td>
<td>Filterable organic carbon</td>
</tr>
<tr>
<td>GL</td>
<td>Gigalitres</td>
</tr>
<tr>
<td>HMW</td>
<td>High Molecular Weight</td>
</tr>
<tr>
<td>HPSEC</td>
<td>High Pressure Size Exclusion Chromatography</td>
</tr>
<tr>
<td>ML</td>
<td>Megalitres</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural Organic Matter</td>
</tr>
<tr>
<td>POC</td>
<td>Particulate Organic Carbon</td>
</tr>
<tr>
<td>SEC</td>
<td>Size exclusion chromatography</td>
</tr>
<tr>
<td>SEC-OCD</td>
<td>Size exclusion chromatography with organic carbon detection</td>
</tr>
<tr>
<td>SEC-UV</td>
<td>Size exclusion chromatography with ultraviolet detection</td>
</tr>
<tr>
<td>SEC-UV-OCD</td>
<td>Size exclusion chromatography with ultraviolet and organic carbon detection</td>
</tr>
<tr>
<td>SUVA</td>
<td>Specific Ultra Violet Absorbance</td>
</tr>
<tr>
<td>THM</td>
<td>Trihalomethane</td>
</tr>
<tr>
<td>TKN</td>
<td>Total Kjeldahl nitrogen</td>
</tr>
<tr>
<td>TTHM</td>
<td>Total trihalomethane</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VHA</td>
<td>Very hydrophilic acids</td>
</tr>
<tr>
<td>WCWA</td>
<td>Water Corporation of Western Australia</td>
</tr>
<tr>
<td>WGWTP</td>
<td>Wanneroo Ground Water Treatment Plant</td>
</tr>
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</table>
1 INTRODUCTION

The high and variable levels of natural organic matter (NOM) in coloured source waters throughout different regions of Australia can contribute to disinfection management and treatment problems (e.g. high chlorine decay rates, high concentrations of disinfection by-products (DBPs), biofilm regrowth and aesthetic issues associated with these problems) (Westerhoff et al., 2004; Uyak et al., 2008; Franzmann et al., 2001). Several treatment strategies have been investigated by water utilities especially in Western Australia (WA) and South Australia (SA), but the heterogeneity and varied dynamics of NOM in Australian source waters has challenged existing treatment processes. Consequently, only advanced and expensive strategies (e.g., adsorption using activated carbon) have consistently provided the preferred efficiency of NOM removal from coloured waters.

There is a clear need to better understand the fundamental characteristics of NOM in surface waters of high colour so that (i) existing schemes can be better managed, and (ii) new, cost effective water treatment process can be developed for sufficient removal of NOM.

The characterisation of NOM is a complex and demanding analytical challenge due to the wide molecular size distribution and the heterogeneous and variable nature of the material (Picolo, 2001; Her et al., 2003). Analytical methods range from simple, rapid methods requiring little or no sample preparation, but which provide only basic information, to methods that are complicated, expensive and laborious, but which provide detailed structural chemical information. No single technique exists to determine the chemical structure and functionality of NOM, and all methods have considerable limitations and drawbacks: generally, the more complex the technique, the more detailed the information that is yielded. In this project, the high frequency of monitoring required to derive accurate data to predict trends and the number of sites (six) meant that the study was, of necessity, limited to analytical techniques that are rapid and robust. The information collected includes determination of molecular weight profiles using size exclusion chromatography with ultraviolet and organic carbon detection (SEC-UV-OCD), measurement of NOM spectral properties using UV-visible and three dimensional fluorescence scans and determination of hydrophobic and hydrophilic fractions of the NOM. These measurements, when considered in combination, provided very detailed information, both in terms of the structure and functionality of NOM and in terms of ‘fingerprinting’ information.

Models capable of predicting the hydrodynamics and chemical dynamics within water bodies were applied to one source in the study, Bolganup, to assist in planning source management and water treatment strategies. The DYRESM model is a hydrodynamic model which predicts stratification and the effects of inflows and outflows over seasonal time scales. CAEDYM is a water quality model that couples directly to DYRESM and deals with chemical and biochemical processes including nutrient cycles (carbon (C), nitrogen (N), phosphorus (P), silicon (Si)), dissolved oxygen (DO), primary production, particles and exchange of gases with the atmosphere. The CAEDYM model includes only very basic considerations of organic carbon and does not take into account the additional, more detailed, information on the organic carbon characteristics collected in this study. One of the aims of the project was, therefore, to refine the model to make use of this additional data.

The modelling describes the transport and fate of DOC and includes hydrodynamic effects (inflows, outflows and meteorological forcing), as well as microbial degradation of DOC and UV photolysis. The degradation of DOC by UV light has implications for phytoplankton growth, as DOC has a significant impact on the light properties within reservoirs, and light is a fundamental requirement for phytoplankton productivity. Therefore, the breakdown of DOC by UV light could lead to a significantly enhanced light climate, which could then impact on the phytoplankton population. Aquatic ecological models, such as those to be employed in this study, have yet to consider potential UV impacts and feedback with DOC and other water quality parameters, such as phytoplankton biomass. In this study, we investigate the role of UV light on the degradation of DOC, and determine the extent to which this could be actively promoted by manipulating residence times of the reservoirs. It has implications in determining the DOC load to the off-take water, the fate of catchment-derived DOC in the reservoir and the potential to actively manage DOC levels in the reservoir. A two-band (A and B) UV degradation model of DOC, specifically looking at the DOC breakdown attributable to the UV-A and UV-B bandwidths, and how this might vary as a function of DOC source, is being developed and applied by CWR (Harris and Antenucci, 2008).
1.1 Aim

The primary objective of the project was to better understand the origin, structure, reactivity and temporal dynamics of NOM in the six surface waters under study. The questions of interest were:

1. What is the origin of the NOM in these waters?
2. What are the fundamental characteristics of the NOM (e.g. in terms of molecular weight distribution, hydrophobic/hydrophilic nature, UV-visible and fluorescence spectral properties, organic nitrogen and phosphorous content)?
3. Does NOM character vary throughout the year? What causes this variation? Can it be modelled?
4. What, if any, relationships exist between NOM character and physical, inorganic and biological water quality characteristics (e.g. pH, DO, hardness, alkalinity, nutrients (N and P), phytoplankton numbers and chlorophyll)?
5. What is known about the treatability of the various NOM fractions (i.e. size exclusion chromatography (SEC), hydrophilic/hydrophobic fractions) and how may better treatment strategies for dealing with the NOM of highly coloured waters be identified.
2 METHODS USED

2.1 Sampling Program

Sampling was conducted on a monthly basis for six different surface water sites as listed in Table 1. Figure 1 shows the geographical locations of the study sites in Western Australia.

Table 1 Project Sampling Schedule and Details

<table>
<thead>
<tr>
<th>Study Site</th>
<th>Region</th>
<th>GPS Co-ordinates of Deepest Point (Latitude / Longitude)</th>
<th>Sampling Period</th>
</tr>
</thead>
</table>
The sampling program for the South West region was not run as long as the others due to budget constraints and some sampling events for Harding Dam were not able to be completed due to unavoidable Water Corporation of Western Australia (WCWA) personnel absences. Prior to the sampling program, depth sounding equipment was used to locate the deepest point of each water source. On each sampling occasion, water samples were collected from the surface and from the bottom of each water body, from each location, from the designated point. At Walpole River only surface samples were collected due to the shallow water depth. Depth samples were taken with a van Dorn depth sampler. Additional sampling for Bolganup Dam was carried out at the inflow from August 2007 for a period of four months (This inflow was not flowing for the entire year).

![Geographical locations of study sites](image)

**Figure 1** Geographical locations of study sites (Provided by Google Earth).
2.2 Background Information for Study Sites

Bolganup Creek Dam is located on the south coast of Western Australia (approximately 410 km south of Perth) in the Porongurup Range, and supplies the drinking water for the Porongorup caravan park and has supplied some surrounding localities in the past (Water Corporation, 2005a; Trolio, 2009 personal communication). The catchment for Bolganup Creek Dam has an area of 5 km$^2$ and varies in elevation from 290 M AHD at the reservoir to about 500 M AHD at the head of the catchment. The Bolganup Dam catchment lies completely within a National Park, which is dominated by Karri (Eucalyptus diversicolor) forest with an understorey of lichens and small native shrubs (Water Corporation, 2005a). A summary of the landform and vegetation is found in Appendix I. Water inflow to the reservoir is mostly from surface runoff over the winter months (Water Corporation, 2005a).

Figure 2 Aerial photograph of Bolganup Dam (Provided by Google Earth).
Denmark River Dam is located in the Great Southern region of Western Australia, approximately 54 km west of Albany. Denmark River Dam, along with Quickup River Dam has in the past supplied drinking water for the township of Denmark (Water Corporation, 2005b). Use of Denmark River water has been discontinued, except for periods when water levels in Quickup Dam, the main water source for Denmark township, are low. In 2007/08, water from Denmark River was blended with 80% water from Quickup Dam. Water Corporation is introducing advanced water treatment for Denmark River water, including ultrafiltration and UV treatment (Trollo, personal communication, 2009). The catchment area is 567 km², with the dam covering an area of 21.9 ha with a storage volume of 451 ML. Water flow into the dam is from roughly equal contributions of surface and subsurface flows (Water Corporation, 2005b). Forests in the catchment comprise Jarrah (Eucalyptus marginata) and Marri (Corymbia calophylla), with some stands of Karri in the lower reaches. Banksia and Sheoak dominate the upper Western part of the catchment (see Appendix I for summary of landform and vegetation). Approximately 17% of the catchment has been cleared for agriculture. Historically, raw water salinity, colour, iron and aluminium concentrations have exceeded Australian Drinking Water Guidelines (Water Corporation, 2005b).

Figure 3 Aerial photograph of Denmark River (Provided by Google Earth).
Quickup River Dam is the primary drinking water supply for the township of Denmark. The catchment has an area of 28 km$^2$, with the reservoir covering an area of 50.7 ha and having the ability to hold 1,189 ML (Water Corporation, 2005c). Surface runoff over the winter months contributes 65% of water inflow to the reservoir and approximately 35% of water inflow is due to subsurface flows (Water Corporation, 2005c).

Like other south Western Australian water supplies in this study, the Quickup Dam catchment is dominated by forests of Jarrah, Marri and Karri (Water Corporation, 2005c). A summary of landform and vegetation can be found in Appendix I. The majority of the Quickup River catchment (99%) is covered with State Forest (Water Corporation, 2005c). The water quality from Quickup Dam raw water has typically been considered good, with only colour and pH being outside the Australian Drinking Water Guidelines (Water Corporation, 2005c).

Figure 4 Aerial photograph of Quickup Dam (Provided by Google Earth).
The Quinninup Dam catchment covers an area of approximately 36 km², and lies within the Shire of Manjimup (approximately 340 km south of Perth) (Water Corporation, 2005d). The dam was formed by constructing an earth impoundment on Little Quinninup Brook and has a storage capacity of 717.5 ML (Water Corporation, 2005d). It supplies the drinking water for the township of Quinninup. Communities of Karri and Jarrah forest surround the Dam, and residential subdivisions are in close proximity, however, the majority of the catchment is State Forest.

Although the Water Corporation owns Lot 187, which encompasses the dam and the surrounding 30 m buffer, it has been reported that a number of recreation activities occur in and around the dam, as well as the surrounding catchment (Water Corporation, 2005d). Some of these activities may be occurring illegally, since recreation in the dam is prohibited (Trolio, personal communication, 2009).

![Quinninup Dam](image.png)

**Figure 5** Aerial photograph of Quinninup Dam (Provided by Google Earth).
The Walpole River Weir is used to supplement drinking water supplies to the township of Walpole (approximately 423 km south of Perth and 120 km west of Albany) (Water Corporation, 2005e). Butlers Creek Dam is the additional water supply for Walpole.

The Walpole River Catchment has been extensively cleared and developed, with landuse including agriculture, dairy and grazing, state forest, Walpole-Nornalup National Park, landfill site now used for waste transfer and an agricultural airstrip (Water Corporation, 2005e). Cattle stocking is prevalent in the catchment, and cattle can access the feeder streams that are in close proximity to the off-take (Water Corporation, 2005e).

The Walpole River basin has broad drainage floors of sedimentary rock, covered with swamp terrain, and associated sands that have a high tendency to leach phosphorus but a low risk of eroding (Water Corporation, 2005e). Surrounding the basin are hills consisting of flat swampy terrain on sedimentary rock with broad drainage floors in lower reaches of streams. Surrounding the basin, the remainder of the catchment comprises hills consisting of laterite and some igneous rock outcrops. The soils are sandy or gravely duplex soils that have a higher phosphorus holding capacity (Water Corporation, 2005e).

Figure 6 Aerial photograph of Walpole River (Provided by Google Earth).
Harding Dam is located in the Pilbara region, North Western Australia, approximately 40 km southeast of Karratha (Water Corporation, 2004). It operates in conjunction with the Millstream borefield to supply drinking water to the towns of Karratha, Dampier, Roebourne, Wickham, Point Samson, Cape Lambert and the Burrup Peninsula (Water Corporation, 2004).

The Harding Dam Catchment has an area of approximately 1100 km$^2$, with the dam having a storage capacity of 63.8 ML and surface area of 14 km$^2$ (Water Corporation, 2004). Water inflow into the dam is irregular and dependent upon intense rainfall events which occur during cyclones and thunderstorms in the summer months.

Harding Dam is surrounded by dolerite boulders. The vegetation changes across the catchment, with Spinifex hummock grasslands on the shallow scree hill slopes, Spinifex on the erosional slopes, and a mixture of mulga shrublands and grasslands on the depositional plains (Water Corporation, 2004). River gums and Cadjebuts line the major creeks and drainage lines (Water Corporation, 2004).

Figure 7 Aerial photograph of Walpole River (Provided by Google Earth).
2.3 Sample Collection and Measurement of Depth Profiles

The following precautions were taken to preserve sample integrity:

- For biodegradable dissolved organic carbon (BDOC), dissolved organic carbon (DOC), ultraviolet (UV), analyses, amber glass sampling bottles were pre-annealed at 550°C overnight.
- Water samples for phytoplankton number analysis were preserved with Lugol’s solution (ca. 1%v/v in total volume) (Saraceni & Ruggiu 1969).
- Chlorophyll-a samples were collected in amber bottles, preserved with MgCO₃ (ca. 0.01%w/v in total volume) and immediately wrapped in aluminium foil to exclude all light.
- Samples for metals analysis were collected in high density polyethylene containers.
- All containers were pre-rinsed three times with the sample before collection to prevent contamination. Samples were chilled in eskies with ice bricks immediately after collection.
- Samples were filtered on-site through a 0.45μm PALL™ cartridge filter.

Depth profiles for the Great Southern water sources were collected using a ‘Hydrolab Sonde’ water quality meter. Parameters measured were pH, conductivity, light penetration, turbidity, DO, and temperature. Instrumentation and expertise to operate the Hydrolab Sonde were provided by the Department of Environment (DoE) Albany. Depth profiles for the South West water sources were not collected due to lack of equipment. Some depth profile data for Harding Dam was also recorded using a ‘Hydrolab’ water quality meter by WCWA personnel.

2.4 Chemical and Microbiological Analyses

Characterisation of NOM was carried out by analysing for DOC, BDOC, SEC-UV-OCD, UV-visible scans and three dimensional UV-fluorescence scans Curtin Centre for Water Quality (CWQRC) and NOM fractionation Australian Water Quality Centre (AWQC).

Biodegradable dissolved organic carbon (BDOC) analyses were carried out according to a method originally described by Joret and Levy (1986). This method was further developed and validated at Curtin University, in collaboration with researchers from CSIRO Land and Water, and with support from WCWA. The method is based on inoculation of water samples with biomass grown on Siran sintered glass beads and subsequent measurement of any decrease in DOC over a time scale of seven days. The inoculum biomass was generated within bioreactors at Wanneroo Ground Water Treatment Plant (WGWT) providing a microbial population indigenous to West Australian waters. The difference between the original and final DOC represents the quantity of DOC utilisable by the biomass, and therefore, the BDOC (i.e., the fraction of DOC which is labile in terms of microbiological degradation). The method is described in detail by Zappia et al., (2008).

Excitation-emission matrix (EEM) fluorescence spectroscopy was carried out in order to show changes in specific components of NOM, particularly fulvic and humic substances and algal-derived organic matter. Temporal changes in fluorescence spectra were compared with other indicators of these NOM components (e.g. chlorophyll-a, resin fractionation, SEC-UV-OCD). These comparisons assist in general interpretation of data and consistency between measurements from the various techniques adds confidence to the body of NOM characterisation data collected.

All fluorescence measurements were made using a dual beam Varian Cary Eclipse Fluorescence Spectrophotometer with a xenon flash lamp on water samples (0.45μm filtered) in a quartz cell (1 cm). Excitation emission matrices (EEMs) were gathered by collating emission spectra at a range of excitation wavelengths. Emission and excitation spectra were scanned in 2 nm steps from 380 to 500 nm and 190 to 380 nm, respectively. Slit widths (5 nm resolution) and lamp voltage (800 V) were held constant in all spectra.

The collected assays were converted and imported into Origin 7.5 (OriginLab Corporation, 2006) to generate a colour contour plot (3D plot). Plot scales and settings were kept constant to enable direct comparisons between and within sites. The 3D contour plots were used to assess changes in the fluorescence characteristics of the water over time and between sites.
Rapid adsorption/fractionation was conducted using a procedure which was developed by Chow et al. (2004, 2005). The method is based on adsorption of NOM onto a series of three resins, each of which adsorbs a different fraction of the NOM, according to its hydrophobic properties. The water is first passed through DAX-8, which retains the most hydrophobic NOM, then XAD-4, which retains slightly hydrophobic material, and finally, IRA 958, which retains charged hydrophilic acids. In between each resin adsorption step, subsamples are collected and analysed for DOC. In this way, it is possible to determine the concentrations of each of four operationally defined NOM fractions, each of which have varying properties, and to characterise the NOM in terms of the proportions of these fractions.

Size Exclusion Chromatography with Ultraviolet and Organic Carbon Detection (SEC-UV-OCD) was conducted using a method developed as part of CRCWQT Project 2.3.1.1. In this method, DOC components are separated based on their molecular size and then detected on-line, first by a UV absorbance detector, then by a custom built organic carbon detector (OCD). The UV detector is a diode array detector, capable of providing complete scans across the entire UV-visible spectrum (190 – 800 nm). The OCD utilises a continuous flow UV/persulfate oxidation procedure to convert DOC components at high conversion rates into carbon dioxide, which is then separated from the aqueous stream and detected as CO₂ gas by Fourier transform infrared (FTIR) spectroscopy. In this way, molecular weight profiles of both DOC and UV-absorbing DOC are obtained concurrently. The method is described in detail by Allpike et al., (2007). The technique provides information on the quantity of DOC and UV-visible spectral properties of any given molecular weight fraction.

Other characteristics. Aggregate DOC concentration was measured using a Shimadzu TOC-V₆₅₅ Total Organic Carbon Analyser with a Shimadzu ASI-V Autosampler, which employed the standard persulfate method. UV-visible scans were measured using a Shimadzu UV-1700 PharmaSpec spectrophotometer. UV-visible scans were conducted over the wavelength range 190-1100 nm. External commercial laboratories carried out tests for phytoplankton numbers (Dalcon Environmental), filterable organic carbon (FOC), chlorophyll-a, conductivity, total anions, turbidity, total manganese, aluminium, sodium, potassium, calcium, magnesium, sulphate, chloride, silica, alkalinity and nutrients (total Kjeldahl nitrogen (TKN), nitrate, nitrite, total P, filterable reactive P) (SGS Environmental, Queens Park, WA). Bromide was analysed at the CWQRC using ion chromatography.

2.5 Meteorological Data

All meteorological data were sourced from the Bureau of Meteorology (BoM). There was not always a BoM station within close proximity to all of the study sites (Table 2), however, the nearest station was selected for all sites. For example, the BoM station was quite close for the Walpole study site (4 km). In contrast, one of the BoM stations for the Denmark site was 42 km away). This may have had an effect on how closely climate data can be related to events within a study site, as climatic conditions can change significantly over short geographical distances.

Due to the regional locations of the study sites a full range of data was not always available from every station (e.g. a station may only have precipitation data available). Data from November 2005 to January 2008 was sourced, comprising of: cumulative monthly precipitation, maximum / minimum / average mean air temperature and, when available, monthly evaporation. Table 2 provides an indication of which BoM stations were utilised for the respective study sites.
Table 2 Available meteorological data and BoM stations for respective study sites.

<table>
<thead>
<tr>
<th>Study Site</th>
<th>Parameter (*)</th>
<th>BoM Station</th>
<th>Approximate Station distance from study site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinninup Dam</td>
<td>T &amp; P</td>
<td>Manjimup</td>
<td>22km NNW</td>
</tr>
<tr>
<td></td>
<td>T, P &amp; E</td>
<td>Pemberton</td>
<td>18km W</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>Deeside</td>
<td>16km ENE</td>
</tr>
<tr>
<td></td>
<td>T &amp; P</td>
<td>Shannon</td>
<td>17km SSE</td>
</tr>
<tr>
<td>Walpole River Dam</td>
<td>T &amp; P</td>
<td>North Walpole</td>
<td>2km ENE</td>
</tr>
<tr>
<td>Bolganup Dam</td>
<td>T &amp; P</td>
<td>Mount Barker</td>
<td>20km WNW</td>
</tr>
<tr>
<td>Denmark River Dam</td>
<td>P</td>
<td>Denmark</td>
<td>4km S</td>
</tr>
<tr>
<td></td>
<td>T, P &amp; E</td>
<td>Albany Airport</td>
<td>42km ESE</td>
</tr>
<tr>
<td>Quickup Dam</td>
<td>P</td>
<td>Denmark</td>
<td>6km SSW</td>
</tr>
<tr>
<td></td>
<td>T, P &amp; E</td>
<td>Albany Airport</td>
<td>39km ESE</td>
</tr>
<tr>
<td>Harding Dam</td>
<td>T &amp; P</td>
<td>Roebourne</td>
<td>24km N</td>
</tr>
</tbody>
</table>

Note (*) Temperature = T, Precipitation = P, Evaporation = E

2.6 Modelling

Sufficient meteorological data was collected to enable modelling to be carried out on all of the reservoirs, but the scope of the project allowed modelling for one site only. Bolganup Dam was chosen because it was sufficiently deep for it to become clearly stratified and complete data sets for depth profiles were available throughout the study period.
3 RESULTS AND DISCUSSION

3.1 Bolganup Creek Dam

Bolganup Creek Dam underwent regular cycles of stratification and mixing (Figure 8). Stratification occurred during the summer months, while over turn and mixing of the water body occurred during winter, and corresponded to peak rainfall periods. Greater mixing of the Bolganup Dam water body occurred during winter 2006, than for winter 2007 as shown by the complete meeting of dissolved oxygen concentrations and temperature for both the top and bottom of the dam for 2006 only (Figure 8).

During stratification, bottom waters became progressively anoxic, and reducing conditions were created. Under these conditions, iron was released into the water column from the sediments (Figure 9). Manganese also exhibited a similar trend to iron. Sulphate underwent reduction during stratification periods (Figure 9). During October 2007 an ‘orange’ scum was apparent on the surface of Bolganup Dam (Figure 10). It is unclear whether this scum was of biological or chemical origin. The scum may have been an iron complex or precipitate of some type; dissolution of precipitated iron from the bottom sediments would have occurred during stratification, mobilising iron into the water within the epilimnion. Subsequent turnover of the dam may have then transported ferrous iron throughout the water column where elevated oxygen levels were able to oxidise it to ferric, yielding a visible surface precipitate. This precipitate could have then been transported to the edges of the dam by the wind. Alternatively, the scum may be due to an algae, possibly *Botryococcus*, which are known to produce this type of coloured foamy material (Trolio, personal communication 2009).
**Figure 8** Trends in dissolved oxygen, temperature, rainfall and NOM character (UV$_{254\text{nm}}$ absorbing species) for Bolganup Creek Dam.  
* = size-exclusion chromatogram profile changed between 15/8/06 and 12/9/06 (see text).
Figure 9 Change in unfiltered iron and sulphate concentration for Bolganup Dam water (top and bottom) during the course of November 2005 – November 2007.
The nature of UV$_{254nm}$ absorbing compounds of the NOM in both the top and bottom waters of the dam, as studied using size-exclusion chromatography, did not differ significantly during the course of the study (Figure 8), except for some variation in the high molecular weight (HMW) components.

After the mixing period in 2006, the nature of the UV$_{254nm}$ absorbing species of NOM (Figure 8) for both top and bottom NOM changed, as observed by an increased response for the HMW species at approximately 47,000 Da. Upon further investigation using high performance size-exclusion chromatography, coupled with a DOC detector, it was shown that the HMW species in this peak comprised some carbon as well as strongly UV absorbing material, giving it a very high specific UV absorbance (Figure 11).

Specific UV absorbance (SUVA) at 254 nm, a measure of the UV absorbance at 254 nm per mg of DOC in 1 L of sample, is an indication of the aromatic, hydrophobic character of NOM (Traina et al., 1990, Novak et al., 1992). The relatively high SUVA values (Figure 12) indicated that the HMW peak may have contained inorganic matter as well as organic carbon.

This bimodal molecular weight distribution has been observed for other NOM sources in Western Australia. Allpike et al., (2005) attributed the high molecular peak to possible incorporation of inorganic material into NOM, particularly iron or sulphur as “dirty sulphur”. These authors suggested that even though the sample had been filtered, it could still contain colloidal material that would give an apparent UV response. Other compounds such as silicates, iron oxyhydroxides and aluminium complexes may contribute in this way to the high SUVA values (references in Allpike et al., 2005).
Figure 11 Size exclusion chromatograms of Bolganup Dam NOM (16/5/07) with UV\textsubscript{254nm} and DOC detection. The DOC concentration for NOM in top waters was 11 mg CL\textsuperscript{-1} and bottom waters, 15 mg CL\textsuperscript{-1}.
Figure 12 Changes in colour and aromatic content (SUVA) of NOM from the top and bottom of Bolganup Creek Dam from November 2005 – November 2007.
Interestingly the UV$_{254nm}$ absorbing species of NOM contained in the water from the inlet flowing into the dam did not contain a significant high molecular weight peak (Figure 13). The absence of the high molecular weight peak in the inlet NOM was consistent for all inlet samples analysed (July-August 2007). This suggests that the higher molecular weight component in the dam is not attributable to material washed in from surface run off but forms within the body of the lake. Alternatively, it may have represented NOM that had been previously transferred into the dam.

**Figure 13** Size-exclusion chromatograms of UV$_{254nm}$ absorbing NOM from Bolganup Dam inlet, top and bottom, sampled November 2007.

The observation of a lake and its adjacent inlet having different NOM characteristics is not unique, and has also been noted elsewhere, for example, Redberry Lake (Oligotrophic saline lake in Saskatchewan; Waiser and Robarts, 2000). In the study conducted by Waiser and Robarts (2000), lake DOM was older than the younger inflowing organic matter, and heavily influenced by in-lake chemical alterations. Residence time of water in this lake is discussed in Appendix II (Harris and Antenucci, 2008).

SUVA and colour increased for bottom water samples during stratification (Figure 12) in Bolganup Dam. In addition, DOC concentrations increased in bottom waters during stratification, and less notably, top water (Figure 14). The increase in DOC concentration may have been due to input from the initial rainfall event after summer (as suggested by fluorescence data; Section 3.7), however it may have also been due to release from sediments during stratification, as higher rainfall events in winter did not result in further DOC increase. In addition, the higher rainfall in 2007, compared with 2006 did not correspond to a higher DOC content (Figure 12). Studies conducted by Chadwick et al., (2006) found that DOC concentrations can increase in the hypolimnion during stratification, due to either decomposition of NOM associated with recently fallen particles or release of sediment-bound DOC associated with dissolution of iron and manganese hydrous oxides from the sediments.

DOC is less prone to mineralisation under anoxic conditions and the higher concentrations observed in the bottom waters may also have been due to preservation in this zone, while DOC in the surface layers was degraded and mineralised to CO$_2$. 

30
An increase in the biodegradable component of DOC (BDOC) coincided with the increase in total DOC (Figure 15), providing a food source for heterotrophic bacteria. During May 2006, when the first spike in DOC concentration occurred in the bottom waters, a sharp increase in phytoplankton numbers also occurred. The increase in phytoplankton numbers was due principally to unknown taxa. It may be possible that some of the DOC, and BDOC (particularly as the BDOC concentration increases in the bottom waters directly after the phytoplankton bloom) could have originated from the phytoplankton. Certainly, studies have shown the phytoplankton can contribute to an increase in the BDOC pool (Kragh and Sondergaard, 2004). Extracellular release from phytoplankton has been shown to produce DOC (Baines and Pace, 1991; Sondergaard et al., 2000). Traditionally, autochthonously derived DOC is considered more bioavailable than allochthonously derived DOC (Sondergaard and Middelboe 1995).

The changes in the composition of DOC shown by size-exclusion chromatography profiles, SUVA, colour, and DOC/BDOC concentrations, were not reflected by the fractionation measurements, which did not change substantially throughout the study period (Figure 16). This apparent discrepancy highlights the difficulties faced in NOM characterisation and the value of using different analytical techniques to gain a broader understanding of NOM character.
Figure 15 Changes in DOC, BDOC, and phytoplankton numbers in the top and bottom of Bolganup Creek Dam from November 2005 – December 2007.
Figure 16 Changes in NOM fractions in the top and bottom of Bolganup Creek Dam from November 2005 – November 2007.
3.2 Denmark River Dam

Denmark River Dam volume did not fluctuate substantially during the study period (448.66 – 400.35 ML), and exhibited some stratification during the summer months (Figure 17).

![Dissolved oxygen (%) and water precipitation (mm/month)](image)

**Figure 17** Trends in dissolved oxygen, temperature, water precipitation during Nov 2005 – Nov 2007.

Much like other dams across South-Western Australia in this study, NOM character (as analysed by size exclusion chromatography) in Denmark River Dam was bimodal in nature (Figure 18), having a larger molecular weight peak centred on approximately 47,000 Da, and broader, smaller molecular weight peak centred on approximately 5,700 Da. The abundance of these two peaks varied over time, and between top and bottom. Figure 18 shows the peak height ratio of peak 1 to peak 2 (47,000 Da to 5,700 Da peak ratio) over time for top and bottom NOM. The higher the peak ratio value, the larger the 47,000 Da peak is to the broader 5,700 Da centred peak. Typically, the proportion of peak 1, or higher molecular weight substances increases during stratification, with the bottom NOM generally having a higher proportion of peak 1 than the top NOM. This supports the suggestion that the increase in UV absorbance in this peak may be caused by incorporation of reduced sulphur and/or iron into organic matter, since stratification would cause sulphate reduction in the anoxic zone. The increase in peak 1 coincides with an increase in iron, but sulphate concentrations did not alter substantially between top and bottom waters throughout the study period. However, sulphate is generally in large excess compared with reduced sulphur compounds and sulphate reduction may therefore not affect sulphate concentrations. Reduced sulphur compounds were not analysed in this study.
Figure 18 Trends in the peak ratios of peak 1 to peak 2 (47,000 Da to 5,700 Da peak ratio) over time for top and bottom NOM during Nov 2005 – Nov 2007.

Size exclusion chromatograms of the 29/11/2005 and 16/01/2007 top and bottom NOM are shown to illustrate bimodal nature of NOM, and different ratios of peak 1 to peak 2.

A weak linear relationship between the size exclusion chromatogram peak ratios and SUVA occurred for bottom waters ($r^2 = 0.769$, $n=23$), but not top waters ($r^2 = 0.051$, $n=23$) indicating that the larger molecular weight peak had a large impact on SUVA. During stratification, the peak ratio of the bottom NOM (Figure 17), and SUVA (Figure 19) increased. Minimal change occurs to the top water NOM (excepting February 2007). During stratification, reducing conditions result in the dissolution of iron and manganese oxides (Hamilton-Taylor and Davison, 1995) releasing these species into the water column (Figure 19), consistent with the observed increase in iron concentrations during stratification. Alternatively, other inorganic components may have been incorporated into the NOM upon release from the sediments during stratification. Iron, manganese, calcium, and some organic nitrogen concentrations increased in bottom waters, and may have contributed to the increase in high molecular weight species. The sample integrity and the stability of the reduced species that may comprise peak 1 also should be considered: long sample storage times prior to analysis may have occurred in some instances, which may have led to degradation of the UV-absorbing material comprising this peak, so these results need to be interpreted with caution.
Figure 19 Trends in SUVA, iron and manganese for top and bottom NOM during Nov 2005 – Nov 2007.

During oxic conditions, the iron and manganese concentrations decreased (Figure 19), indicating the formation of oxides that precipitate out of solution.
In addition, increases in DOC concentrations did not appear to be linked with rainfall events (Figure 20). Approximately one month after the peak rainfall period in July 2006 (Figure 17), a rise in top and bottom water DOC concentrations occurred. Rainfall quickly diminished after this period; however, the DOC concentrations remained high until the winter months, where DOC concentrations decreased. The predominant source of DOC may therefore have been due to transport down the river from higher up in the catchment, resulting in the delayed response. Additionally, if minimal DOC contributions are occurring during rainfall events, then the observed decreases in DOC concentrations during these times may be due to a dilution effect.

Despite fluctuations in DOC concentrations during the study period, there was minimal compositional change within the fractions of NOM (Figure 21). Very hydrophobic acids were the dominant fraction.

Figure 20 Trends in rainfall and DOC for top and bottom water in Denmark River Dam during Nov 2005 – Nov 2007.
Characterisation of Natural Organic Matter in Highly Coloured Surface Waters

Figure 21 Changes in NOM fractions in the top and bottom of Denmark River Dam from November 2005 – November 2007.

Increases in DOC concentrations generally did not correspond with peaks in phytoplankton blooms (Figure 22), indicating that the majority of DOC came from other sources. Phytoplankton blooms appeared to correlate to total phosphorus inputs into the system. Denmark River is impacted by agricultural activities which may contribute to phosphorus loadings. These results show that phytoplankton growth appears to be limited by phosphorus concentrations, as would be expected.

Studies have also shown however, that an increased supply of fine sediments such as silts and clay can increase internal phosphorus loading of rivers and dams (Olive et al., 1994). The initial increase in phosphorus concentrations of top and bottom water during 2006 may have been due to increased loading from inflow into the dam after rainfall, as peaks occurred just after the initial autumn rainfall, however, this does not explain the large increase in concentration in bottom waters during summer 2007.

The large increase in phosphorus concentration for the bottom waters during summer 2007 may have been due to the formation of anoxic conditions during stratification, resulting in the release of phosphorus from sediment. Studies have shown that sediments can act as both a sink and source for nutrients (Baldwin and Williams, 2007) through adsorptive and desorptive exchange between the sediments and water column (Webster et al., 2001). The anoxic conditions formed in the hypolimnion for Denmark during summer resulted in solubilisation of phosphorus.
Figure 22 Trends in DOC, phytoplankton and total phosphorus in top and bottom waters of Denmark River Dam during Nov 2005 – Nov 2007.

The increased phytoplankton for both top and bottom waters in April 2006 was due to increased numbers of Chrysophyceae (data not shown: detailed phytoplankton counts data is available on request) The taxa responsible for the increase in phytoplankton numbers in bottom waters January 2007 (corresponding with the increase in total phosphorus) was Cryptophyceae, making up 90.2% of the phytoplankton population. Cryptophyceae are able to compete for phosphorus when it is limiting, allowing them to dominate over other algae. The remaining 9.8% was due to Bacillariophyceae.

The Denmark River catchment is predominantly agricultural land, tree farming on private land, and State Forest on Crown Land (Water Corporation, 2005b). Historically, increased salinity and turbidity due to land clearing has been of concern for the Denmark River catchment. Certainly the sodium and chloride concentrations in the dam would exceed the Australian Drinking Water Guidelines (180 mg/L sodium, 250 mg/L chloride) (ADWG, 2004) without further treatment, however, the concentrations did not vary significantly over the course of the study, excepting a spike in concentration during September 2007 (Figure 23). This peak in conductivity may have been a result of prolonged rain just prior to this period which allowed transportation of salts from higher up in the catchment to the dam.

Turbidity fluctuated during the course of the study (Figure 24), but remained relatively low (mean 7.07 NTU, median 6.4 NTU). Turbidity is quite variable across Australian waters, and varies with space and time. For example, studies by Armstrong and Mackenzie in 2002 found that the turbidity in the Wollondilly River water supply weir in New South Wales (NSW) ranged from 1 to 380 NTU, with a median of 12 NTU; and the Wollondilly River just above Lake Burrarorang had a median turbidity of 4 (Armstrong and Mackenzie 2002).
Figure 23 Changes in conductivity, sodium, and chloride concentration in the top and bottom waters of Denmark River Dam from November 2005 – November 2007.
Figure 24 Changes in turbidity in the top and bottom waters of Denmark River Dam, and rainfall from November 2005 – November 2007.
3.3 Quickup River Dam

Stratification and mixing periods for Quickup River Dam were not as well defined or obvious as the other South-Western Australian Dams studied. Differences in dissolved oxygen saturation (%) between top and bottom samples were apparent during summer months (Figure 25); more clearly observed during the summer of 2005/2006 than in the 06/07 summer. Typically, the other water quality parameters were comparable for both the top and bottom samples for most of the sampling period (Figure 25 and 26). This was likely due to Quickup River Dam being shallower than the other dams studied (a maximum depth of 5 m to a minimum of 3.2 m during the course of the study).

The nature of the UV absorbing species of the NOM in Quickup Dam changed during the course of the study period as either having a unimodal distribution, bimodal distribution with the HMW peak having a lower peak height than the second broader peak, or a bimodal distribution where the HMW peak had a greater peak height than the lower molecular weight peak (Figure 25).

![Figure 25](image-url) Trends in dissolved oxygen, temperature, rainfall and NOM character (UV$_{254nm}$ absorbing species) for Quickup River Dam.

[A blue asterisk indicates a size exclusion chromatogram consisting of one broad molecular weight peak. A red asterisk indicates a size exclusion chromatogram with bimodal distribution, where the first (higher molecular weight) peak height is smaller than the second, broader peak. A green asterisk indicates a size exclusion chromatogram with bimodal distribution, where the first (higher molecular weight) peak height is greater than the second, broader peak.]
There was no apparent trend in the nature of UV absorbing species in size exclusion chromatography results. The DOC concentration was similar throughout the top and bottom waters in Quickup River Dam, and decreased during the study period (Figure 26). This decrease could not be explained by the fluctuations in rainfall and water level of the dam (Figure 27). Despite the slight rise in DOC concentration after rainfall periods during winter (likely introduced from surface and groundwater runoff, and input from the immediate area into Quickup River into the dam), the overall trend was a decrease in DOC concentration and water level of the dam (Figure 27). The peaks in DOC occurring during autumn/winter also correlated with bioavailable DOC peaks (Figure 28), indicating that the DOC was likely diagenetically younger material. It would be expected that at low water levels, evaporation of DOC (with increasing salinity) may occur, as has been reported in other studies (Curtis and Adams, 1995; Anderson and Stedmon, 2007). While there was certainly an increase in salts over time, as indicated by the conductivity (Figure 29), an increase in DOC concentration was not observed.

Figure 26 Changes in SUVA, DOC and iron concentrations in top and bottom waters of Quickup Dam from November 2005 – November 2007.
**Figure 27** Changes in dam volume and water precipitation for Quickup Dam from November 2005 – November 2007.

**Figure 28** Changes in BDOC and DOC for Quickup Dam from November 2005 – November 2007.

Other processes such as mineralisation of DOC through exposure to solar radiation, and/or microbial degradation may have contributed to the loss of DOC. Alternatively, or additionally, DOC may have precipitated out of solution, by complexation with inorganic components (Alberts et al., 2004). It is well established that changing salinity can result in aggregation of DOC (Søndergaard et al., 2003), subsequently removing it from solution. Indeed, increases in salinity (as indicated by conductivity), and inorganic components such as magnesium and calcium (as indicated by hardness) were noted during the course of the study (Figure 29). Further studies would have to be conducted to determine the contribution of this process to the removal of DOC.
The nature of the fractions of DOC did not change significantly during the course of the study. A slight decrease in the very hydrophobic acid content of NOM occurred, with a slight increase in slightly hydrophobic acids (maximum difference at September 2007) (Figure 30).

Figure 29 Changes in hardness, conductivity and water precipitation for Quickup Dam from November 2005 – November 2007.
Figure 30 Changes in very hydrophobic acids (%) in the top and bottom of Quickup Dam from November 2005 – November 2007.
3.4 Quinninup Dam

Due to resourcing limitations, Quinninup Dam (otherwise known as Karri Lake; Water Corporation, 2005e) water quality was only monitored from November 2005 to May 2007. During this time, the majority of rainfall occurred during winter 2006 (Figure 31). Dissolved oxygen and temperature were not monitored for this site because suitable equipment was not available. Even though these parameters could not be measured, changes in the concentrations of other characteristics such as iron and sulphate would suggest that the water body underwent stratification during autumn (Figure 32). Stratification of the bottom waters leads to anoxic conditions and subsequent reductive dissolution of oxidised species of iron, and sulphate reduction (Boehrer and Schultze, 2008).

DOC concentrations were similar between top and bottom waters of the dam, excepting April-May 2006 and mid-February to mid March 2007, when DOC concentrations in the bottom waters were higher than in the top waters. The DOC concentration increased in both the top and bottom waters during April-May 2006, however, only bottom water DOC concentration increased mid-February to mid March 2007 (Figure 31). The increases in DOC concentration did not correspond to rainfall, indicating that it did not originate from allochthonous inputs in surface water run-off.

The DOC increase was not likely due to phytoplankton, as DOC and phytoplankton counts did not increase at the same time (Figure 33). Increases in DOC occurred predominantly in the bottom waters during stratification periods. Studies have shown that humic substances can follow the movements of iron during its redox cycling in the hypolimnion and sediment (Tipping and Woof, 1983), and it is highly likely that during anoxic conditions formed during stratification, release of organic matter can occur alongside dissolution of iron into the water column. Studies conducted by Chadwick et al., (2006) also found that DOC concentrations increased in the hypolimnion during stratification, and attributed it to either decomposition of NOM associated with recently fallen particles or release of sediment-bound DOC associated with dissolution of iron and manganese hydrous oxides from the sediments.

The predominant taxa responsible for the high phytoplankton counts were Cyanobacteria. The increase in phytoplankton counts in the top water, January 2007 was also due to Cyanobacteria, but an increase in Chlorophyceae also occurred. Cyanobacteria are limited by phosphorus, and it was seen that after a spike in phosphorus concentration in top waters March 2006, an increase in phytoplankton numbers followed in April-May 2006 (Figure 33).

The molecular weight distribution, as indicated by the UV$_{254nm}$ absorbing species of NOM in top waters of the dam remained similar throughout the study (Figure 31), having a small, higher molecular weight peak eluting first (peak 1), followed by a broad distribution of lower molecular weight species (peak 2; e.g. Diagram A, Figure 31). The ratios of the peak height for peaks 1 and 2 were plotted for the course of the study (Figure 31). Like Denmark River Dam, peak 1 had a large impact on the SUVA, resulting in a similar trend for SUVA and peak ratios.

Changes in the intensity of peak 1 were likely due to the incorporation of inorganic components during stratification as previously discussed. There was a marked increase in the height of peak 1, leading to the higher peak ratio for bottom waters during the stratification period in 2007 (Figure 31). Interestingly, however, an increase in peak ratio did not occur during stratification in 2006 (Figure 31). Size exclusion chromatogram profiles certainly differed for the bottom water NOM during February to May 2006, having a broad peak 1 (stratification period) (Figure 34). Peak broadening occurs due to overloading of the analytical system and therefore indicated the presence of a high abundance of material comprising this peak. The broader peak 1 for bottom water NOM occurred for the majority of the stratification period in 2006 (sample event 3 to 6 inclusive; February to May 2006), consistent with other observations that it is present in samples from anoxic environments.

During stratification periods, an increase in aluminium, organic nitrogen, total phosphorus, calcium, iron, reduction in sulphate, and increase in alkalinity occurred (e.g. Figure 32). Increase in peak 1 height or width may have been due to colloidal or inorganic material as discussed by Allpike et al., (2005).
Figure 31 Changes in DOC, water precipitation, SUVA, size exclusion chromatogram peak areas and size exclusion chromatograms of UV\(_{254}\) absorbing NOM in the top and bottom of Quinninup Dam from November 2005 – May 2007. A = molecular weight distribution of top and bottom water NOM 30/11-05. B = molecular weight distribution of top and bottom water NOM 12/12-06.
Figure 32 Changes in unfiltered iron and sulphate concentration, and total alkalinity for top and bottom waters of Quinninup Dam from November 2005 – May 2007.
Figure 33 Changes in phytoplankton, DOC, and total phosphorus for top and bottom waters of Quinninup Dam from November 2005 – May 2007.
Figure 34 Examples of size exclusion chromatograms of UV$_{254\text{nm}}$ absorbing species of NOM taken from bottom waters of Quinninup Dam, 15/02/2006 and 10/04/2006.
Despite changes in SUVA and size exclusion chromatograms of Quinninup NOM, no substantial changes occurred for the fractions of NOM (Figure 35). This would support the suggestion that inorganic compounds played an important role in the character of UV$_{254nm}$ absorbing NOM character. VHA comprised 80-90% of DOC throughout the study period, indicating the strong humic (allochthonous) character of the DOC in this lake.

**Figure 35** Changes in fraction of NOM for top and bottom waters of Quinninup Dam from December 2005 – May 2007.
3.5 Walpole River Dam

Walpole River Dam was very shallow, with depths ranging from a minimum of 0.92m to a maximum of 1.59 m during the course of the study. As such, there was no top and bottom sample taken, but rather, the sample taken from the water column was assumed to be representative of the whole water column. Sampling was only possible until May 2007 due to resource limitations for the project.

Landform (Appendix I, Table I), coupled with extensive clearing and development of the catchment (Water Corporation 2005d) enabled DOC inputs after rainfall events to quickly enter the dam. Consequently, DOC concentration closely following rainfall patterns (Figure 36). DOC concentrations promptly decreased during summer, presumably due to precipitation or microbial and photochemical degradation. Inorganic content increased during the summer periods as indicated by increases in conductivity, hardness, and iron concentrations (Figure 37). Missing data points did not allow trends in BDOC to be explored, however, the data that is present suggests that the DOC loss due to microbial action may be significant with 12-32% of the DOC being bioavailable. As carbon is consumed by bacterioplankton, recalcitrant DOC can be newly produced (Kragh and Sondergaard 2004). Bioavailability of DOC decreased during summer, presumably due to the consumption of bioavailable components without replenishment from younger NOM (Figure 38). This suggests that the decrease in DOC occurred largely due to biodegradative mineralisation processes and lack of replenishment.

The nature of the UV$_{254}$ absorbing species of the NOM varied over the course of the study (Figure 36), again, having a similar molecular weight profile to the other study sites in South-Western Australia. There was no apparent trend in UV$_{254}$ absorbing species over the course of the study.

Figure 36 Change in water precipitation, DOC and size-exclusion chromatograms of NOM (UV$_{254}$ signal) in Walpole River Dam from November 2006 to May 2007.
**Figure 37** Change in conductivity, alkalinity and iron concentrations for Walpole River Dam from November 2005 to May 2007.
Figure 38 DOC and BDOC and % DOC as BDOC in Walpole River Dam from November 2006 to May 2007.
The aromatic nature and very hydrophobic acids fraction of NOM, as indicated by SUVA decreased during April 2006 and 2007 (Figure 39), but otherwise remained reasonably constant throughout the study period. An increase in conductivity is also noted at this time (Figure 37). It is well recognised that humic substances (UV-absorbing, chromophoric components of NOM) undergo conformational changes with variations in ionic strength, with an apparent loss of molecular size or shape with increasing ionic strength (DeHaan et al., 1987; De Nobili and Yona, 1999; Piccolo, 2001). An increase in conductivity and therefore ionic strength may have ‘closed’ the NOM structure, leading to an apparent loss of aromaticity (as indicated by SUVA). Very hydrophobic acids dominated the NOM fractions (Figure 39).

**Figure 39** Change in SUVA and NOM fractions for Walpole River Dam from November 2006 to May 2007.
3.6 Harding Dam

Harding Dam was stratified during most of the study, excepting May-June 2006, when mixing occurred (Figure 40). Interestingly, despite a large rainfall event in January 2006 (Cyclone event, 295.8 mm/month), turnover of the water body did not occur until much later (May 2006). The trigger for the turnover was most likely a decrease in temperature in the surface layers, which closely followed air temperature (Figure 40).

Figure 40 Trends in dissolved oxygen, temperature, rainfall and NOM character (UV\textsubscript{254nm} absorbing species) for Harding Dam. Turnover of the lake is indicated by the arrow.
A decrease in surface temperature would bring the epilimnion temperature closer to that of the hypolimnion, thereby facilitating mixing.

After the cyclone event, salt concentrations first decreased rapidly as a result of the inflow of freshwater. However, in the subsequent months (Jan – May 2006), the salinity increased again, relatively rapidly, in both the top and bottom waters of Harding Dam (as indicated by conductivity and TDS March - May 2006; Figure 41). This may have been due to the inflow of accumulated salts (during summer) in peripheral pockets or in pools at the extremities of the catchment of the dam during overturn (May 2006). The lag period during Jan/Feb suggests that the influx of saline water was more likely to come from distant, rather than local, parts of the catchment.

![Harding Dam - Conductivity](image1)

![Harding Dam - Total dissolved solids](image2)

**Figure 41** Change in conductivity and total dissolved solids for top and bottom waters in Harding Dam from December 2005 to December 2007.

Excepting the period before overturn, a negative linear relationship existed between dam level and conductivity (Figure 42), indicating that after June 2006, the increased conductivity was due to evapo-concentration of salts.
Figure 42 Negative linear relationship between conductivity and dam volume after sampling event 7 (15/06/2006).
[A = all data points in top and bottom water (n = 38). B = data points up to and including event 7 removed (n = 24).]
Typically UV$_{254\text{nm}}$ absorbing species of NOM, as analysed using size-exclusion chromatography, did not alter significantly during the course of the study, or between top and bottom of the dam (Figure 40). Figure 40, shows a slightly higher concentration of approximately 62,500 Da molecular weight species in the bottom waters than the top, however, this trend was not always the case, and varied between top and bottom waters over time. In all circumstances, the 62,500 Da peak height was low.

Interestingly, DOC concentration was consistent throughout the water body (top and bottom waters), even during stratification periods. The DOC concentration decreased slightly after the cyclone event, likely due to dilution (Figure 43), and afterwards increased slowly over time with evapococoncentration. DOC concentration did not increase after rainfall, indicating that allochthonous inputs may not be the major source of DOC in the dam.

A slight increase in DOC occurred during April 2007 in both the top and bottom waters of the dam. This may have been due to an increase in phytoplankton during this time (Figure 43). The predominant taxa responsible for this increase in phytoplankton numbers was Cyanobacteria. In the bottom waters, *Merismopedia* species dominated, whilst the top water had blooms of *Merismopedia* sp., *Cyanodictyon* sp. and *Anabaena inaequalis*. *Merismopedia* were detected in relatively large numbers, but they are very small in size (1.5 – 2 µm) and, therefore, each individual organism did not contribute much biomass. Hence, even though they were detected in large numbers, they may have only accounted for similar biomass and DOC contribution as cyanobacteria in top waters. The increase in DOC concentration for bottom waters was therefore higher than top waters, but not proportionately equal to the difference in phytoplankton numbers between top and bottom waters. Comprehensive analysis of phytoplankton data was beyond the scope of this project but detailed raw data on phytoplankton numbers is available from the authors on request.

The phytoplankton blooms may have been triggered by an increase in phosphorus concentrations (Figure 43). There was no apparent reason for the increase in phosphorus in top waters during November 2006.
Figure 43 Changes in phytoplankton numbers, DOC, water precipitation and total phosphorus concentration in top and bottom waters of Harding Dam from December 2005 to December 2007.
Very hydrophobic acids dominated the composition of NOM for Harding Dam, however, the overall percentage VHA was much lower than for the South Western Australian study sites (Figure 44).

Figure 44 Changes in NOM fractions for top and bottom waters of Harding Dam from December 2005 to December 2007.
3.7 Fluorescence Analysis

Fluorescence spectroscopy is one of a variety of powerful methods that can be used to detect differences in the character of NOM. Aromatic moieties, particularly polyaromatics, are amongst the most intense fluorophores and these structures appear to be well-represented in humic and fulvic materials or VHA. Although the fluorescent properties of some compounds are extremely strong, making the technique very sensitive for those compounds, many organic compounds do not fluoresce. Therefore, fluorescence detects only a select portion of NOM, largely the humic and fulvic materials and, to a lesser extent, nitrogen-containing compounds generally attributed to proteinaceous material or wastewater-derived organic matter. Since the fluorescent response is dependent on the structure of the OM, the analytical response cannot be considered quantitative (per mass unit of C). Differences in the character of NOM are apparent from shifts in the maximum Emission and Excitation wavelengths.

Excitation-emission matrix (EEM) fluorescence spectra for all six study sites from December 2005 to July 2007 were prepared in order to assess changes in the character of NOM in these sources. The graphics program Origin 7.5 (OriginLab Corporation, 2006) was used to process these data. Initially a “full” scan was taken which involved collection of fluorescence intensity data over an excitation range of 190-450 nm and emission of 300-600nm. “Full” EEM spectra results of the first sampling event for all six study sites are shown in Figure 45. Study site spectra from the Great Southern (Bolganup, Denmark and Quickup) and South West (Quinninup and Walpole) regions are very similar in appearance, indicating that the fluorescing compounds present in these samples are also very similar.
Figure 45 “Full” EEM fluorescence spectra for all sample sites for sampling event #1 (Dec 2005).
Location of the fluorescence peak maximum is independent of wavelength as it represents one excitation/emission combination resulting in maximum fluorescence (Coble, 1996). Identification of this peak maximum and its relative intensity provides significant quantitative and qualitative information in terms of the type of organic matter that is present. EEM spectra for each study site, for the project duration has been assessed and summarised in terms of characteristic fluorescence peak maxima (Table 3).

Table 3 Summary of approximate peak maxima, derived from EEM fluorescence spectra

<table>
<thead>
<tr>
<th>Excitation</th>
<th>Peak I Maxima</th>
<th>Peak II Maxima</th>
<th>Peak III Maxima</th>
<th>Peak IV Maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission</td>
<td>340 nm</td>
<td>260 nm</td>
<td>230 nm</td>
<td>310 nm</td>
</tr>
<tr>
<td></td>
<td>460 nm</td>
<td>460 nm</td>
<td>430 nm</td>
<td>420 nm</td>
</tr>
<tr>
<td>Present in which source</td>
<td>Bolganup, Denmark, Quickup, Walpole, Quinninup</td>
<td>Bolganup, Denmark, Quickup, Walpole, Quinninup &amp; Harding</td>
<td>Bolganup, Denmark, Quickup, Walpole, Quinninup &amp; Harding</td>
<td>Harding</td>
</tr>
<tr>
<td>Persistence</td>
<td>Most persistent peak in all sites</td>
<td>Present in all sites for most months of the year</td>
<td>Present in all sites for some months of the year</td>
<td>Seemingly unique to Harding</td>
</tr>
</tbody>
</table>

Figure 46 “Reduced” EEM fluorescence spectra and indication of characteristic peak maxima (Top samples for Denmark and Harding have been used as examples).

A “reduced” EEM fluorescence scan, depicted in Figure 46, was decided upon soon after the analytical program for this project began as it was clear that this provided data over a sufficiently broad wavelength range. In addition to this, greater resolution was possible due to the reduced scan range of 190-380nm excitation and 380-500nm emission.

Although Peak II and III seem to be “common” for Harding Dam and the southern study sites it should be noted that there is a slight shift to the lower end of the emission spectrum for Harding water with respect to the location of these peaks. This is consistent with all of the Harding EEM spectra when compared to that of the southern study sites. In addition to this, the location of Peak IV (exclusive to Harding Dam) which is also in the low end of the emission spectrum (Ex310/Em420nm) may have some similarities to algal organic matter (Ex342/Em415nm) as found by Her et al., (2003).
The fluorescence intensity of a sample is to some extent related to the amount of organic matter present, for example Harding Dam generally has the lowest level of DOC to in relation to all of the other study sites (<4mg/L as opposed >10mg/L) and this is reflected by the resultant low intensity EEM spectra (Figure 45).

For all study sites, except Harding, the Peak I maximum (ca. Ex340/Em460) was present in significant intensities. This peak was indicative of humic substances: previous fluorescence characterisation studies of organic matter have shown that these substances fluoresce in the excitation range of ca. 300-400 nm and emission range of ca. 400-500 nm (Smith and Kramer, 1999). Thus, the organic matter in this region (South West/Great Southern) would appear to have a strong “back-bone” of humic material which changed little with seasonality; however the apparent fulvic acid component seemed to vary with time, in differing magnitudes, for the different sources.

The peak maxima identified in Table 3 moved slightly over time for each of the study sites. This would indicate that the character of fluorescing organic material changed with respect to seasonality; however this study shows that the shifts were not significant thus the sink of organic material in these sources did not greatly change over time. To illustrate this all of the Peak I and II maxima from Bolganup Dam (i.e., top and bottom samples for all sampling events) were plotted with respect to cited literature indicating organic matter character by fluorescence peak maxima (Figure 47). Selection of peak maxima was done manually by assessing the shape of the peak then taking into account the intensity matrix of that peak. The method was slightly problematic as it was, at times, difficult to separate local intensity maxima from the global maximum. A more thorough method such as the use of a statistics program would be recommended for future work or method development at Curtin University.

The above figure confirms that the fluorescing character of organic matter in Bolganup Dam did not change significantly over the 24-month sampling period. The fluorescing peak maxima for Bolganup Dam agree very well with the wavelength pairs reported by Her et al., (2003) for Suwannee River humic and fulvic acids.

To monitor the seasonality of fluorescence data two excitation-emission pairs were selected which are representative of Suwannee River humic acid (Her et al., 2003). The employed “fixed” points were Ex330/Em452 nm and Ex260/Em457 nm. A macro was used to extract the relevant points from EEM fluorescence spectra of each sample. The results for Bolganup Dam’s fixed fluorescence analysis can be seen in Figure 48.
Even though studies by Her et al., (2003) defined two excitation-emission points (Peak I and II) to be important in terms of humic acid representation; for the sake of comparisons in this study only one peak was considered for simplicity. Peak II was chosen because it generally had the greater intensity. As in the example of Bolganup Dam, it can be seen that the trend of Peak I and II followed each other quite closely when comparing top and bottom samples (Figure 48). Hence, even though absolute values between peaks I and II may have varied, the general trends, which were of interest in this study, did not.

In the data from Bolganup Dam an interesting inverse relationship can be seen between DOC concentration and fluorescing humic acid abundance in the lower part of the water column. Normally it would be assumed that fluorescing humic acids would increase with increasing DOC concentration, however this was not the case. A coincidental change in pH, which may affect fluorescing properties, was not observed in the bottom waters as a possible explanation either. Upon first rains (March and June 2006) there was an immediate increase in fluorescing character suggesting that some of the material wash-in from run-off was of a fluorescent nature.

Figure 48 Fixed fluorescence (Peak I and II) analysis of Bolganup Dam and comparison to bulk DOC/pH.

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**Figure 48** Fixed fluorescence (Peak I and II) analysis of Bolganup Dam and comparison to bulk DOC/pH.
Quinninup dam exhibited the same relationship that was observed for Bolganup Dam, where a DOC increase in the bottom waters occurred after a decrease in the fluorescing humic acid abundance. This event also coincided with bottom water anoxia which may have had an effect. Indeed, studies have shown that iron (III) can result in increased absorbance and reduced fluorescence properties of NOM (Pullin et al., 2007). It is likely that iron released during stratification may have affected the fluorescence properties of the DOC.

Figure 49 Fixed fluorescence (Peak II only) analysis of Quinninup Dam and comparison to bulk DOC/ pH.
An assessment of Harding Dam, with respect to fluorescence results has been made in Figure 50.

**Figure 50** Fluorescence assessment of Harding Dam; Fixed (Peak II only), EEM spectra and comparison to bulk DOC.
During the major rainfall event of January/February 2006 bulk DOC did not change in Harding Dam. This indicates that surface run-off did not significantly contribute to the DOC sink of the dam and that alternate mechanisms and pathways exist for its occurrence. Figure 50 also indicates that DOC in the dam before the rainfall event had very low fluorescent intensity, suggesting that the DOC present at this point was of different character than any incoming DOC contributions made by inflows or run-off. After the rainfall event, the gradual increase in DOC concentration was most likely due to evapoconcentration and/or possibly algal origins. Given that there was not a measured increase in DOC after the rainfall event it was surprising that a significant and rapid increase occurred for fluorescing material measured at peak II (Ex260/Em457). This is shown in the EEM spectra before the rainfall event, where the characteristic fluorescence peaks are of low intensity, but during the rainfall event (January/February 2006) the intensity for these peaks significantly increased. Increases in fluorescing material occurred both in the upper and lower parts of the water column. These findings indicate that fluorescence is a sensitive technique as even though the amount of DOC available was reduced the technique was still more than able to show changes in the organic matter character.

3.8 NOM characteristics and implications for water treatment

3.8.1 Trihalomethane Correlations

Trihalomethanes (THMs) are highly important in terms of drinking water quality and treatment. Where available, THM data has been extracted from the Water Corporation WA database corresponding to when the raw water samples were collected for this study. Comparisons were made between raw water bromide and DOC values against respective THM values, as discussed in the following paragraphs.

Speciation of the THMs formed upon disinfection of organic matter is influenced by the inorganic components present. Bromide occurs naturally in many Western Australian drinking water sources, with concentrations ranging from around 0.02 to 2 mg L\(^{-1}\) (Heitz et al., 2004), and is difficult to remove with conventional water treatment practices. Since bromide ions readily undergo oxidation by chlorine to form bromine, and bromine reacts faster with NOM than chlorine (Westerhoff et al., 2004), brominated THMs predominate under these circumstances.

3.8.1.1 Harding Dam

In this source, concentrations of raw water bromide and total THM (TTHM) in the treated water followed a similar trend (Figure 51) to conductivity and total dissolved solids (Figure 41), steadily increasing after the cyclone in January 2006. The steady increase in THMs did not appear to correlate as strongly with a rise in DOC concentration, as it did with bromide concentration. Even though a progressive increase in bromide concentration occurred after the December 2005 cyclone it was quite homogeneous in terms of concentration throughout the water column.

The water at Harding Dam is treated extensively to remove NOM, using polyaluminium chloride flocculation coupled with microfiltration. However, even after treatment, a correlation still exists between bromide and DOC in the raw water and THM levels in the treated water. This shows the strong influence of raw water quality on water that is distributed to the consumer, despite the treatment process. Both raw and treated water quality deteriorated as the drought period extended over more than two years. As shown in Figure 51, the increase in bromide concentration appeared to drive THM formation and bromide incorporation into THMs. Studies elsewhere have shown that brominated THMs are more important than their chlorinated analogues in terms of adverse human health effects and steps should be taken to decrease their concentration (Bull et al., 2006).
Figure 51 Comparison of raw water bromide and DOC concentrations against THM values for Harding Dam (Dec 2005 to Dec 2007).
3.8.1.2 Quinninup Dam

For Quinninup no definitive relationships were observed between THM levels and bromide/DOC levels in the raw water (Figure 52). This was partly because of the low frequency of THM measurements.

![Quinninup (Retic Wheatley Coast Rd SP) Br Incorporated into THMs vs Raw Water Br](image)

![Quinninup (Retic Wheatley Coast Rd SP) Total THMs vs Raw Water DOC](image)

**Figure 52** Comparison of raw water bromide and DOC concentrations against THM values for Quinninup Dam (Dec 2005 to Dec 2007).

3.8.1.3 Walpole River

The formation of THMs in treated water from Walpole River appears to be more closely related to DOC concentration than bromide concentration (Figure 53) in the raw water. In contrast to observations at Harding Dam, there does not seem to be any correlation between the level of brominated THMs in treated water and bromide in the raw water.

It is possible that the type of DOC at Walpole or its relatively high loading (ca. 15mg/L as opposed to Harding at generally <5mg/L DOC) and subsequent high DOC to bromide ratio, means that the reaction of chlorine with DOC could be more rapid than the reaction of chlorine with bromide. In this circumstance, chlorine would be incorporated into THMs in preference to bromine. Studies have shown that the quantity and composition of NOM can affect the formation of THMs (Uyak et al., 2008).

Interestingly, the water supplied to the township of Walpole is from Walpole Weir during summer, but during other times of the year, it is a mix of Walpole Weir and Butler’s Creek Dam. The mixing of the two water sources did not appear to affect the trend of DOC concentration relating to total THM concentration.
3.8.1.4 Quickup Dam Water Treated at Denmark Water Treatment Plant (DWTP)
At Denmark the observations were similar to those noted in the Harding system. Bromide concentrations in the raw water seemed to correlate with the observed THM levels of the sample point (Gilbert Ave) following treatment at Denmark Water Treatment Plant (DWTP) (Figure 54). No correlation was observed between THM levels and DOC concentration measured in the raw water, probably because of the extensive treatment for DOC removal that occurs at DWTP. As noted at Harding, the primary driver of THM levels is bromide because this cannot be removed by treatment.

Until December 2007 raw water treated at DWTP was almost exclusively sourced from Quickup Dam. Due to diminishing recharge rates of Quickup Dam, water from Denmark River Dam was sourced and combined with reduced amounts of Quickup Dam water to alleviate demand on this source (Cheryl Davenport, personal communication). However, this change did not occur until the end of the present studies and therefore, it is not relevant for the data discussed here and shown in Figure 54. It should be noted that since this time, Water Corporation has commissioned advanced water treatment for Denmark River water, including ultrafiltration and UV processes (Trolio, personal communication, 2009).
3.8.2 Assessment of Suitable Off-take Depths for Minimisation of Iron and Manganese

Iron and manganese are two important elements to consider with respect to water treatment, primarily because precipitation of the oxidised forms of these metals in distribution systems can cause discoloured water problems. The aesthetic limits for iron and manganese are 0.3 mg/L and 0.1 mg/L, respectively (Australian Drinking Water Guidelines (ADWG)). There is no limit set for iron with respect to health; however manganese has a health risk limit of 0.5 mg/L.

The study described in this section was carried out to provide a guide on the most suitable off-take levels for minimisation of iron and manganese concentrations at each site. The concentrations of these metals were at a minimum during periods of maximum oxygen saturation. In addition, the conditions that caused minimum concentrations of iron and manganese also represented conditions (i.e. periods and water depths) where DOC was at a minimum (i.e. higher oxygen saturation promotes the suppression of organic carbon in the sediments). As organic carbon removal is a key aspect of any drinking water treatment process the monitoring of dissolved oxygen is a potentially important surrogate for the level of treatment required for a particular site at a given point in the season.

Figure 54 Comparison of raw water bromide and DOC concentrations against THM values for Denmark River (Dec 2005 to Dec 2007).
The average “top” and “bottom” levels (for the full sampling period) of total iron and total manganese for all six study sites are summarised in Table 4. For most study sites significantly higher levels of iron and manganese were found in the hypolimnion, correlating to extended periods of anoxia and thus release of these metals from the sediments. Quickup Dam was different to the other study sites as the concentration of these metals remained constant throughout the water column, but this may be due to the relatively shallow nature of this source (deepest point average depth ca. 4.5m from Nov 2005 to Nov 2007), meaning that clear stratification was rarely attained.

Table 4 Average total iron and total manganese levels in “top” and “bottom” samples for all study sites.

<table>
<thead>
<tr>
<th></th>
<th>Iron (average mg/L)</th>
<th>Manganese (average mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Denmark</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top (n=23)</td>
<td>1.8</td>
<td>0.14</td>
</tr>
<tr>
<td>Bottom (n=23)</td>
<td>3.8</td>
<td>0.19</td>
</tr>
<tr>
<td><strong>Bolganup</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top (n=22)</td>
<td>1.3</td>
<td>0.015</td>
</tr>
<tr>
<td>Bottom (n=22)</td>
<td>4.2</td>
<td>0.041</td>
</tr>
<tr>
<td>Inlet (n=4)</td>
<td>0.11</td>
<td>0.0075</td>
</tr>
<tr>
<td><strong>Quickup</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top (n=23)</td>
<td>3.3</td>
<td>0.017</td>
</tr>
<tr>
<td>Bottom (n=23)</td>
<td>3.4</td>
<td>0.017</td>
</tr>
<tr>
<td><strong>Quinninup</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top (n=18)</td>
<td>0.90</td>
<td>0.070</td>
</tr>
<tr>
<td>Bottom (n=18)</td>
<td>3.9</td>
<td>0.130</td>
</tr>
<tr>
<td><strong>Walpole</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top (n=18)</td>
<td>1.6</td>
<td>0.045</td>
</tr>
<tr>
<td>Bottom (n=18)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Harding</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top (n=21)</td>
<td>0.056</td>
<td>0.027</td>
</tr>
<tr>
<td>Bottom (n=21)</td>
<td>0.27</td>
<td>0.31</td>
</tr>
</tbody>
</table>

To minimise the treatment of water with respect to iron and manganese removal, it is clear that off-take levels should be in the epilimnion. To better define this; iron and manganese concentrations in bottom waters were compared to oxygen saturation in the same water to determine the oxygen concentration that best minimised the presence of these elements. Then, using depth profiling data (Denmark, Bolganup, Quickup and Harding only) the depth at which oxygen saturation fell below the identified critical oxygen concentration was recorded for each month. This enabled the construction of a seasonal profile for periods and depths at which iron and manganese would be problematic.

The determination of appropriate off-take levels for Denmark River is summarised in Figure 55.
In Denmark River, during periods of mixing; dissolved oxygen increased up to 70% saturation in the hypolimnion and the lowest concentrations of iron and manganese occurred during this period. Therefore at a nominated oxygen saturation of >40%, iron and manganese levels are sufficiently minimised for water treatment purposes. It is optimal to have the off-take >1m depth all year round, however during mixing periods of the year (ca. May through to Sep) the optimal depth can increase to as deep as 6-7m.

**Figure 55** Denmark River: determination of appropriate off-take level.
Similarly, Bolganup Dam has a suitable iron and manganese limiting oxygen saturation level of >50%, as indicated in Figure 56 below.

![Bolganup Iron/ Manganese and DO in the Bottom Waters](image)

![Appropriate Offtake Level for Bolganup](image)

**Figure 56** Bolganup Dam; determination of appropriate off-take level.

Similarly to Denmark River, the optimal off-take level for Bolganup Dam is substantially lower (ca. 11-12 m) during seasonal periods of mixing (ca. May through to September). All-year-round suitable dissolved oxygen levels occur at shallower than 2 m depth but generally start to drop into anoxic conditions below this level.

As previously mentioned, Quickup Dam is quite different to all of the other study sites (except Walpole River) in that iron and manganese levels in the hypolimnion are not elevated with respect to that of the epilimnion (iron: 3.3 mg/L top and 3.4 mg/L bottom, manganese: 0.017 mg/L top and bottom). As shown in Figure 57, only at the very beginning of the study (April 2006 and before) was there a period when anoxic conditions were apparent in the hypolimnion. It appears that the decrease in dam volume (ca. 1150 ML to 800 ML) in April 2006 prevented major stratification, in combination with the large dam surface area which would lead to the development of wind currents and subsequent circulation. For Quickup Dam there is no significant relationship between oxygen saturation and iron/manganese levels. Even though this is the case, it would not be recommended to situate the off-take for this water source deeper than 1m, as data indicates that if the dam level rises above 800 ML it still has the potential to stratify, thus potentially elevating levels of iron and manganese in sub-levels of the water column.
An oxygen saturation of >50% was sufficient to limit iron and manganese levels in the hypolimnion of Harding Dam as indicated in Figure 58. Plotting of oxygen levels below 50% saturation shows that an off-take level of 5m and shallower is suitable, as sufficient oxygen is maintained regardless of seasonality. However, typical “seasonality” does not apply to Harding Dam as the predominant means of recharge for this source is major rainfall events, mostly associated with cyclonic activity.

The significant decrease of suitable off-take level which occurred from May to September 2006 is attributed to overturn of the dam (hypolimnic oxygenation) which was most likely due to an ambient air temperature trigger as opposed to the large rainfall event which occurred almost four months previously. Due to the lack of availability of equipment, few depth profiles for the last stages of the sampling regime for Harding dam were collected, thus it is difficult to comment on the period following July 2007.

A substantial increase in total manganese (and total iron to a lesser extent) occurred in January 2007 which persisted until May 2007 (ca. 1.0 mg L\(^{-1}\) Mn) before dropping back to normal levels (ca. 0.1mg/L Mn). A potential explanation for this is that high levels of oxygen saturation throughout the whole water body during the May – September 2006 overturn precipitated irregular quantities of mobile manganese from the bulk water, then on returning to anoxic conditions the newly precipitated manganese was easily reduced and remobilised.
Figure 58 Harding Dam: determination of appropriate off-take level.
3.9 Quality Assurance and Validation of Data

During analysis of the samples for this project a number of quality control (QC) protocols were established to ensure good quality results. As the analytical requirements of this project were wide and varied it was difficult to incorporate QC samples to cover all analytes, however the best available measures were taken. This process was viewed as being of great importance as reliable and correct data are essential for valid interpretation of trends.

3.9.1 Data Base Cross-correlations

Midway through the sampling and analytical regime for this project a statistical method was utilised to assess the data. Correlation coefficients were calculated for each parameter against the next using a large spread-sheet. As in Figure 59 below for Bolganup Dam top samples, correlation coefficients were calculated using data pairs from the first thirteen sampling events for manganese and dissolved oxygen (% saturation).

![Bolganup Dam Top Manganese vs %DO](image)

**Figure 59** Bolganup Dam: correlation between manganese and dissolved oxygen (% saturation).

In this example the correlation coefficient of these parameters suggests a strong negative relationship which makes logical sense, as an elevated oxygen level would oxidise any available manganese, leading to precipitation and decrease in manganese concentrations in the epilimnion.

Each parameter was compared against another in this manner so relationships between the parameters could be highlighted. A separate spreadsheet was derived for each parameter for the “top”, “bottom” and then “top/ bottom”. As indicated below (Figure 60) a colouring system was utilised to readily show if there was a; “strong positive” relationship (Green, \( r^2 = +0.75 \) to +1.00), “strong negative” relationship (Red, \( r^2 = -0.75 \) to -1.00) or a “weak” relationship (Yellow, \( r^2 = -0.25 \) to +0.25).
Following construction of each database the strong positive and negative relationships between each parameter were assessed to see if the result was expected or if it highlighted an interesting parameter relationship that should be examined more thoroughly. This technique was principally used as a QC tool, as it is assumed that some parameters should be positively or negatively related (e.g. air temperature and rainfall “should” have a negative relationship) and if they were not then the data should be scrutinised to determine why this was the case. It was through this process that errors in the database could be highlighted and rectified.

It should be noted that individual analytical methods included their own method validation and QC and that this part of the work was intended to cross check for data entry errors and other systematic errors, as well as to identify genuine trends in data.

Some of the strong negative/positive relationships between parameters, observed for Bolganup top samples are listed in Table 5.

---

**Figure 60** Example of a correlation data matrix for Bolganup Dam top samples.
Table 5 Strong positive and negative correlations for Bolganup Dam top samples.

<table>
<thead>
<tr>
<th>Bolganup Dam Top Parameter Correlations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strong Positive Correlations</strong></td>
</tr>
<tr>
<td>$R^2 = +0.75$ to $+1.00$</td>
</tr>
<tr>
<td>Rainfall and Turbidity</td>
</tr>
<tr>
<td>Salinity and Mg/ Na, Cl, Total Anions/ Conductivity</td>
</tr>
<tr>
<td>BDOC and Total-N (Kjeld.)/ Chlorophyll-A/ Phaeophytins</td>
</tr>
<tr>
<td>Ca and K/ Mg/ Na/ Hardness (as CaCO3)</td>
</tr>
<tr>
<td>Temperature&lt;sub&gt;in Field&lt;/sub&gt; and Temperature&lt;sub&gt;BOM&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

3.9.2 Dissolved Organic Carbon (DOC): Comparison of data from different laboratories

DOC was analysed at three different laboratories to allow for inter-laboratory comparisons. It was found that all three laboratories yielded consistently different results and that, although trends in the results were very similar, quantitatively the differences exceeded experimental error (generally around +/- 5%). It was this comparative process that led to the following conclusions:

- DOC samples must be analysed promptly after collection as storage time was found to have an effect on result reliability.
- Depending on the analytical method employed to measure DOC, standards or quality control samples should be measured in conjunction with actual samples. A QC sample to match the matrix effects of the sample being analysed is ideal (e.g. high inorganic carbon matrix).

If samples are to be stored (refrigerated) before analysis they should be filtered (0.45μm membrane) first. It was found that after storing two identical samples (one was 0.45μm membrane filtered and the other unfiltered) the level of DOC determined in the “raw” sample was less than that for the “filtered” sample (prior to analysis, after storage, both samples were 0.45μm filtered through a cartridge filter). This observation was noted for top and bottom samples of four different water sources (e.g. Harding Dam in Figure 61). Blank analyses of the filter did not show any DOC leaching from the filters which would have accounted for the observed differences.

![Harding Dam Top and Bottom DOC Analysis](image)

**Figure 61** Effect of storing “raw” and “filtered” samples on Harding Dam DOC analysis.
4 SUMMARY AND CONCLUSIONS

- DOC inputs varied between sites and to different degrees each year. Significant increases in DOC concentration were noted for Bolganup, Quickup and Quinlinup during stratification periods. Denmark had a delayed increase in DOC after rainfall, indicating that inputs from upstream were significant. DOC concentrations in Walpole strongly correlated with rainfall, indicating that allochthonous inputs are an important source of DOC for this site. Autochthonous sources of DOC were likely to dominate in Harding Dam.

- Conditions of anoxia led to increases in DOC and in concentrations of metals in the water column, the latter due to reductive dissolution of precipitated metals from the sediment. Some indicators (e.g. fluorescence measurements) suggested that changes to DOC with decreasing DO were qualitative as well as quantitative.

- Rapid fractionation of organic matter revealed that very hydrophobic acids dominated the composition of NOM from all sites, particularly those from southern sites. The VHAs in South Western Australian sites ranged from approximately 70% for Bolganup, up to approximately 80% for Quickup and Quinlinup. The NOM composition in Harding Dam was significantly different, with percentage VHAs ranging from 40-70%.

- The use of different analytical techniques was advantageous in understanding the character of NOM. For example, high performance size-exclusion chromatography coupled with DOC detection provided extra information on the composition of high molecular weight peaks found in South Western Australian study sites.

- A dissolved oxygen level of ca. >50% saturation was shown to significantly reduce the quantity of iron, manganese and DOC present in raw water, thus reducing the level of treatment required. Careful observation of dissolved oxygen levels in relation to placement of the off-take for a water source may lead to savings in the cost of chemicals for treatment.

- A study of the influence of raw water quality on the quality of distributed water found that bromide concentrations impacted strongly on levels of TTHMs at sites where there was significant treatment to remove DOC (Harding and Denmark). At sites with high DOC, the concentration of DOC, rather than bromide, dominated THM concentrations. This was presumably because DOC reacted preferentially with chlorine, preventing oxidation of bromide and formation of reactive bromine. At sites where DOC had been removed by treatment, reaction of chlorine with bromide occurred, leading to higher proportions of bromine-containing THMs. Since brominated disinfection by-products are thought to be more toxic than their chlorinated analogues, steps should be taken to reduce bromide in relevant sources (e.g. bromide concentrations reached almost 1.0 mg/L at Quickup and 0.5 mg/L at Harding).

The following points summarise observations specific to each sampling location.

**Bolganup:** In-lake DOC transformations were observed: the character of DOC in samples of inflow water, as determined by HPSEC, was different to that of samples taken from within the lake. The major difference was the absence of high MW, high SUVA material in DOC in the inflow samples. In this lake, DOC increased in the bottom water during stratification. Possible mechanisms to explain this observation include release of sediment organic carbon bound to Fe or other minerals, or release of DOC through phytoplankton decay. DOC in bottom waters would be preserved during periods of anoxia, leading to increased concentrations, relative to concentrations during periods of mixing, when DOC mineralisation would occur. In this lake, phytoplankton appeared to contribute to increased DOC, particularly increased BDOC.

Evidence of the formation of sulphur-bound NOM (or Fe(II)-bound NOM) species in anoxic bottom waters was provided by the presence of a very high SUVA peak in the high AMW (SEC) range. This peak was present only in samples of bottom waters that were taken when the dam was stratified.
**Denmark:** Increases in phosphorus concentration during precipitation events may indicate input from agricultural land. Additionally, phosphorus was likely bound to Fe in sediments and released to bottom waters during anoxic conditions. Phytoplankton (Chrysophyceae) appeared to respond to phosphorus input but there was no evidence that increases in phytoplankton counts contributed to increased DOC load. Periodic increases in salinity that were not directly related to local rainfall events were probably due to inflows of saline water from the extremities of the catchment. This was also noted for other rivers, particularly Harding River Dam.

**Quickup:** Although some stratification was observed, this dam was not clearly stratified every season due to its shallow depth (3-5m) during the study period. DOC was well correlated with BDOC, indicating diagenetically young organic carbon and high turnover rates. In addition, the %DOC as BDOC varied substantially, indicating complex processes in this dam. A decrease in DOC with increasing salinity was observed, possibly due to precipitation of DOC with inorganic species such as Fe, Ca or Mg.

**Quinninup:** This water body was strongly stratified during winter, as evidenced by increases in iron and alkalinity, with a concomitant decrease in sulphate (depth profiles for DO, temperature, etc could not be measured at this dam). An observed increase in DOC concentrations in late summer/early autumn was probably due to release of Fe-bound DOC in sediments.

There was no evidence that DOC increase was linked to phytoplankton numbers but an increase in cyanobacteria was linked with a phosphorus spike. Phosphorus in bottom waters appeared to be bound to Fe and this was released during anoxic conditions but the impact on cyanobacteria appeared to be low.

**Walpole:** This dam is very shallow and water quality appeared to be substantially impacted by surface runoff. Concentrations of DOC and other solutes were strongly impacted by local rainfall events. There was some evidence that DOC decrease occurred due to biodegradative processes.

**Harding:** This dam was stratified for most of the study period, with only one overturn event observed. Overturn does not appear to be seasonal although ambient temperature appeared to be a factor in the mixing event that did occur. Water quality was strongly influenced by rare but extreme rainfall events.

DOC concentrations were consistent throughout the water body during the course of the study, even after the rainfall event. However, a slight increase in concentration was observed over this period, probably due to evapoconcentration. DOC did not increase after the rainfall event, suggesting that allochthonous sources were not dominant. The response of DOC concentration to algal counts supported this evidence, that autochthonous DOC was probably the major source.

The character of DOC in Harding Dam was markedly different to that in the southern sources in this study. The content of VHA was consistently lower than for the other WA study sites.

**Fluorescence measurements** showed strong peak maxima in the wavelength region corresponding to humic and fulvic substances for all study sites except Harding Dam. Harding samples exhibited weak maxima for fulvic and humic substances and weak maxima for proteinaceous, probably algal-derived organic matter. These findings were consistent with other indicators of organic matter character for the six study sites. The fluorescent properties of NOM changed during turnover and anoxia events in southern sites, and the major rainfall event in Harding Dam, suggesting that changes in the structure of this material occurred. This may be related to the nature of binding of NOM to inorganic materials such as Fe or S and is consistent with other indicators of NOM character. For Harding Dam, the change may have been a reflection of the input of fresh organic matter.
5 RECOMMENDATIONS

- At Harding Dam both raw and treated water quality deteriorated with extended drought conditions, indicating that the treatment process was not adequate during low dam water levels. Since this source is prone to drought, relying on major rain events that typically occur only once every 2-3 years, the method of treatment should be investigated to determine whether additional treatment could provide improved water quality during periods of low water levels. In particular, the concentrations of brominated THMs in treated water were shown to increase with increasing source water bromide concentration. Studies elsewhere have shown that brominated THMs (and other brominated DBPs) are more important than their chlorinated analogues in terms of adverse human health effects and steps should be taken to decrease the concentration of bromide in source water during low dam water levels. Since this time, Water Corporation has moved to increase treatment to reduce THMs in the West Pilbara distribution system, as described by Trolio et al., (2007).

- At some sites in this study, insufficient data was available to enable conclusions to be drawn on the influence of source water changes on THM concentrations in distributed water. In order to better study the impact of changes in source water quality on treated and distributed water, more frequent monitoring of post-treatment water should be conducted.

- Recommendations on suitable off-take levels for minimisation of Fe, Mn and DOC are given in Section 3.8.

- The use of the hydrodynamic models DYRESM-CAEDYM added considerable additional information on sources of DOC at the Bolganup site. Sufficient data has been collected at other sites to enable the use of these models. CAEDYM-DYRESM models should be investigated for use at the other five sites in this study to predict water quality changes and DOC dynamics.

- Although substantial information has been collected and analysed in this project, on the variations in water quality within sites and between sites, this has not yet been as effectively translated into treatability outcomes as originally intended. Further work is still required to better understand the impact of water quality changes on treatability, perhaps with more targeted approaches aimed at specific water types. This would better address the final aim in Section 1.1. “What is known about the treatability of the various NOM fractions (i.e. size exclusion chromatography (SEC), hydrophilic/hydrophobic fractions) and how may better treatment strategies for dealing with the NOM of highly coloured waters be identified.”
6 ACKNOWLEDGEMENTS

A very special thanks must be extended to all those who contributed to the extensive sampling regime of this project, especially Geoff Bastyan from the Department of Environment (Albany) who would take time out of his busy schedule every month to embark on yet another sampling event. Geoff provided most of the equipment that made it possible for us to obtain the necessary samples and depth profiling data as well as a wealth of knowledge in the subject of environmental monitoring. Also from the Albany region, Adrian Stratico and Steve Childs of Water Corporation are to be commended for their generous assistance with the requirements of this project and providing a safe working place for us to operate in.

Thanks very much to Aaron Campbell and Jason Dearl from Water Corporation’s South West region for organising all of the necessary logistics to allow safe sampling of Quinninup Dam.

Last but not least, the efforts of Kevin Cutmore (aka Chippy) of Water Corporation’s North West region are greatly appreciated and without his dedication and great attitude the study of this interesting water source (Harding Dam) would not have been possible.

The time and efforts of external reviewers, Dr Daniel Couton and Dr Rino Trolio is much appreciated. Their insightful comments served to improve the quality of this report. Thank you.
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CHARACTERISATION OF NATURAL ORGANIC MATTER IN HIGHLY COLOURED SURFACE WATERS


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Water Corporation (2005b) Denmark catchment management strategy. A report from the customer service division, great southern region.

Water Corporation (2005c) Quickup River catchment management strategy. A report from the customer service division, great southern region.


8 APPENDIX I

Vegetation and Landform of Study Sites

Table 6 Vegetation and landform of the study sites.

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<th>Surrounding vegetation and landform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bolganup Dam</td>
<td><strong>Surrounding vegetation:</strong> Karri forest with an understorey of lichens and small native shrubs.</td>
</tr>
<tr>
<td></td>
<td><strong>Landform:</strong> Located on the slopes of the Porongurup Range, which comprises</td>
</tr>
<tr>
<td></td>
<td>granite massifs with colluvial slopes over Archean basement rocks.</td>
</tr>
<tr>
<td>Denmark Dam</td>
<td><strong>Surrounding vegetation:</strong> Forests of Jarrah, Marri, with some stands of Karri in the lower reaches.</td>
</tr>
<tr>
<td></td>
<td>Sheoak and banksia cover the western part of the upper catchment.</td>
</tr>
<tr>
<td></td>
<td>Approximately 17% of catchment cleared for agriculture.</td>
</tr>
<tr>
<td></td>
<td><strong>Landform:</strong> Laterite plateau consisting of sands and ironstone gravels over mottled clays.</td>
</tr>
<tr>
<td></td>
<td>The hilly uplands of mottled soils and gravels comprise approximately 20% of catchment. Valleys with</td>
</tr>
<tr>
<td></td>
<td>slopes of yellow podsolic soils and red earths (15% of catchment). Swamps flats with poor drainage</td>
</tr>
<tr>
<td></td>
<td>(10% of catchment).</td>
</tr>
<tr>
<td>Harding Dam</td>
<td><strong>Surrounding vegetation:</strong> Vegetation changes across the catchment. Spinifex</td>
</tr>
<tr>
<td></td>
<td>hummock grasslands on the shallow scree hill slopes.</td>
</tr>
<tr>
<td></td>
<td>Spinifex on the erosional slopes, and a mixture of mulga shrublands and</td>
</tr>
<tr>
<td></td>
<td>grasslands on the depositional plains. Tall river gums and Cadjebuts line major drainage lines.</td>
</tr>
<tr>
<td></td>
<td><strong>Landform:</strong> Lower Proterozoic Fortescue Group (consisting mainly of volcanic rocks) is intruded</td>
</tr>
<tr>
<td></td>
<td>by Cooya Pooya Dolerite.</td>
</tr>
<tr>
<td></td>
<td>Solonised and alluvial soils.</td>
</tr>
<tr>
<td>Quickup Dam</td>
<td><strong>Surrounding vegetation:</strong> Forests of Jarrah, Marri and Karri dominate the catchment.</td>
</tr>
<tr>
<td></td>
<td><strong>Landform:</strong> Laterite plateau consisting of sands and ironstone gravels over mottled clays.</td>
</tr>
<tr>
<td></td>
<td>Drainage is influenced by granite outcrops that form rounded hills about 200 m high.</td>
</tr>
<tr>
<td></td>
<td>Yellow podsolic soils and red earths.</td>
</tr>
<tr>
<td>Quinninup Dam</td>
<td><strong>Surrounding vegetation:</strong> State forest areas with largely Jarrah stands. Karri forest surrounds</td>
</tr>
<tr>
<td></td>
<td>the dam.</td>
</tr>
<tr>
<td></td>
<td><strong>Landform:</strong> Located on the Darling Plateau, consisting of crystalline rock, quartzite and</td>
</tr>
<tr>
<td></td>
<td>consolidated sediments.</td>
</tr>
<tr>
<td>Walpole River</td>
<td><strong>Surrounding vegetation:</strong> Extensively cleared and developed land.</td>
</tr>
<tr>
<td></td>
<td><strong>Landform:</strong> The Walpole River basin consists of flat swampy terrain on sedimentary rock, with</td>
</tr>
<tr>
<td></td>
<td>broad drainage floors in lower reaches of streams.</td>
</tr>
</tbody>
</table>

Appendix II

Bolganup Reservoir Biogeochemical Modelling Study

Final Report

J. E. Harris and J. P. Antenucci
CERTIFICATE OF APPROVAL FOR ISSUING CWR DOCUMENTS

DOCUMENT AND PROJECT DETAILS:

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Document no. (ED, WP): CWR 2228
Document author(s): J.E. Harris and J.P Antenucci
Project title: Characterisation of NOM in Highly Coloured Surface Waters
Project manager: Dr Steve Capewell, A/Prof Anna Heitz
Client organisation: Water Corporation
Client contact: Dr Steve Capewell
Synopsis: Final Report

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<td>1st Sept</td>
<td>M.Hipsey</td>
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RELEASE STATUS:

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EXECUTIVE SUMMARY

Bolganup Reservoir is located on Bolganup Creek, about 40km north of the town of Albany and 20km east of Mt Barker. The reservoir has a storage volume of 235ML and supplies water to Albany and surrounding localities. Dissolved Organic Carbon (DOC) concentrations are relatively high in the reservoir, and this has implications upon treatment with chlorine. When chlorine is used for disinfection of water, it reacts with naturally present organic matter in the water to produce disinfection byproducts (DBPs), which can have adverse health impacts during long periods of exposure.

A one-dimensional hydrodynamics model (DYRESM) coupled with a biogeochemical model (CAEDYM) developed by CWR was applied to Bolganup Reservoir to examine the DOC dynamics. DYRESM-CAEDYM was capable of reproducing stratification, salinity, pH, DO, nitrogen and phosphorus species, carbon compounds and phytoplankton biomass in the reservoir.

Internal loading, particularly of refractory DOC, accounts for the greatest source of DOC to the reservoir. This refractory DOC is predominately the very hydrophobic fraction (VHA), which is a highly aromatic compound. Associated with this compound, is a high Specific UV Absorbance (SUVA) indicating higher potential for DBP production and thus a larger amount of chlorine is required to treat this water. Additionally, phytoplankton biomass has the potential to make a significant contribution to the DOC pool within the reservoir.
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1 INTRODUCTION

Bolganup Dam and Reservoir are located on Bolganup Creek, about 40km north of the town of Albany and 20km east of Mt Barker. The reservoir covers an area of 4ha and has a storage volume of 235ML (see Figure 1.1). Annual inflow to the reservoir is estimated to be 300ML, primarily through runoff between May and August (Marchesani, 1993). Bolganup Catchment lies within the Porongurup National Park, which is dominated by karri forest with an understorey of lichens and small native shrubs. The catchment has an area of 5km² and varies in elevation from 290m AHD at the reservoir to about 500m AHD at the head of the catchment (Water Corporation, 2004).

Bolganup Dam is one of four water sources operated by the Water Corporation as part of the Lower Great Southern Town Water Supply Scheme, which supplies public drinking water to Albany and surrounding localities. Water from Bolganup Reservoir is transferred to the Mt Barker water treatment plant where it is clarified to reduce colour, iron, aluminium and turbidity levels. It is then transferred to Mt Barker service reservoir where it is blended with water from other sources in the Lower Great Southern Town Water Supply Scheme that has been delivered from storages in Albany. The stored treated water is then chlorinated before being supplied to the towns of Mt Barker and Kendenup. There is an offtake in the Bolganup to Mt Barker delivery main near the reservoir where water is chlorinated at the transfer pump station before being supplied to the town of Porongurup.

Water from Bolganup Reservoir has generally been of good quality, with the exception of colour, turbidity, iron and aluminium (Water Corporation, 2004). Dissolved Organic Carbon (DOC) is a complex and heterogeneous mixture of organic compounds with various physical and chemical properties, functionally defined as organic matter which can pass through a 0.45µm filter. When chlorine is used for disinfection of water, it reacts with naturally present organic matter in the water to produce disinfection byproducts (DBPs). Research has suggested that high levels of DBP exposure over many years could increase the risk of cancer and liver, kidney and nervous system problems in animals, as well as miscarriage and birth defects. There is therefore concern over the relatively high levels of DOC in Bolganup Reservoir, and whether the levels of DBP produced on reaction with DOC are under Australian Drinking Water Standards.

The primary objective of the current study is to develop an understanding of the dynamics of DOC in Bolganup Reservoir using a one-dimensional hydrodynamic and ecological modelling (DYRESM-CAEDYM). Specifically, the major sources of DOC to the reservoir will be determined, and the controls on DOC cycling examined. Enhanced understanding of these processes will allow managers to predict changes to organic carbon quality in offtake waters and therefore assist in the planning of treatment and management of the water source.
Figure 1.1 Map of Bolganup Reservoir indicating the reservoir sampling location (34° 40' 17.85"S, 117° 52' 42.51"E) and the inlet sampling location (34° 40' 19.15"S, 117° 52' 33.94"E).
2 DATA ANALYSIS

2.1 Morphometric Data

An elevation-storage curve for Bolganup Reservoir is presented in Figure 2.1. The maximum depth of the reservoir is 13.65m (298.55m AHD), with a volume of 235ML and a surface area of 39,290m². One offtake is present in the reservoir, which floats approximately 1m below the water surface.

![Surface Area vs. Depth](image1)
![Volume vs. Depth](image2)

Figure 2.1 Bolganup Reservoir Storage curves showing a) Surface Area and b) Volume as a function of height above AHD.

2.2 Meteorological Data

Meteorological data available consisted of air temperature, wind speed, wind direction, relative humidity and rainfall. Data was available at two stations in the proximity of Bolganup reservoir; Mount Baker BOM station 22km WNW of Bolganup (-34.6256 117.6344) and Albany Airport BOM Station 30km SSW of Bolganup (-34.9431 117.8008). Air temperature, wind speed and relative humidity were available at Albany BOM station at 30 minute intervals while only minimum and maximum values were available at Mt Barker BOM station. Vapour pressure was calculated on a daily basis using air temperature and relative humidity data. These data are presented in Figure 2.2 for the period November 2005 to December 2007. The data shows the typical seasonality expected of a site with a Mediterranean climate with warm dry summers and cool mild winters.
Daily total rainfall data were available at Mt Barker BOM station. These data are presented in Figure 2.3 for the period November 2005 to December 2007. The total 2005 rainfall was 0.86m, approximately equal to the annual average for the catchment which is 0.82m (Water Corporation, 2005). The total 2006 and 2007 rainfall was significantly lower than the long term average- 0.4m in 2006 and 0.56m in 2007. There were no exceptionally large rainfall events in 2006 and 2007 and the rainfall was relatively consistent throughout the year, rather than concentrated in the winter months.

Radiation data were taken from Karrivale BOM station (9958), 3.5km west of Bolganup. Radiation was not measured directly at this site; it was derived from satellite data, with an average error of this technique of 0.17%. The data was available in the form of total daily global solar exposure- this value was comprised of incoming short wave (direct) radiation, long wave (diffuse) radiation and infra-red (Figure 2.4).

North-westerly winds dominated the winter climate due to a combination of the subtropical ridge being located north of Albany and a land breeze effect. Sea breezes in summer were experienced from the south- west through to the south- east, however, the south easterly winds were the most common. Wind speeds were generally greatest in summer, although winter winds displayed more variability with high peaks in speed due to the passing of fronts. Variable wind speeds and directions were experienced during sampling events.

Figure 2.2 Daily averaged meteorological data at Albany BOM station (9741) between 29th November 2005 and 31st December 2007. a) Air temperature, b) Wind speed, and c) Vapour pressure.
2.3 Water Storage Data

Water level measurements were available at a weekly interval between October 1999 and December 2007. Over this time period, water depth ranged from 8.65m to 13.6m, while during the study period between November 2005 and December 2007, water depth ranged from 12.45m-13.6m (Figure 2.5). This indicates 2005-2007 was a period of high water level with little variability.

The daily Bolganup storage volume record was constructed by interpolation between the available measurements between 2005 and 2007 (Figure 2.6). The reservoir was at full capacity at the end of 2005, as well as in July 2006 and for short periods at the end of 2007 (Figure 2.7). It is likely that the ungauged dam overflow was active during these times.
Figure 2.5 Bolganup Reservoir water level between October 1999 and December 2007. Red line indicates the study period water level (Nov 05-Dec 07).

Figure 2.6 Reservoir volume during the study period constructed from measured data points (green points).

Figure 2.7 Bolganup water level during the study period (maximum depth is at 285m AHD).
2.4 Calibration and Verification Data

Water column physical, chemical and biological data for Bolganup Reservoir were sourced from the Curtin Centre for Applied Organic Geochemistry (CAOG) between November 2005 and December 2007. Physical, biological and chemical sampling was carried out on twenty-three occasions during this period, with an approximate monthly interval between sampling. Profile data were obtained for salinity, temperature, dissolved oxygen (DO), pH and photosynthetically active radiation (PAR). Various biological and chemical data were available at surface and bottom depths (Table 1). For full field method collection details, see Heitz et al., (2008).

Table 1 Biological, chemical and physical data available at the surface and bottom of the water column during the sampling period (2005-2007).

<table>
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<th>Data</th>
<th>Variable</th>
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<td></td>
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<td></td>
<td>Chl a</td>
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<td>DOC VHA</td>
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2.4.1 Vertical Structure

Bolganup is a fresh reservoir with salinity values less than 0.24ppt during the study period (Figure 2.8). Water temperature ranges from 10-22°C, with a distinct thermocline at a depth of 2-3m evident over the summer period from November to April (Figure 2.9). As the first rains occur in April, the thermocline deepens until the water column is homogeneous by June. Salinity is slightly less in the surface layer than bottom layers, likely due to evaporation in summer. Temperature is therefore playing a larger role in the density structure of the reservoir.

Dissolved oxygen (DO) concentrations in the reservoir range from 0-10 mg/L, with anoxic conditions present below the thermocline in summer (Figure 2.10). The pH closely matches this pattern with neutral conditions (pH 7-8) throughout the water column in winter and more acidic conditions (pH 5.5-6.5) below the thermocline in summer (Figure 2.11).

Photosynthetically active radiation (PAR) sharply declines with depth, with 90% of the light being absorbed in the top 50cm of the water column (Figure 2.12). Similarly, Secchi depths are shallow, ranging from 0.84-1.62 m.

Alkalinity in Bolganup Reservoir ranges from 7-20 mg/L, characteristic of fresh water bodies, indicating a low buffering capacity (Figure 2.13). Alkalinity is generally higher in the bottom waters, and steadily increases throughout the summer period, until the first rains where a marked drop in alkalinity can be observed. Water hardness ranges from 30-53 mg/L (Figure 2.14), which is classified as slightly hard water under the Australian Drinking Water Guidelines (2004). Water is generally harder in the surface waters and hardness declines when the first rains occur. Colour ranges from 55-200 TCU, with higher values in the bottom water samples, particularly before rains occur (Figure 2.15).

![Figure 2.8 Salinity profiles measured in Bolganup reservoir between January and August 2007. Red points represent the measured profiles and contouring has occurred between these points.](image-url)
Figure 2.9  Temperature profiles measured in Bolganup reservoir between December 2005 and December 2007. Red points represent the measured profiles and contouring has occurred between these points.

Figure 2.10  Dissolved Oxygen (DO) profiles measured in Bolganup reservoir between December 2005 and December 2007. Red points represent the measured profiles and contouring has occurred between these points.

Figure 2.11  pH profiles measured in Bolganup reservoir between December 2005 and December 2007. Red points represent the measured profiles and contouring has occurred between these points.
Figure 2.12 Photosynthetically active radiation (PAR) profiles measured in Bolganup reservoir between December 2005 and December 2007. Red points represent the measured profiles and contouring has occurred between these points.

Figure 2.13 Total Alkalinity as calcium carbonate measured in Bolganup reservoir between December 2005 and December 2007.

Figure 2.14 Hardness as calcium carbonate measured in Bolganup reservoir between December 2005 and December 2007.
2.4.2 Nutrients

Mean TN and TP concentrations are moderate ranging from 0.46-1.2 mg/L and 0.013-0.06 mg/L respectively (Figure 2.16 to Figure 2.17). Bottom concentrations are on average 31% and 32% greater than surface concentrations respectively (based on mass concentration). TN: TP ratios are similar in the surface and bottom of the water column, with on average 26 and 22 times more TN than TP in the surface and bottom respectively. This ratio indicates a mesotrophic ecosystem with respect to total nutrients. In comparison, DIN:DIP ratio’s differ significantly in the surface and bottom of the water column, with a 24:1 ratio in the surface and a 64:1 ratio in the bottom of the water column. This indicates a greater release of $NH_4$, $NO_2^-$, and $NO_3^-$ combined than $PO_4$ in the hypolimnion.

Mean inorganic nitrogen concentrations in Bolganup Reservoir are generally low, according to Kalff (2002), with $NH_4$ concentrations ranging from 0.008 to 0.44 mg/L, $NO_3^-$ from 0.002 to 0.022 mg/L and $NO_2^-$ from 0.002 to 0.095 mg/L (Figure 2.19 to Figure 2.19). In comparison, inorganic phosphorus concentrations are moderate (Kalff, 2002), with $PO_4$ ranging between 0.002 and 0.013 mg/L (Figure 2.20). Bottom waters have elevated concentrations of particularly $NH_4$ (75% higher in bottom waters), and also $NO_2^-$ (40% higher in bottom waters), indicating their release from the sediment. $NO_3^-$ (28% higher in bottom waters) and $PO_4$ concentrations (20% higher in bottom waters) do not display such a significant difference in surface and bottom waters indicating little release.

Between December and April, surface concentrations of dissolved nitrogen species are at their lowest concentrations due to uptake by phytoplankton growing in the warm surface layers. Bottom $NH_4$ concentrations at this time are elevated, while $NO_2^-$ and $NO_3^-$ concentrations are low in comparison to the rest of the year. Waters below the thermocline are anoxic during this summer period, resulting in nitrification rates slowing. A decline in the nitrification rate results in high concentrations of $NH_4$ and lower concentrations of $NO_2^-$ and $NO_3^-$. Additionally, in the absence of oxygen below the thermocline, denitrification occurs utilising the low concentrations of $NO_3^-$ in the water column, resulting in very low $NO_3^-$ concentrations.
In May, as the first rains occur, the water column begins to mix and dissolved oxygen concentrations in the bottom waters increase. Over the summer, particulate and dissolved forms of nitrogen have been deposited into the sediment and as this oxygen becomes available, they can be acted upon by bacteria and released into the water column. A sharp increase in $NH_4$ occurs in May as this occurs; however, nitrifying bacteria then begin to thrive in this oxygenated environment, reducing the $NH_4$ concentrations for the duration of mixing. $NO_3$ and $NO_2$ concentrations steadily increase in the bottom of the water column due to this nitrification and this suggests that nitrification is occurring at a fast rate. High concentrations of $NH_4$, $NO_3$ and $NO_2$ remain in the surface of the water column until October when warm temperatures return and phytoplankton utilise them.

$TN$ is generally constant in the surface and bottom of the water column throughout the year. This suggests Bolganup is a nitrogen limited system, as despite the presence of fluctuating dissolved components of nutrients, the total pool of nitrogen is constant, indicating whenever inorganic nitrogen becomes available, it is rapidly utilised.

Phosphate and Total Phosphorus concentrations show no temporal trends and surface and bottom concentrations are similar. This indicates little $PO_4$ release from the sediment and a system not limited with respect to phosphorus.
2.4.3 Dissolved Organic Carbon

Filtered DOC and biodegradable DOC (BDOC) concentration data were available during the sampling period. Fractionation of DOC provided measurements of Very Hydrophobic DOC (VHA), Slightly Hydrophobic DOC (SHA), Charged (anionic) DOC (CHA) and Neutral DOC.
Hydrophobic fractions are more likely to be sorbed to soils and minerals, while charged and neutral fractions are more mobile. Filtered DOC minus BDOC can be considered as the refractory portion of DOC (DOCR). Maximum concentrations of DOCR occurred in May to June of each year, near to the end of the stratification period, with concentrations reaching 13mg/L in the bottom of the water column (Figure 2.21). BDOC concentrations closely followed this pattern, with maximum concentrations of 5mg/L reached towards the end of each stratification period (Figure 2.22).

The SHA, CHA and NEU fractions of DOC display little variation (0.18-0.35 standard deviations) in the surface and bottom of the water column during the sampling period (Figure 2.23 to Figure 2.24) In comparison, the VHA fraction accounts for the majority of the filtered DOC as well as the majority of the variation (1.62 standard deviations). VHA comprises 46-83% of the filtered DOC during the sampling period, and on average accounts for 70% of the DOC (Figure 2.25). This result is common in West Australian waters; VHA generally accounts for 60-82% of total DOC (CRC for Water Quality and Treatment). Maximum VHA concentrations occur in the surface of the water column in January to February 2006 and April to June 2007, and in the bottom of the water column between May and June 2006 and January to June 2007. Elevated concentrations of VHA under stratification accounts for the increasing filtered DOC concentrations during this period. Uncharacteristically low concentrations of VHA, SHA, CHA and NEU DOC were measured in June 2006. This result appears to be in error, as the total DOC during this event is not significantly lower than other measurements as the fractionation data suggest and as such these data points have been excluded from the figures below.

Specific UV absorbance (SUVA) is defined as the UV absorbance at 254nm per mg of DOC in a 1L sample. A high SUVA indicates a large portion of the organics present in the water column are aromatic and hydrophobic. Aromatic compounds have a greater tendency to react with disinfectants to create DBP’s and as such, a high SUVA indicates a higher potential for DBP formation. It is important to note however that SUVA measurements are also influenced by other inorganic material, such as reduced sulphate and iron, which also absorb UV at this spectrum. SUVA is relatively constant in the surface of the water column with an average of 4.5 mg/L/m (Figure 2.26). In the bottom of the water column, SUVA values peak during stratification periods, reaching 8.5 mg/L/m in 2007. The increase in SUVA in February to April 2007 appears to be unrelated to VHA concentrations, and it is likely to reflect the high iron concentrations measured during this sampling event. However, following this increase, the SUVA increases again in the hypolimnion in May 2007, and appears to be related to the increase in the VHA component during this stratification period. Similarly, the increase in SUVA from January to May 2006 correlates with the increase in VHA during this period in the hypolimnion under stratification.

DOC concentrations in the bottom of the water column increase under stratification and this increase is primarily due to the VHA fraction of DOC. VHA is a highly aromatic compound and thus an increase in SUVA occurs during these periods. This increase is not associated with rainfall entering the reservoir (Figure 2.26), and appears to be internally loaded into the system.
The DOC within Bolganup reservoir appears to be a relatively constant, unchanging pool of DOC with respect to chemical characterisation. Refer to Heitz et al., (2008) for a detailed chemical analysis of DOC.

**Figure 2.21** Refractory DOC (DOCR) measured in the top and bottom of Bolganup reservoir during sampling events.

**Figure 2.22** Biodegradable DOC (BDOC) measured in the top and bottom of Bolganup reservoir measured during sampling events.
Figure 2.23  DOC fractions (VHA, SHA, NEU, CHA) measured in the surface of Bolganup reservoir during sampling events.

Figure 2.24  DOC fractions (VHA, SHA, NEU, CHA) measured in the bottom of Bolganup reservoir during sampling events.
Figure 2.25 Percentage DOC as VHA measured in the surface and bottom of Bolganup reservoir during sampling events.

Figure 2.26 Specific UV absorbance (SUVA) measured in the surface and bottom of Bolganup reservoir during sampling events. Green circles indicate rainfall measured in Mt Barker since the last sampling event.
2.4.4 Phytoplankton

Total Chlorophyll a concentrations and total phytoplankton cell counts are presented in Figure 2.27 to Figure 2.28. Surface Chlorophyll a concentrations are generally low in the reservoir (<2 µg/L). Surface counts were higher than bottom counts, except in May 2006, where bottom counts reached 30,080 cells/mL of an unknown species. Total cell counts and Chlorophyll a concentrations were greatest over the summer and spring period (December to April 2006), with lower counts throughout the winter months.

Phytoplankton samples over the study period were co-dominated by chlorophytes (40%), primarily *Actinastrum sp.* and *Sphaerocystis sp.*, and cyanobacteria (49%), primarily *Aphanocapsa sp.* and *Synechocystis sp.* Cell counts for each of these individual phytoplankton phyla are presented in Figure 2.29 to Figure 2.31. Cyanobacteria have the highest cell counts in the reservoir, reaching 14,000 cells/mL during the summer period. Chlorophyte abundances peak in spring and autumn, reaching cell counts of 5000 cells/mL in March 2006. Cryptophytes (primarily *Cryptomonas sp.*) are also a minor background phyla in the reservoir, with cell counts remaining at 200 cells/mL for the majority of the year.

![Figure 2.27](image1.png)  
**Figure 2.27** Total Chlorophyll a concentration measured in the top and bottom of Bolganup Reservoir measured during sampling events.

![Figure 2.28](image2.png)  
**Figure 2.28** Total phytoplankton cell density measured in the top and bottom of Bolganup Reservoir measured during sampling events.
Figure 2.29 Cyanobacteria cell counts measured in the top and bottom of Bolganup Reservoir measured during sampling events.

Figure 2.30 Chlorophyte cell counts measured in the top and bottom of Bolganup Reservoir measured during sampling events.

Figure 2.31 Cryptophyte cell counts measured in the top and bottom of Bolganup Reservoir measured during sampling events.

2.4.5 Additional Data

Chloride concentrations are greatest in the surface of the water column, with values ranging between 85 and 135 mg/L (Figure 2.32). Sulfate concentrations are less than 10 mg/L (Figure 2.33), calcium less than 3 mg/L (Figure 2.34), potassium less than 2.2 mg/L (Figure 2.35) and magnesium less than 9.5 mg/L (Figure 2.36). Aluminium concentrations reach 0.9
mg/L (Figure 2.37). Iron concentrations increase over the summer period (up to 8 mg/L), with a marked decline in concentrations when the first rains occur (Figure 2.38). Manganese concentrations follow a similar pattern to iron, with concentrations less than 0.006 mg/L (Figure 2.39).

![Figure 2.32 Chloride concentrations in the top and bottom of Bolganup Reservoir measured during sampling events.](image)

![Figure 2.33 Sulfate concentrations in the top and bottom of Bolganup Reservoir measured during sampling events.](image)

![Figure 2.34 Calcium concentrations in the top and bottom of Bolganup Reservoir measured during sampling events.](image)
Figure 2.35  Potassium concentrations in the top and bottom of Bolganup Reservoir measured during sampling events.

Figure 2.36  Magnesium in the top and bottom of Bolganup Reservoir measured during sampling events.

Figure 2.37  Aluminium concentrations in the top and bottom of Bolganup Reservoir measured during sampling events.
Figure 2.38  Iron concentrations in the top and bottom of Bolganup Reservoir measured during sampling events.

Figure 2.39  Manganese concentrations in the top and bottom of Bolganup Reservoir measured during sampling events.
4 DYRESM-CAEDYM MODELLING

4.1 Introduction

DYRESM is a one-dimensional hydrodynamics model for predicting the vertical distribution of temperature, salinity and density in lakes and reservoirs over seasonal and inter-annual time scales. The model is horizontally averaged, and accounts for surface thermodynamics, inflows and outflows and internal mixing processes driven by these forcing mechanisms. CAEDYM is a water quality model that couples directly to DYRESM, and includes process descriptions for the dominant nutrient cycles (carbon, nitrogen, phosphorus and silica), dissolved oxygen, primary production, organic and inorganic particles and the exchange of gases with the atmosphere. DYRESM-CAEDYM was successfully applied to Mundaring Weir during investigations conducted there in 2001/2002. DYRESM-CAEDYM has been developed by CWR, and is distributed widely via the internet to more than 1500 users across 59 countries.

4.2 Representation of the Carbon cycle in CAEDYM

CAEDYM models labile (DOCL) and refractory (DOCR) fractions of DOC as state variables. Particulate organic carbon is also partitioned into labile (POCL) and refractory (POCR) components. Figure 4.1 presents a simplified schematic of the carbon cycle, with the main processes involved in the sediments and water column in Bolganup reservoir being:

- Atmospheric fluxes of DIC.
- Carbonate buffer system induced DIC variations.
- Mineralisation of DOCL and DOCR to DIC.
- Biological uptake of DIC by phytoplankton.
- Dissolved sediment fluxes of DIC, DOCL, and DOCR.
- Decomposition of POCL to DOCL and POCR to DOCR.
- Biological mortality and excretion into the DOCL and POCL pools.
- Settling and re-suspension of POCL, POCR and internal carbon.
4.3 Input data

4.3.1 Morphometric Data

The daily Bolganup storage volume record was constructed by interpolation between the available measurements between 2005 and 2007 (see Figure 2.1).

4.3.2 Meteorological Data

DYRESM was forced with daily meteorological data from a combination of Albany and Mt Barker BOM stations. Variables included short wave radiation, cloud cover, air temperature, vapour pressure, rainfall and wind speed.

Air temperature and vapour pressure data were daily averages of the 30-minute data at Albany BOM station, as presented in Figure 2.2. There were only minimal gaps in the recorded data (a few hours at maximum), and for these instances data was used from a previous day to fill the record. Daily rainfall data at Mt Barker BOM station were used as an estimate of rainfall received at Bolganup. Following initial simulations, this rainfall volume resulted in the water level not being accurately reproduced, and as such, the rainfall measurements were reduced. The water level was calculated well by the model when the rainfall measured at Mt Barker was halved (Figure 4.2). It is likely Bolganup reservoir receives less rainfall than Mt Baker due to it being located in a rain shadow behind the Porongurup Ranges.

Total daily global solar exposure data were taken from Karrivale BOM station (9958), as shown in Figure 2.4. Assuming the infra-red component is small, the incoming radiation data...
was split into short wave and long wave components. This was accomplished by firstly fitting a sine curve to the seasonal peaks in the radiation record to represent the clear sky radiation input and it was assumed that the cloud cover percentage was the percentage difference between the clear sky estimate and the measured value. Daily short and long wave radiation were provided to the model at a daily time step (Figure 4.3).

Figure 4.2 Estimated daily rainfall at Bolganup Reservoir from 29th November 2005 to 31st December 2007. Rainfall at Mt Barker BOM station has been halved to create this record.

Figure 4.3 Short and long wave (cloud cover) radiation calculated from daily global total incoming radiation measured at Karrivale BOM station from 29th November 2005 to 31st December 2007.
4.3.3 Inflow, Outflow and Storage Data

Outflow volumes from the offtake and water storage volumes were available at 5-10 day intervals from the Water Corporation. Outflow was assumed to be taken at a constant daily rate between available volumes (Figure 4.4). Inflow to the reservoir is not gauged, and thus weekly inflow has been calculated as follows (Figure 4.5):

\[
\text{Inflow} = \Delta \text{Volume} - \text{Outflow} - \text{Rainfall} + \text{Evaporation}
\]  

(Eq. 1)

Weekly evaporation was calculated from Albany BOM station and multiplied by the surface area of the reservoir (4 ha). Weekly inflow was averaged over a monthly time period to smooth the series and remove negative values which can arise from the calculation of water balance.

When the dam was overflowing, it was not possible to obtain an inflow volume using this method. The estimated inflow values from when the dam was not overflowing were therefore used to obtain a mean percentage of rainfall which enters the reservoir as inflow. Excluding the summer period, 5.6% of the rainfall measured at Mt Barker enters the reservoir as inflow. The summer period was excluded in this calculation due to the large calculated percentage of rainfall which enters as inflow due to negligible amounts of rainfall. Therefore, 2.8% of the halved Mt Barker rainfall was used to estimate inflow volume when the dam was overflowing.

Figure 4.4 Daily Bolganup Outflow volume from 1st January 2005 to 30th January 2007.
4.3.4 Chemical and Biological Data

Water temperature in Bolganup Creek has been calculated as a four-day moving average of the air temperature data presented in Figure 2.2. A relatively frequent moving average has been used due to the small size of the reservoir, thus heat exchange is expected to be rapid. Water quality of the inflow into Bolganup Reservoir was measured on four occasions between August and November 2007. CAEDYM was initially forced with an average of these measurements during all other times of the simulation. Seasonal variations may occur in the inflowing conditions which were not able to be captured by these measurements in the spring period. Following initial simulations, it was found that using an average of measured inflow nitrate and nitrite concentrations resulted in surface concentrations in the reservoir being over-predicted. Nitrate and nitrite concentrations are generally correlated with rainfall, and in Bolganup reservoir, this was also the case with concentrations relating to inflow volume as follows:

$$NO_x = 0.0015 \times Inflow - 0.0986$$  \hspace{1cm} (Eq. 2)

This relationship was therefore used to estimate inflowing nitrate conditions during the remainder of the simulation when measurements were not available in the field.

Inflow data included temperature, salinity, dissolved oxygen, pH, Dissolved Organic Carbon (refractory and labile), Particulate Organic Carbon (refractory), Particulate and Dissolved Nitrogen (labile), Particulate and Dissolved Phosphorus (labile), Ammonium, Nitrate and nitrite, Phosphate, Silica, Total alkalinity and Dissolved Inorganic Carbon.

Organic phosphorus and nitrogen have been calculated as the difference between total nutrients and inorganic nutrients, and assumed to be dissolved and labile material. DOC was partitioned into refractory and labile components, with filtered DOC minus BDOC forming the refractory pool and BDOC forming the labile pool. The majority of the particulate organic carbon can be assumed to be coming from the catchment and therefore was modelled as refractory. Dissolved Inorganic Carbon was calculated using Total alkalinity and pH.
In order to maintain the high light extinction coefficients in the reservoir, suspended solids load was assumed based on a 1:1 ratio between suspended solids concentration and turbidity. CAEDYM accommodates more than one independent SSOL group to model a distribution of particles with different sizes and densities. Total suspended solids have been divided equally into large (diameter of 8µm) and small (diameter of 3µm) suspended solid fractions.

### 4.4 Validation of DYRESM-CAEDYM with field data

#### 4.4.1 Configuration

DYRESM-CAEDYM was forced with data presented in Section 4.2. Three phytoplankton groups have been simulated (Chlorophytes, Cyanobacteria and Cryptophytes) due to their dominance in the reservoir (see Section 2.4.4). Initial conditions for the simulation were from the first sampling event carried out by COAG on the 29th November 2005. All simulations were conducted over a 762 day period from 29 November 2005 to 31 December 2007, using a 60 minute model time step.

Validation results presented in this section include water level, temperature, salinity, PAR, DO, pH, phytoplankton, nutrients and organic carbon.

#### 4.4.2 Simulation Results

##### 4.4.2.1 Water Level

Predictions of the water level are shown in Figure 4.6. Water level was predicted reasonably well, with a maximum error between field and simulated measurements of 25cm. Note that in these simulations, the inflow was calculated by averaging the inflow over a monthly period, which results in slight discrepancies in the modelled water level below. This was done to smooth the series, which had the effect of removing negative values which can arise from the calculation of daily water balance.
4.4.2.2 Temperature

Initial simulations predicted a deeply mixed water column, with the thermocline at approximately 6m depth, rather than 3m as measured in the field (Figure 4.7). Reducing the photolytic decay rate of DOCR in the surface of the reservoir to 0.00003/day resulted in an improved representation of the temperature structure (Figure 4.8). DOCR is capable of absorbing a significant portion of UV light, and thus reducing its photolytic rate of decay to DIC results in higher concentrations of DOCR in the surface of the water column, limiting light penetration to depth. Reducing the rate of DOCL to DIC mineralisation from 0.01/day to 0.003/day further improved the temperature structure by reducing the depth of the thermocline (Figure 4.9). DYRESM-CAEDYM well represents the temperature structure of Bolganup reservoir, with the water column becoming fully mixed at the start of July and stratification evident from October to April of each year. This sensitivity analysis indicates that the dynamics of the DOC play a very strong role in the stratification of the reservoir.
Figure 4.7  Measured (top) and initially simulated (bottom) water temperature from 29th November 2005 31st December 2007. Photolytic decay of DOCR 0.3/day. Red points in the top panel indicate sampling points.

Figure 4.8  Measured (top) and initially simulated (bottom) water temperature from 29th November 2005 31st December 2007. Photolytic decay of DOCR 0.00003/day. Red points in the top panel indicate sampling points.
Figure 4.9  Measured (top) and simulated (bottom) water temperature from 29th November 2005 to 31st December 2007. Photolytic decay of DOCR 0.00003/day and DOCL to DIC mineralisation 0.003/day. Red points in the top panel indicate sampling points.

4.4.2.3 Salinity

A comparison of the simulated and measured salinity is presented in Figure 4.10. Salinity is relatively well represented in the reservoir, with values generally 0.02ppt higher than the measured data. As explained in Section 2.4.1, salinity is not the key determinant of the density structure of the reservoir, and thus this difference is negligible.

Figure 4.10  Measured (top) and simulated (bottom) salinity from 29th November to 31st December 2007. Red points in the top panel indicate sampling points.

4.4.2.4 PAR

Photosynthetic active radiation measured in the field and simulated in the model are shown in Figure 4.11. Light penetration is well predicted by the model, with PAR being absent below 2m in the field and the model. Surface values (top 25cm) are greater in the field than in the simulation.
4.4.2.5 Dissolved Oxygen

Figure 4.12 shows the dissolved oxygen measured in the field and that computed by the model. The model reproduces the loss of oxygen below the thermocline in summer, followed by the mixing of well oxygenated water to depth in July. Timing and magnitude of DO draw-down are well reproduced by the model, however, surface concentrations are generally 2 mg/L higher in the surface of the water column in the model than that measured in the field.

4.4.2.6 pH

pH in the field and simulation are presented in Figure 4.13. The lowering of pH in the hypolimnion in summer is well predicted by the model, although slightly over-estimated with pH approximately 0.5 units too low in the hypolimnion in the simulation. The field results
show patchiness of pH in the hypolimnion. Bacterial breakdown of DOC produces \( \text{CO}_2 \) resulting in patches of water with more acidic conditions. The model does not reproduce this patchiness, and instead pH is relatively uniform in the hypolimnion under stratification.

![Figure 4.13 Measured (top) and simulated (bottom) pH from 29th November to 31st December 2007. Red points in the top panel indicate sampling points.](image)

4.4.2.7 Phytoplankton

Total Chlorophyll \( a \) simulation results are presented in Figure 4.14. Total Chlorophyll \( a \) includes Chlorophyte, Cryptophyte and Cyanobacterial biomass. Temporal variation in Chlorophyll \( a \) is well represented by the model, with higher concentrations in summer and autumn of each year. The model predicts a Cryptophyte bloom in November to May 2007, which is not supported by the field data. This is likely to be due to elevated phosphorus concentrations prior to the bloom (see Section 4.3.2.8).
4.4.2.8 Nutrients

Ammonium ($NH_4^+$) concentrations in the field and simulation are presented in Figure 4.15. The increase of $NH_4$ concentrations in the hypolimnion throughout the summer due to sediment release processes was well reproduced by the model, with concentrations being overestimated by 0.1mg/L in the first summer and underestimated by 0.3mg/L in the second summer. The sharp decline in bottom concentrations during mixing in July due to dilution was captured by the model. Surface values were also well reproduced, with slight increases in the winter months due to mixing with hypolimnetic water.

Nitrate ($NO_3^-$) concentrations were well predicted by the model, with surface concentrations increasing during inflow events such as in autumn and winter of 2007 (Figure 4.16). Concentrations in the hypolimnion increase during winter mixing due to increased rates of nitrification and reduced rates of denitrification associated with an oxygenated sediment-water interface.

CAEDYM does not simulate Total Nitrogen (TN) or Total Phosphorus (TP) as state variables but derives these as the sum of the total inorganic components ($NO_3^-$ and $NH_4^+$, or FRP) plus the particulate organic components (PON or POP) plus the dissolved organic components (DON or DOP). TN concentrations were relatively well reproduced by the model, with concentrations increasing throughout summer, decreasing in June as mixing occurs and then gradually increasing until January, primarily caused by $NH_4$ (Figure 4.17).
Temporal patterns in phosphate ($PO_4$) are difficult to discern in the field measurements (Figure 4.18). In the model, $PO_4$ concentrations increase in the surface during summer due to phytoplankton release. In October, these concentrations rapidly reduce due to a Cryptophyte bloom which utilises the nutrients (see Section 4.3.2.7). TP concentrations also display few temporal patterns in the field data (Figure 4.19). The model predicts TP to slowly increase in the surface of the water column, due to the increasing $PO_4$ concentrations. In the hypolimnion, TP reduces, due to mineralisation of DOPL to $PO_4$. The range of TP and $PO_4$ concentrations simulated by the model corresponds well to those measured in the field.

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Figure 4.15 Measured (top) and simulated (bottom) Ammonium concentrations in the surface and bottom of Bolganup reservoir.
Figure 4.16 Measured (top) and simulated (bottom) nitrite/nitrate concentrations in the surface and bottom of Bolganup reservoir.

Figure 4.17 Measured (top) and simulated (bottom) Total Nitrogen (TN) concentrations in the surface and bottom of Bolganup reservoir.
Figure 4.18  Measured (top) and simulated (bottom) phosphate concentrations in the surface and bottom of Bolganup reservoir.

Figure 4.19  Measured (top) and simulated (bottom) Total Phosphorus (TP) concentrations in the surface and bottom of Bolganup reservoir.
4.4.2.9 Carbon

BDOC was well reproduced by the model, with maximum concentrations of approximately 5 mg/L in the hypolimnion towards the end of stratification periods (Figure 4.20). Note that the field data pattern is not as clear as the simulation data, but does show increases from January to April each year in the bottom waters, which are replicated by the simulation results. DOCR was also well reproduced by the model, with maximum concentrations of 13.5 mg/L reached in the hypolimnion during stratification periods (Figure 4.21). Sediment flux rates of DOCL and DOCR which best reproduced the field results were 0.06g/m²/day and 0.05g/m²/day respectively.

Figure 4.22 illustrates the dominant processes predicted by CAEDYM that influence the organic carbon concentrations in the hypolimnion. DOCL mineralisation to DIC occurs at a rate up to 0.0003 mg C/L/hr, with higher rates occurring in summer when water temperatures are warmer. DOCL and DOCR flux out of the sediments at up to a rate of approximately 0.0002 mg C/L/hr, with maximum fluxes occurring during periods of stratification.

Both particulate organic carbon (POC) and refractory DOC must be processed into low molecular weight, labile, dissolved molecules before they can be absorbed across bacterial membranes (Read et al., in preparation). This processing involves extracellular enzymatic hydrolysis though a stepwise degradation process (Arnosti, 2004). The rate of this processing may be limited by nutrients or specific vitamins and essential amino acids required for bacterial growth (Arnosti, 2004, Reimann & Søndergaard, 1986). Depending on the rate of these processes, the labile material is likely to be utilised by the bacteria, and remaining refractory DOC may accumulate in the sediments, and diffuse into the overlying water. In the case of Bolganup reservoir, both labile and refractory DOC appear to be diffusing out of the sediments, due to the increasing concentrations of both under stratification. This could be due to growth limitation of the bacteria by certain nutrients or vitamins, resulting in not all of the DOC being utilised by the bacteria. Alternatively, a groundwater rich inflow may be injecting an additional source of DOC into the hypolimnion which the modelling has not considered.

Phytoplankton biomass makes a significant contribution to the DOCL pool, with up to 0.0002 mg C/L/hr being contributed during peak biomass in January to April 2006. At this point in time, chlorophyll a in the model reaches 6µg/L (refer to Figure 4.14). This equates to 1mg of chl a per L being capable of contributing 36 mg of C per litre to the hypolimnion. Although, in the field data, chl a did not reach this magnitude, it demonstrates the influence phytoplankton production can have on organic carbon in the reservoir.
Figure 4.20 Measured (top) and simulated (bottom) BDOC in the surface and bottom of Bolganup reservoir.

Figure 4.21 Measured (top) and simulated (bottom) DOCR in the surface and bottom of Bolganup reservoir.
Figure 4.22 CAEDYM modelled organic carbon dynamics. a) Dominant processes influencing b) DOCL and c) DOCR concentrations in the hypolimnion. Processes include DOCL mineralisation to DIC, DOCL contribution from phytoplankton, and DOCL and DOCR flux from the sediments.
5 Conclusions

This report outlines the results of investigations into dissolved organic carbon (DOC) dynamics in Bolganup reservoir. The findings of this work include:

1. Significant concentrations of DOC (0.11g DOC/m²/day), primarily in a highly refractory form, flux out of the sediments under anoxic conditions between October and May of each year.
2. DOC flux from the sediments can be explained in terms of bacterial production. DOC is transported into the hypolimnion from overlying waters, and depending on the rate of the stepwise degradation processes of POC and high molecular weight DOC, refractory and labile portions of DOC may accumulate in the sediment and diffuse into the overlying waters.
3. The refractory DOC fluxed from the sediments is predominately of the VHA component, and is highly aromatic in nature. Associated with this compound, is a high Specific UV Absorbance (SUVA) indicating higher potential for DBP production and thus a larger amount of chlorine is required to treat this water.
4. The DOC in Bolganup reservoir is sourced primarily by that released from the sediments. The DOC in the sediments would have entered the reservoir either in previous inflow events, prior to the study period, or may have been accumulated in the sediments prior to construction of the dam. It is likely that inflow events continue to deliver small concentrations of POC and refractory DOC to the reservoir, although this was not evident during the study period.
5. DYRESM-CAEDYM is capable of predicting stratification, salinity, pH, DO, nitrogen and phosphorus species, carbon compounds and phytoplankton biomass in Bolganup reservoir.
6 RECOMMENDATIONS

DOC concentrations in Bolganup reservoir are primarily coming from the sediments of the reservoir. The volume of water in the hypolimnion of the reservoir will therefore play an important role in the magnitude of DOC concentrations. During periods of high water level, it could be expected for DOC concentrations to be significantly lower in the hypolimnion due to increased dilution. These periods provide optimal periods for abstraction with minimal treatment costs.

An increase in phytoplankton biomass in the reservoir has the potential to significantly contribute to DOC concentrations. Nutrient input to the reservoir should therefore be monitored and kept minimal to avoid phytoplankton growth in the reservoir.

Future work in Bolganup reservoir should involve the collection of sediment cores and examination of the fractions of DOC within the sediment.
7 ACKNOWLEDGEMENTS

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8 REFERENCES


Characterisation of Natural Organic Matter (NOM) in Highly Coloured Surface Waters

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